

# Pitch-Mesophase-Carbon Transformation Diagrams for a Variety of Pitches

by

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**Abstract.** Diagrams, comprising glass transition and decomposition temperatures plotted as a function of C/H and/or volatile content of pyrolysis residues have been determined for pitch. In the two phase region separation has been carried out by hot centrifugation and data for each phase is included in the diagram.

## Introduction

The concept of a Transformation Diagram to describe the transformation of a pitch via the liquid crystalline mesophase to carbon has been outlined previously<sup>1-3</sup>. Characteristic temperatures, usually glass transition temperatures,  $T_g$ , and decomposition temperatures,  $T_o$ , are plotted against some measure of the extent of pyrolysis such as volatile content or C/H. This concept is further examined here and has been applied to the pyrolysis of a number of carbon precursors. In previous work it was possible only to determine a single value of  $T_g$  for two phase mesophase pitches and this was considered to be characteristic of the continuous phase<sup>4</sup>. In the work reported here the technique of hot centrifugation<sup>4</sup> has been used to separate the two phases physically, enabling the characteristic temperatures for each phase to be included in the diagram. This latter approach is very useful as it enables changes in the properties of each phase to be followed and also facilitates comparison of properties of the mesophases from different precursors. In an attempt to detect any differences in the mesophase characteristics of materials that show the fine mosaic type of optical texture two such precursors, gilsonite and a coal extract, were included in the study. The other materials, which all gave mesophase with a coarse optical texture, were acenaphthylene pitch, a coal tar pitch (Rutgers), an ethylene cracker tar pitch and Ashland A240 (low S).

## Experimental

Precursors were heat treated in open crucibles in a nitrogen atmosphere in a tube furnace at a linear heating rate of  $5 \text{ K min}^{-1}$ . At the required temperature, samples were withdrawn to the cooled end of the tube where they were quenched. The coal extract was heat treated at heating rates of 3 and  $0.1 \text{ K min}^{-1}$ .

The quenched samples were sectioned vertically and examined microscopically for the distribution and the internal microstructure of the mesophase.

Following the removal of the vertical section the whole of the remainder was ground and intimately mixed. The pyrolysis products were analysed chemically; volatile contents and decomposition temperatures were determined thermogravimetrically at  $5 \text{ K min}^{-1}$  to  $800^\circ\text{C}$  and glass transition temperatures were determined using a Stanton Redcroft Thermomechanical Analyser. A nitrogen atmosphere and linear heating rate of  $5 \text{ K min}^{-1}$  was used with a flat ended probe and a weight of only 1g. In this way the change in thermal expansion coefficient at the glass transition could be observed. The values determined in this way agreed with previous measurements by broad line proton NMR.  $T_g$ 's of the coal extract were determined as described previously<sup>4</sup>.

In the two phase region below the phase inversion point the mesophase and isotropic liquids were separated by hot centrifugation. This method is superior to solvent fractionation since it avoids problems due to retention of solvent which would markedly affect properties such as  $T_g$ . It is essential that the temperature of centrifugation be high enough and maintained through the centrifugation long enough that the sedimented mesophase retains its fluidity and can fully coalesce without any entrainment of isotropic liquid. This could be achieved with the materials that gave rise to the coarse optical texture but not with gilsonite (separation of the coal extract has not been attempted). The mesophase in this case was not sufficiently fluid at temperatures below the decomposition temperature. The separated fractions were also characterised as described above.

## Results and Discussion

The results for each pyrolysis series have been combined into transformation diagrams using both C/H and volatile content as a measure of extent of pyrolysis. The features for the Ashland A240, the coal tar pitch and the ethylene cracker pitch were similar and the diagram for the latter pitch is shown in fig. 1. This will be discussed as an

illustrative example for all three pitches.  $T_g$  values for each phase are plotted against the volatile content of the whole two phase mixture (not against the volatile contents of the separate phases). Similarly the decomposition temperatures (expressed as  $T_{0.5}$  i.e. temperature at which the wt loss is of 0.5% of the sample) refer to the whole sample to indicate when that sample begins to change composition. The difference in temperature between this line and the  $T_g$  lines indicates the temperature range over which each phase is fluid and chemically stable. This temperature range is of the order of 230°C for the starting pitch and is maintained at about this level up to the phase inversion point after which it begins to decrease. In the two phase region it can be seen that the  $T_g$  for the mesophase does not change very significantly until the phase inversion region is reached. This suggests that the mesophase composition is not changing substantially. The volatile contents and C/H's of the mesophase samples are all fairly constant at about 15% and 1.86±0.05 respectively which is consistent with this view. Just before the phase inversion region (at 15% volatile content of the whole sample) the characteristic properties of the mesophase begin to change. The  $T_g$  of the isotropic liquid, however, increases steadily in the two phase region as its composition moves towards that of the mesophase. The difference between the two  $T_g$ 's, which is of the order of 70°C, for this precursor in the early stages of mesophase growth decreases gradually as the phase inversion region is approached. This result suggests that the changes in the apparent viscosity observed in 'in situ' rheological measurements<sup>3,5</sup> are largely due to changes in the viscosity of the isotropic phase and the changing volume fraction of mesophase at temperatures below the phase inversion point.

