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Investigation of graphitizing carbons from organic compounds by various experimental techniques

T Hossain and J Podder
Department of Physics, BUET, Dhaka, Bangladesh

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Abstract : Graphite making organic compounds such as polynuclear aromatics, high rank coal always pass through a liquid or plastic state-structural transition of optical anisotropy, called carbonaceous mesophase, the life time of which is limited by its hardening to a semi-coke. X-ray analysis shows that the inter-layer spacing of graphitic carbons decreases with increasing temperature and becomes 3.354 Å or nearly so in the graphitization temperature range 2500°C to 3000°C Sensitive tint technique of polarized-light microscopy has been found most suitable to study the initial formation of spherules, their coalescence and the growth of mosaic texture during the mesophase period Differential thermal analysis (DTA) trace having an initial large endotherm with activation energy of the order of 60 K cal/mole or above, has been proved to be an another effective tool for detecting graphitizable organic materials and in determining the mesophase intervals A sharp fall in resistivity with temperature is found to be an another indicator for the graphitizable organic materials exhibiting semi-conducting behaviour.

Keywords : Carbon graphitization, XRD, DTA

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1. Introduction

During the heat-treatment of carbon containing materials to high temperatures, the removal of non-carbon atoms, usually oxygen, hydrogen, nitrogen or sulphur, as well as some carbon constitutes the process what is known as 'Carbonization'. This process follows a rearrangement of order within the remaining carbon atoms which may ultimately develop a three-dimensional order very close to the well-defined structure of pure graphite is termed 'Graphitization'. In fact graphitization occurs in the temperature range 2500°C to 3000°C.

X-ray analysis [1] shows that the carbon-atoms in graphite are arranged in layers. Each layer is a continuous net-work of planar, hexagonal rings; the carbon atoms within a

layer are held by strong covalent bonds 1.415 Å long. The different layers, 3.354 Å apart, are held to each other by weak forces of Van der Waals' type. In the graphitic carbons, the apparent inter-layer spacing decreases with increasing temperature [2].

Organic solid materials ultimately producing synthetic graphite usually pass through a fusion stage during carbonization. This is one but not the only condition for the graphitizability of organic solid compounds. Many workers [3–7] have demonstrated the formation of carbonaceous mesophase in the temperature range 350–600°C as precursor to graphitization. This mesophase is a liquid or plastic-state structural transition in which the large lamellar molecules formed by thermal cracking and aromatic polymerization become aligned in a parallel array to form an optically anisotropic liquid crystal, the life time of which is limited by its hardening to a semi-coke.

In the initial stages of nucleation, the carbonaceous mesophase appears as small spherules suspended in the optically isotropic matrix and as carbonization progresses with increasing temperature and time, the growing mesophase spherules, being denser than the isotropic parent phase, sink to the bottom of the container. While sinking two or more spherules coalesce to produce larger droplets, eventually leading to a bulk mesophase as shown in Figure 1. When viewed microscopically with cross polarizers, the bulk mesophase usually displays a complex ensemble of extinction contours. The polarized-light extinction

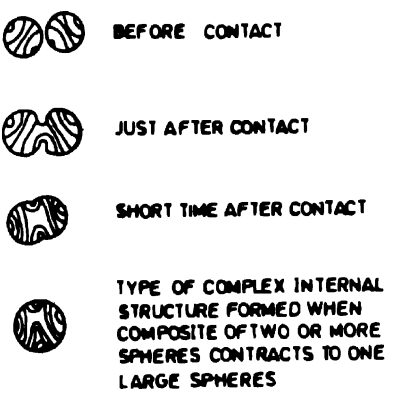

Figure 1. Rearrangement which appear to occur when two spheres coalesce.

contours display nodes and the characteristic Maltese Cross patterns. Using sensitive tint technique of polarized-light, changes in pleochroism for coalesced and for deformed mesophase forming mosaic texture are observed.

