CHAPTER II

EXPERIMENTAL

2.1 Introduction

The present work involved:

(i) Studies on chemical modification of petroleum pitch with nitric acid and Their Characterization

(ii) Studies on chemical modification of petroleum pitch with sulphuric acid and their Characterization

(iii) Development of carbon fibers from low softening point petroleum Pitches and their Characterization

(iv) Characterization of mesophase pitch based carbon fibers

The modification of petroleum pitch by chemical modification method using various oxidizing agent at room temperature and effect on its properties were studied using various techniques, instruments and procedures which are given in this chapter.

2.2 Studies on Chemical Modification of Petroleum Pitch With Nitric Acid and Their Characterization

2.2.1 Materials Used

* Low softening point Petroleum pitch, Supplied by: M/s. Graphite India Limited, Banglore

* Nitric acid, AR grade (70wt %), Qualigens Chemicals, India

2.2.2 Modification of Petroleum Pitch by Nitric Acid Treatment

The commercially available low softening point petroleum pitch obtains from Graphite India Limited, Banglore. Characteristics of the petroleum pitch are given in Table 2.1
Table 2.1 Characteristics of petroleum pitch

<table>
<thead>
<tr>
<th>Softening Point °C*</th>
<th>% Coke yield</th>
<th>% Ash content</th>
<th>% C</th>
<th>% H</th>
<th>% N</th>
<th>% S and O by diff.</th>
<th>C/H ratio</th>
<th>% QI content</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>39.23</td>
<td>0.63</td>
<td>89.78</td>
<td>8.58</td>
<td>0.03</td>
<td>1.61</td>
<td>0.871</td>
<td>0.95</td>
</tr>
</tbody>
</table>

*QI: Quinoline Insoluble, *Ring-ball method

Pitch in form of solid lumps were well grinded and made into powder form and sieved using sieve shaker machine. The particle size of the pitch obtained were < 300 µm for the better chemical reaction between pitch molecules and nitric acid. 100 gm of pitch powder was treated with 200ml nitric acid solution of different concentration for different time periods at room temperature. Concentration of nitric acid was varied from 10 wt% to 50 wt%. The various time periods from 60 min to 300 min interval were used for stabilized. The mixture of pitch and nitric acid solution was well stirred throughout the chemical treatment time periods with magnetic stirrer. After the chemical treatment, pitches were filtered and washed with distilled water until complete removal of unreacted nitric acid. The modified pitches were neutralized and checked with pH strips for the confirmation of removal of unreacted nitric acid. Figure 2.1 shows the schematic diagram of the procedure used for modification of pitch. The modified pitches after neutralization of acid were dried in oven at a 60ºC for 10 hrs.

2.2.3 Pyrolysis of Non-Treated and Nitric Acid Treated Pitches

The non-treated and nitric acid treated pitches were pyrolysed at 450ºC to study the effect of nitric acid treatment on the formation of mesophase structure. 2gm
of pitch was heat treated in an alumina crucible at a heating rate of 40ºC/hrs upto 150ºC, followed by further heat treatment up to 450ºC at a heating rate of 20ºC/hrs with 1hrs soaking time in programmable temperature controlled furnace in nitrogen atmosphere. The flow of nitrogen was maintained at 0.5 ml/min throughout the reaction.

2.2.4 Carbonization of Non-Treated and Nitric Acid Treated Pitches

The non-treated and nitric acid treated pitches were carbonized at 950ºC in nitrogen atmosphere for the measurement of coke yield. Weighed 2 gm pitch was taken in alumina crucible and transferred into stainless steel container of the furnace. The pitches were carbonized in programmable temperature controlled furnace in nitrogen atmosphere at a heating rate of 40ºC/hrs up to 150ºC followed by further heat treatment to 450ºC at a heating rate 20ºC/hrs and upto 950ºC at a heating rate of 30ºC/hrs with 1hrs soaking time.