Included in the transformation diagram are the temperatures (pyrolysis temperatures) at which the pyrolysis residues were collected under the linear heating conditions. Thus it is possible to predict the temperature at which a mesophase pitch with particular properties will be produced under these

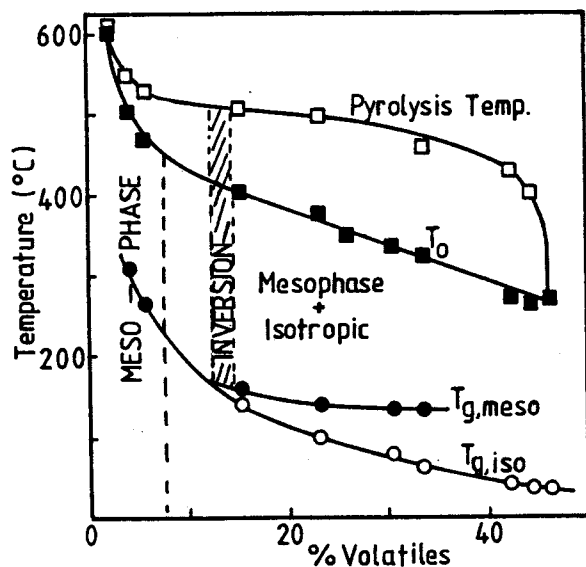


Figure 1. Transformation diagram for ethylene cracker tar pitch.

conditions. The difference between the pyrolysis temperatures and the  $T_g$  values gives an indication of the changing fluidity during pyrolysis. This difference is of the order of 400°C at the beginning of the two phase region but is reduced to about 300°C at the phase inversion point. However, the pyrolysis line is very dependent upon the heating rate and the  $T_g$  lines may also be different for different pyrolysis conditions. This is shown in fig. 2 which is a partial transformation diagram for the coal extract pyrolysed at two different heating rates. Higher  $T_g$  values are obtained at comparable volatile contents at the lower heating rate, due to the changing balance between straight molecular evaporation and release of volatile cracking products, as discussed previously<sup>6</sup>. Moreover, at the slower heating rate the transformation is carried out at lower temperatures (pyrolysis line) with the result that the temperature differences between the pyrolysis temperature and  $T_g$  of the mesophase pitch system are lower, implying higher viscosities in the pyrolysing liquid. It should also be noted that the values of  $T_g$  for the coal extract samples are significantly higher than for the ethylene cracker tar, coal tar, Ashland and acenaphthylene pitches at comparable volatile contents whilst the variation of  $T_g$  with volatile content for gilsonite resembles that for the coal extract.

#### References

1. Rand, B. and Whitehouse, S., Extended Abstracts of the 16th Biennial Carbon Conference, San Diego 1982, American Carbon Society, p.30.
2. Whitehouse, S. and Rand, B., Carbon '82, Extended Abstracts of 6th London Conference on Industrial Carbons and Graphite, London 1982, SCI, p.183.
3. Rand, B., 'Petroleum Derived Carbons', ed. J.D. Bacha, J. Newmand and J.L. White, ACS Symp. Series, in the press.
4. Rand, B. and Whitehouse, S., ref. 1, p.102.
5. Collett, G.W. and Rand, B., Fuel, **57**, 162 (1978).
6. Benn, M., Rand, B. and Whitehouse, S., ref 1, p.52.

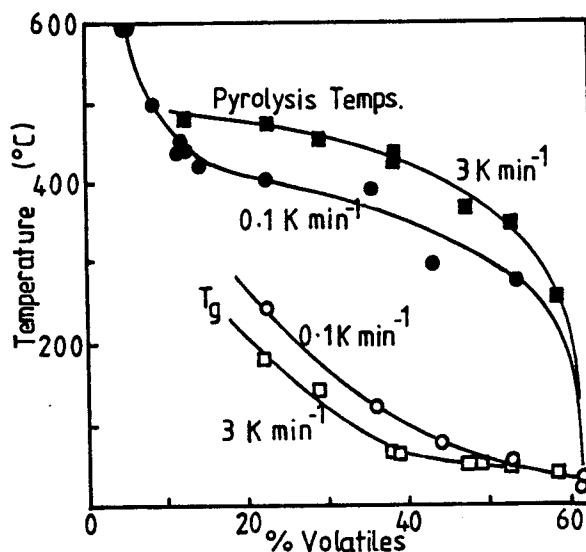


Figure 2. Partial transformation diagrams for coal extract heat treated at two different heating rates.