Differential Thermal Analysis (DTA) as a technique to identify organic compounds producing synthetic graphite was adopted by some workers [8,9]. For graphitizable organic materials, endothermal processes of transformation with effective activation energy over 60 K cal/mole are generally seen to occur in the initial stage of the DTA trace (Figure 2). In the case of an organic compound under heat-treatment, two competing reactions are often found to occur; Cross-linking producing an exothermic reaction and chain stripping and associated reactions, which produce endothermic peaks. The second type often allows

the formation of oriented aromatic rings giving rise to graphitizing carbons. Again, the appearance of an exothermic reaction having activation energy as low as 20 K cal/mole, somewhere in the initial polymer decomposition reaction, ensures that the resulting carbon has non-graphitizing properties (Figure 3).

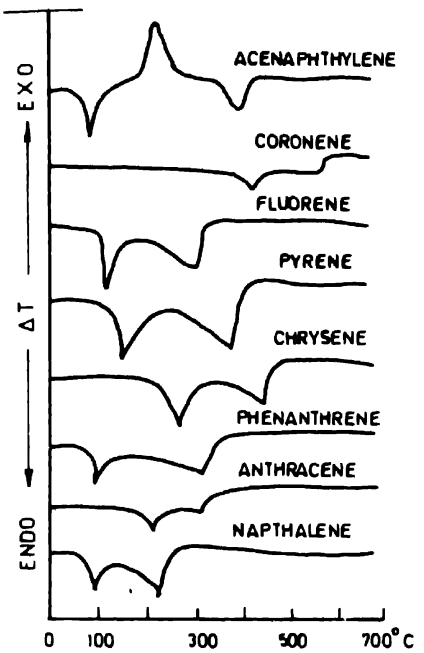

Figure 2. Thermograms of some graphitizable organic materials

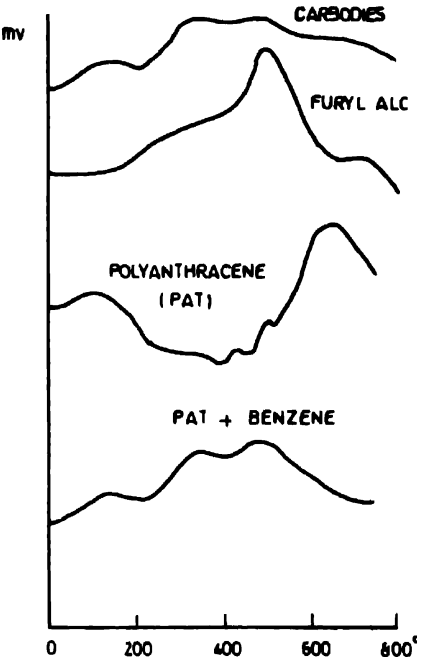

Figure 3. Thermograms of some non-graphitizable organic materials

The temperature interval of the carbonaceous mesophase may be a few degrees or it may be tens of degrees and so very difficult to locate. A combination of differential thermal analysis and polarized-light micrography [10,11] has proved a valuable approach to identify graphitic carbons and for the determination of mesophase interval.

A sharp fall in resistivity [12] is found to be observed indicating semi-conducting nature in the case of organic compounds ultimately producing artificial graphite during carbonaceous mesophase transition. This is usually preceded by random resistivity change due to the emission of various entrapped hydrocarbon gases formed by thermal cracking and aromatic polymerization.

2. Experimental

2.1. X-ray analysis:

The experimental details of X-ray analysis have been described elsewhere [2]. X-ray diffractogram of synthetic graphite derived from North-Western Bangladeshi coals in the

temperature 2700°C has been shown in Figure 6. This diffractogram resembles that of pure graphite indicating that the north-western Bangladeshi coals give rise to synthetic graphite. A recent study of the measurement of inter-layer spacing with increasing temperature undertaken by the authors in the case of pyrene has shown that the inter-layer spacing decreases with increasing temperature indicating that it is graphitic in nature. The diffractograms obtained for pyrene are depicted in Figure 4.