2.3 Chemical Modification of Petroleum Pitch with Sulphuric Acid and Their Characterization

2.3.1 Materials Used

* Low softening point Petroleum pitch; Supplied by M/s. Graphite India Limited, Bangalore

* Sulphuric acid, AR grade (60wt %); Qualigens Chemicals, India

2.3.2 Modification of Petroleum Pitch by Sulphuric Acid Treatment

The commercially available low softening point petroleum pitch was obtained from Graphite India Limited, Bangalore. Characteristics of the petroleum pitch are
given in Table 2.1 Solid lumps of Pitch were well grinded and made into powder form. The pitch powder was sieved using sieve shaker machine and particle of the pitch with size < 300 µm were collected for better chemical reaction between pitch molecules and nitric acid. 100 gm of pitch powder was treated with 200 ml sulphuric acid solution of different concentration for 1hrs time periods at room temperature (30°C). Concentration of sulphuric acid was varied from 10 wt% to 60 wt%. The mixture of pitch and sulphuric acid solution was stirred well for 1hrs using magnetic stirrer. After the chemical treatment of pitches was completed. The solution was filtered and solid washed with distilled water till complete removal of unreacted sulphuric acid. Figure 2.1 shows the schematic diagram of the process used for modifying of pitch using H₂SO₄. The modified pitches were neutralized and checked with pH strips for the confirmation of removal of unreacted sulphuric acid. As the unreacted acid will further react and affect the properties of pitch. The neutralized pitches were dried in oven at a 60°C for 10 hrs.

2.3.3 Pyrolysis of Non-Treated and Sulphuric Acid Treated Pitches

The non-treated and sulphuric acid treated pitches were pyrolysed at 450°C in nitrogen to study the effect of sulphuric acid treatment on the formation of mesophase structure. 2 gm of pitches was heat treated in an alumina crucible at a heating rate of 40°C/hrs upto 150°C, followed by further heat treatment up to 450°C at a heating rate of 20°C/hrs with 1hrs soaking time in programmable temperature controlled furnace in nitrogen atmosphere. The flow of nitrogen was maintained at 0.5 ml/min throughout the reaction.
2.3.4 Carbonization of Non-Treated and Sulphuric Acid Treated Pitches

The non-treated and sulphuric acid treated pitches were carbonized at 950°C in nitrogen atmosphere for the measurement of coke yield. 2 gm accurately weighed was taken in alumina crucible and placed in stainless steel container of the furnace. The pitches were carbonized and carbonization temperature was maintained by programmable temperature controller. The pitches were carbonized in nitrogen atmosphere at a heating rate of 40°C/hrs up to 150°C followed by further heat treatment at 450°C at a heating rate 20°C/hrs and further heat treatment at 950°C at a heating rate of 30°C/hrs with 1hrs soaking time.
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2.4 Development of Carbon Fibers from Low Softening Point Pitches

2.4.1 Materials Used

* Low softening point Petroleum pitch, From M/s. Graphite India Limited, Banglore

* Low softening point coal-tar pitch, From M/s. Sail India Limited, Ranchi

* Nitric acid, AR grade (70wt %), Qualigens Chemicals, India

2.4.2 Fiber Spinning

The pitches were grounded to a fine powder. Table 2.2 shows the characteristics of pitches.

**Table: 2.2 Characteristics of Pitches**

<table>
<thead>
<tr>
<th>Types of Pitch</th>
<th>Softening Point °C</th>
<th>% Coke Yield</th>
<th>% C</th>
<th>% H</th>
<th>% N and O by diff.</th>
<th>C/H ratio</th>
<th>% QI content</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTP</td>
<td>110</td>
<td>37.57</td>
<td>91.16</td>
<td>4.12</td>
<td>0.035</td>
<td>4.685</td>
<td>1.85</td>
</tr>
<tr>
<td>PP</td>
<td>110</td>
<td>39.23</td>
<td>89.78</td>
<td>8.58</td>
<td>0.03</td>
<td>1.61</td>
<td>0.871</td>
</tr>
</tbody>
</table>

*Ring and Ball method, * S, O by difference QI: Quinoline Insoluble,

The coal tar and petroleum pitch were melt spun by laboratory made monofilament steel fiber spinneret having capillary diameter D= 0.5 mm and length L=2mm at 40-45°C higher than the softening point of pitch under 0.8 kg/cm² nitrogen pressure shown in Figure 2.2. 25-30 gm pitch was loaded in to the spinneret container. The container was heated gradually upto melting point of the pitch. The nitrogen pressure was applied to the molten pitch. At a particular temperature the
viscosity of pitch was suitable for the drawing of fibers. The molten pitch was extruded through the orifice hole of spinneret. The fibers were stretched and winding was done on the steel winder. Speed of winder was maintained with speed controller attachment with RPM counter. The bunch of fibers were cut and used for further treatment. The spinning conditions used for pitch fibers preparation are given in Table.2.3

2.4.3 Chemical Treatment of as Spun Fibers

The as spun fibers (CTP, PP) were treated with (70wt %) nitric acid for 2 hrs and 4 hrs at room temperature. After chemical treatment unreacted nitric acid was removed through multiple washing with distilled water. Acid treatments were done carefully to avoid damage to the fibers. The chemical treated fibers were dried at 45°C in oven. These nitric acid treated CTP and PP fibers are designated as 2nCTP, 4nCTP, 2nPP, and 4nPP.