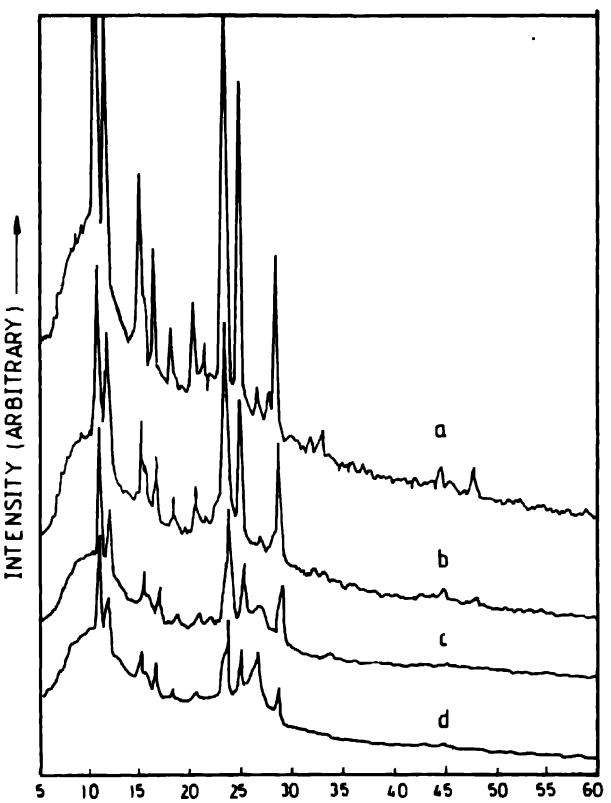

Figure 4. X-ray diffractograms of Pyrene heat-treated at different temperature · (a) raw sample, (b) at 410°C/6 hrs, (c) at 440°C/6 hrs, (d) at 470°C/6 hrs.

2.2. Differential thermal analysis (DTA) :

Details of the DTA technique have been described elsewhere [10]. Selected aromatic samples, which have not yet passed through the carbonaceous mesophase due to prolonged heating at a certain temperature, are subjected to heat-treatment in the Stanton Differential Thermal Analyser. The DTA traces having large endotherms at the beginning (Figure 5) indicate that they are all graphitizable in practice. The DTA traces of the partially carbonized samples are also useful for the determination of mesophase interval.

2.3. Polarized-light micrography:

The technique for micrographic preparation of samples has been described elsewhere [11].

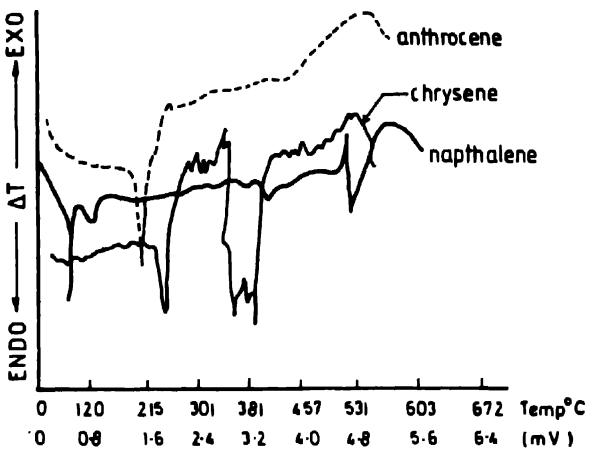

Figure 5. DTA traces of partially carbonised aromatic organic compounds.

Samples so prepared are observed and photographed with a Reichert polarizing microscope using reflected polarized-light. Colour photographs of the mesophase spheres and of subsequent heat-treated samples are usually obtained by High Speed Ektachrome 35 mm reversible film. The coloured mesophase spheres having characteristic Maltese crosses identifying graphitic carbons are produced by the insertion of a gypsum plate inclined to the Analyzer at an angle of 45° and placed between the analyzer itself and the sample under observation. The analyzer and polarizer remain cross with respect to each other. This is the so-called Sensitive Tint Technique.

2.4. D-C conductivity measurement:

The details of the technique of sample preparation for resistivity measurement have been described elsewhere [12].