2.4.4 Stabilization of Pitch Fibers

Oxidative stabilization of the pitch fibers was carried out in air circulating oven. After proper drying the CTP and PP based nitric acid treated pitch fibers were taken in graphite boat and kept in the oven. The temperature of the oven was increased in steps slowly to the desired final temperature. Care was taken that fibers do not melt during stabilization and carbonization reaction. Pitch fibers had low softening point corresponding to that of the parent pitch. These pitch fibers were stabilized in air at a heating rate 100°C/hr up to 350°C and maintained at that
temperature for 30 min. After stabilization the change in weight of fibers was measured. The stabilized fibers are designated as 2sCTP, 4sCTP, 2sPP and 4sPP.

2.4.5 Carbonization and Graphitization of Stabilized Pitch Fibers

The carbonization process of pitch fibers was done at higher temperature to about 1000°C in nitrogen atmosphere. During carbonization volatile materials escaped from the fibers leaving behind dense carbon structure in fibrous form. The carbon fibers formed during carbonization. Flow diagram for the development of carbon fibers is shown in Figure.2.3. The carbonization reaction was carried out in programmable temperature controlled furnace in nitrogen atmosphere. The samples were kept in a quartz tube. The flow of nitrogen was maintained at 0.5 ml/min through out the reaction. The carbonization of stabilized pitch fibers was carried out at a heating rate of 2.5°C/min up to 1000°C under inert atmosphere with 1hr. soaking time at 1000°C. Change in weight of fibers was measured after carbonization. The 1000°C heat-treated pitch fibers were further heat treated at 3000°C under controlled inert gas atmosphere. The carbonized fibers are designated, as 2cCTP, 4cCTP, 2cPP and 4cPP and 3000°C heat-treated fibers are 2GCTP, 4GCTP, 2GPP and 4GPP.
Table 2.3 Spinning conditions for pitch fiber preparation

<table>
<thead>
<tr>
<th>Types of Pitch</th>
<th>Spinning Temperature, °C</th>
<th>Nitrogen Pressure, Kg/cm²</th>
<th>Winding Speed, m/min</th>
<th>RPM of Winder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal Tar</td>
<td>150-155</td>
<td>0.8</td>
<td>335</td>
<td>1000</td>
</tr>
<tr>
<td>Petroleum pitch</td>
<td>150</td>
<td>0.8</td>
<td>335</td>
<td>1000</td>
</tr>
</tbody>
</table>
Figure 2.2 Pitch Fiber Melt-spinning unit
Nitric acid (70%wt) treatment, 2&4 hrs, Room Temp (20-30°C) carbonization at 1000°C in N2, heating rate 2.5°C/min, 1hrs 

Graphitization at 3000°C in argon,

As Spun fibers

Nitric acid treated fibers

Carbon fiber

Stabilized fibers

Low Softening Point Petroleum Pitch

Melt Spinning, 40-50°C higher than the softening point

Stabilization in air at 350°C, Heating rate 100 °C/hr, 30min

Carbonization at 1000°C in N2, Heating rate 2.5°C/min, 1hrs

Graphitic Fibers

Figure 2.3 Schematic diagram for Preparation of carbon fibers
Figure 2.4 Carbonization assembly
2.5 Characterization of Mesophase Pitch Based Carbon Fibers

2.5.1 Materials Used

* 100AR Mesophase pitch based green fibers
* 25S75AR Mesophase pitch based green fibers, supplied by Clemson University, USA

2.5.2 Stabilization and Heat Treatment

Experimental pitch fibers produced from Mitsubishi AR mesophase pitch and SCE mesophase pitch from Clemson University were taken in Green stage and studies on the effect of heat treatment temperature and composition on the properties and microstructure of carbon fibers was made. The fibers are abbreviated as 100AR and 25S75AR. 100AR types as spun fibers were prepared using AR mesophase pitch. 25S75AR types as spun fibers were prepared using mixture of 25%SCE (supercritically extracted AR mesophase pitch) and 75%AR mesophase pitch. A part of the as spun fibers were stabilized in flowing air under optimized conditions of temperature and time. The stabilized fibers were carbonized to 1000°C in programmed way under controlled flow of nitrogen. Part of the fibers was further heat treated at 1500°C, and 2000°C and 3000°C under argon atmosphere.