The resistance is measured by standard dc bridge reading to the nearest microvolt at a heating rate of 2–3°C min^{-1} in the temperature range 105–700°C. The temperature is measured by a calibrated iron-constantan thermocouple.

3. Results and discussions

A comparism of the X-ray diffractogram of synthetic graphite with that of pure graphite (Figure 6) will always ensure identification of organic compounds ultimately producing synthetic graphite. The inter-layer spacing calculated for synthetic graphite obtained from north-western Bangladeshi coals resembles that of pure graphite. Again the inter-layer spacings recently calculated from the diffractograms (Figure 4) at different heat-treatment

temperatures of pyrene in the mesophase region were found decreasing indicating the criteria of an organic compound producing synthetic graphite.

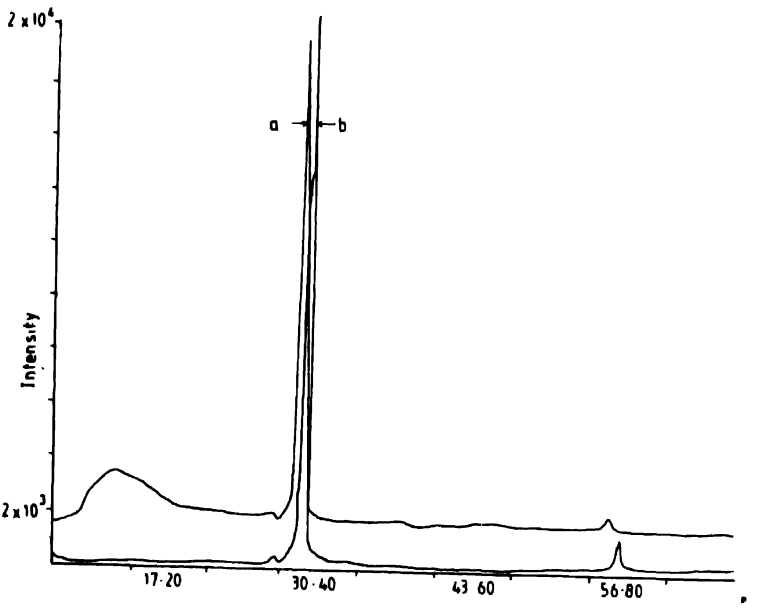

Figure 6. X-ray diffractograms of graphite (a) synthetic graphite derived from coal heat-treated at 2700°C (b) natural graphite

Characteristic of the DTA traces obtained for the different aromatics (Figure 5) is the presence of an initial large endotherm due to melting which is then followed by small fluctuations before a smooth trace. DTA traces of naphthalene, anthracene and chrysene almost show the same trend of behaviour. The temperature at which all the fluctuations terminate, is nothing but the temperature of complete coalescence during mesophase transition of a particular sample. This can be verified by polarized-light microscopy, by viewing through it a sample heat-treated to similar temperature. For example, the polarized-light photomicrograph obtained for chrysene (Plate 2) agree quite well with its respective DTA trace. The temperature at which the mesophase spherules start to develop in the sample has not been ascertained by DTA. The polarized-light photomicrograph (Plate 1) obtained for chrysene shows the temperature at which the mesophase spherules start to develop.

A sharp fall in resistivity with temperature (Figure 7) is found to be observed indicating semi-conducting nature by Bangladeshi coal-peats during carbonaceous mesophase transition. Irregular variations in resistivity usually occur due to the evolution of various entrapped hydrocarbon gases during heat-treatment and due to the rearrangement of the atoms in the molecules of the sample. Because of the rearrangement of the atoms, the energy gap increases and the balance electrons need more energy to jump from balance