2.6 Characterization

2.6.1 Pitch Yield

Pitch yield was calculated from the weight of raw materials taken before modification and weight of pitch after modification by using the following equation.

\[
\text{Pitch yield, \%} = \frac{W_2}{W_1} \times 100
\]

Department of Materials Science
Where, $W_1=$ Weight of raw materials before modification
$W_2=$Weight of pitch after modification

### 2.6.2 Softening Point of Modified Pitches

Change in softening point of non-treated and chemical treated pitch was measured by Ring and Ball method. Figure 2.5 shows the ring and ball method setup. The dimension of stainless steel ball is 25.30 mm diameter and stainless steel ring of inner diameter 25.40 mm with 11.40 mm thickness. The non-treated and chemical treated pitches were melted and a thin coating of pitch was made around stainless steel ball by dipping. The pitch coated stainless steel ball was placed on the stainless steel ring, which was kept in the paraffin oil beaker. The temperature of the paraffin oil was raised slowly. Temperature was measured using thermometer. The temperature, at which the ball starts to pass through the ring, indicates the softening point of pitch. This process was repeated several times to get reproducible results.

### 2.6.3 Coke Yield

Coke yield of the pitch sample (pitch as such, modified pitches) was determined by heating the pitch in nitrogen at 950°C for one hour. Weighed amount of pitch ($W_1$) was taken in alumina crucible and heated to 950°C in nitrogen atmosphere for one hour. After pyrolysis to 950°C the residue obtained was weighed ($W_2$) and from the difference in weight, coke yield was calculated.

$$\text{Coke yield, } \% = \frac{W_1 - W_2}{W_1} \times 100$$
2.6.4 Quinoline Insoluble, Benzene Insoluble and Toluene Insoluble

Content

Quinoline insoluble, Benzene insoluble and Toluene insoluble percentage in pitch as such and modified pitches were determined by using Soxhlet method. An accurately weighted amount of pitch sample was taken in a Whatman thistle. Hot quinoline was dropped on to the pitch sample to dissolve the quinoline soluble. It was repeated for many times. Quinoline showed a change in its colour from clear to black after some cycles of the experiments. After some cycles when colour of the quinoline changed from black to clear, the addition of quinoline was stopped and thistle was taken out. The quinoline insoluble is retained in the thistle. It was washed with hot quinoline and dried in oven at low temperature. It was weighed again. The same method was used to determined benzene insoluble and toluene insoluble percentage in pitches as such as well as in modifies pitches using benzene and toluene.

\[
\text{Quinoline insoluble content, } \%, = \frac{W_2}{W_1} \times 100
\]

Where, \(W_1\) = Weight of pitch before extraction

\(W_2\) = Weight of insoluble content after extraction
2.6.5 Elemental Analysis

C,H,N, elemental analysis of non-treated pitch as well as modified pitch samples was performed using Perkin-Elmer 2400 CHN analyzer with acetonitrile as standard. The method is based on Pregal and Dumas method, samples are combusted in a pure oxygen environment, with the resultant combustion gases measured in an automated fashion.

2.6.6 Density

Density of 100AR and 25S75AR mesophase type pitch based carbon fiber was measured by float and sink method. Density mainly related with the heat treatment temperature given to the carbon fibers. The density of both types of heat-treated fibers was measured using a mixture of organic solvents such as carbon tetrachloride and 1,2 dibromoethane have a density 1.58 gm/cc and 2.18 gm/cc respectively. The experiment carried out on monofilament using five samples.

2.6.7 FTIR Analysis

FTIR analysis of non-treated and nitric acid treated pitch was carried out for the studies on effect of chemical treatment on chemical structure of pitch using SHIMADZU 8300 FTIR Spectrophotometer.

Non-treated and nitric acid treated pitch, were well grounded and made in the powder form. After grinding powder was mixed with dried KBr (spectropic grade) powder and grounded again to make uniform mixture. Thin pellet of these samples was prepared by pressing it in mold. The pellet was placed in FTIR spectrometer sample holder and spectra were recorded.
The non-treated fibers, 2hrs and 4hrs nitric acid treated fibers, stabilized fibers and carbonized fibers were characterized for chemical groups present in the fibers and their transformations by FTIR. The samples in fibrous form were crushed and made into powder. The powder was mixed with KBr in the ratio 1:100 (sample: KBr) and crushed in an agate mortar to make uniform mixture. The mixture was made in to pellet form and analyzed by FTIR. Figure 2.6 show the FTIR Spectrophotometer (Shimadzu 8300)