Plate 1. Mesophase spherules in chrysene at 510°C for 5 hrs

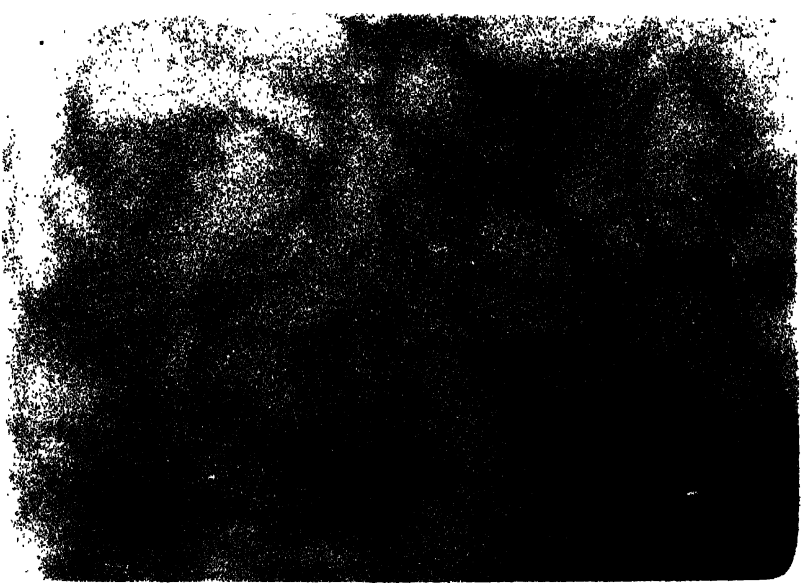

Plate 2. Mosaic formation in chrysene at 530°C for 5 hrs.

bands to unfilled conduction bands. As a result the resistivity increases with temperature at the initial stage. Above this stage, the sample starts decomposing and ordering of the molecules in the parent material begins causing a gradual decrease in the energy gap which

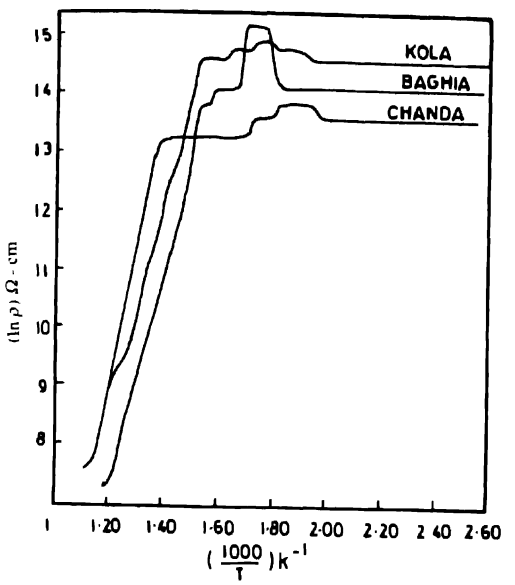

Figure 7. Resistivity variation with temperature

gives rise to intrinsic conduction in the sample. The more the molecules are ordered structurally, the more the conduction becomes significant and hence, the resistivity decreases continuously with increasing temperature indicating the semiconducting nature of the sample during graphitization.

4. Conclusion

The criteria of organic compounds producing artificial graphite may be summarized as follows :

(a) The inter-layer spacing of synthetic graphite obtained from organic materials heat-treated in the graphitization temperature range 2500°C–3000°C will be 3.354 Å or nearly so. In the graphitic carbons, the apparent inter-layer spacing decreases with increasing temperature.

(b) Organic materials ultimately producing synthetic graphite, always pass through a carbonaceous mesophase formation accompanied by temporary liquefaction or plasticizing of the materials in the temperature range 350–600°C. In this liquid-state structural transition, large planer molecules become aligned in a parallel array to form an optically anisotropic liquid crystal. The growing mesophase spherules, the bulk mesophase and also the plastic flow patterns generally show characteristic Maltese Crosses and nodes when viewed under sensitive tint technique of polarized-light microscopy.

(c) For graphitizable organic materials endothermal processes of decomposition with effective activation energy of over 60 K cal/mole are generally seen to occur in the initial stage of the DTA trace.

(d) An organic compound, displaying a sharp fall in resistivity with increasing temperature in the mesophase region, ultimately produce carbons semiconducting as well as graphitic in character.

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