2.7 Thermal Properties
2.7.1 Thermogravimetric Analysis (TGA)
2.7.1a Non-Treated and Nitric Acid Treated Pitch

Thermal characteristics of non-treated and nitric acid treated pitches and their pyrolysis behavior were studied using Mettler thermal analyzer TA 4000 with thermo gravimetric analyzer TG50. 10 mg weighed pitch was taken in the alumina crucible. The measurements were made in nitrogen atmosphere at a heating rate of 20°C/min up to 950°C with controlled flow 200CC/min. Figure 2.7 shows the Mettler Thermogravimetric Analyzer.
Figure 2.5 Softening point measurement Assembly (Ring and Ball)
Figure 2.6 FTIR Spectrophotometer (SHIMADZU FTIR-8300)
2.7.1b Non-Treated and Nitric Acid Treated Pitch Fibers

The thermal behavior of non-treated and 70% conc. nitric acid treated fibers for various time interval were carried out by Mettler thermal analyzer TA 4000 with Thermogravimetric analyzer TG 50 in N₂ at heating rate 10°C/min up to 950°C.

2.7.2 Differential Scanning Calorimetric Analysis (DSC)

2.7.2a Non-Treated and Nitric Acid Treated Pitch and Non-Treated And Nitric Acid Treated Pitch Fibers

Thermal behavior of non-treated and nitric acid treated pitches and fibers were analyzed by mettler thermal analyzer TA 4000 with differential scanning calorimetric DSC 20. Figure 2.8 shows the mettler differential scanning calorimetric DSC 20. 5 mg pitch sample was placed in DSC furnace with reference sample. The measurement was made in to nitrogen atmosphere at a heating rate 10°C/min up to 500°C.
Figure 2.7 Mettler Thermogravimetric Analyzer

Figure 2.8 Mettler Differential Scanning Calorimetric Analyzer
2.8 Microstructure Analysis

2.8.1 Optical Analysis

Leitz LABOULUX 12 POLS Optical microscope with attachment of Leica DFC 300 FX CCD camera shown in Figure.2.9 was used to study the microstructure of semi coke and cokes from pitch as such as well as from modified pitch heat treated at 450°C for 1hrs. Also the optical activity of carbon fiber was analysed. Samples were embedded in epoxy resin in PVC mold. After curing of epoxy resin, the samples were taken out from the mold. The embedded samples were polished with silicon carbide papers of grade 400, 600,800, 1000, and 1200. The polished samples were further polished on polishing machine using different sized alumina powder (BUEHLER USA) of 1micron down to and finally 0.05 micron size. After each cycle of polishing with different grade powder, the sample was cleaned thoroughly with distilled water in an ultrasonic cleaner (Electronica Engineering Co, Bombay Model No ES/250W) for ten to fifteen minutes. These samples were then viewed under optical microscope at different magnification using crosspolarized light.

2.8.2 Scanning Electron Microscopy

Surface morphology of different carbon fibers was studied by HITACHI S3000N Scanning Electron Microscope shown in Figure.2.10. Oven dried fibers samples were mounted on the holder with the help of silver paste. Silver paste acted as an adhesive as well as conducting material. The samples were examined at various magnifications.
Figure 2.9 Polarized light Optical Microscope
Chapter II
2.9 Mechanical Properties

2.9.1 Tensile Strength

The mechanical testing of mesophase pitch based carbon fibers was carried out using Universal Testing Machine INSTRON 4483. The tensile strength was measured by using fiber jaws attachments and capacity of Load cell censor is 10 N. Figure 2.12 shows the fiber testing arrangement.

The fibers were mounted in tensile tab window carefully. The 20 mm gauge length was fixed and precaution was taken to mount fibers in straight line. The fibers were mounted in tensile tab as shown below in Figure 2.11. The tensile stress was applied and breaking strength was calculated with help of the fiber diameter. Tensile strength, tensile modulus of carbon fiber was calculated. Figure 2.13 shows the universal Testing Machine INSTRON 4483.

Cross-section area of carbon fibers \( A = \pi r^2 \)

- Tensile strength = Breaking Load/ Cross-section Area, Gpa
- Strain = Change in Length, mm/ Original Length, mm
- Young modulus of Carbon Fiber = Tensile Strength/ Strain, Gpa
Figure 2.11 Fiber Tensile Tab

Figure 2.12 Tensile testing apparatus
Figure 2.13 Universal Testing Machine INSTRON 4483