Carbonization of 3.5-dimethylphenol-formaldehyde resin and its chemical structure at mesophase appearence

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Introduction)

Some type of pitches such as PVC pitch, petroleum pitch or coal tar pitch which become graphitizable carbon at high temperature, generally forms mesophase during the heat treatment of 400~450°C and the mechanism of its formation was studied by many workers which was well reviewed by Books-Taylor[1] or White[2]. So far it is tacitly recognized generally that mesophase consists of large polycondensed aromatic compounds orienting nearly in parallel each other and still remaining as liquid state. In most of the cases this view may be true but it was not yet chemically confirmed.

This report pursued the change of chemical structure of 3.5-dimethylphenol-formaldehyde resin during its heat treatment, which shows mesophase formation as fine mosaic structure at 430°C, and estimated the chemical structure of mesophase.

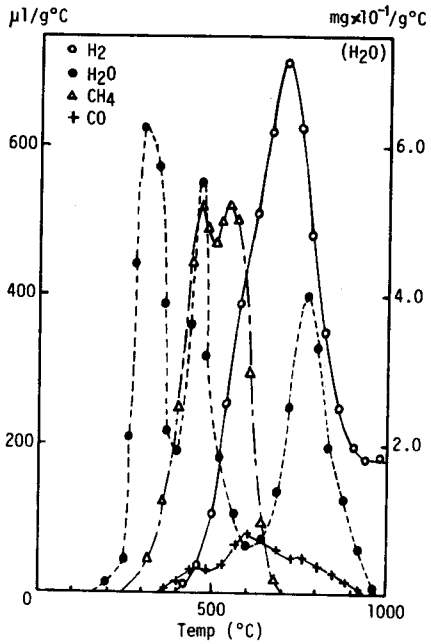
(Experimentals)

The resin has been prepared from 1:1 mol ratio of 3.5-dimethylphenol and formaldehyde (36% aqueous solution) using 10ml of ammonia (23% aqueous solution) per 1 mol of phenol as catalyst and reacting at 90~98°C for 3 hours under nitrogen atmosphere. Then it was cured at 130~140°C on oil bath for 10 hours.

This sample was carbonized with 3°C/min and evolving gases were analysed by gaschromatography every 20°C employing active charcoal for CO and CO_2 and molecular sieve 5A for another gases. Water was decomposed by zinc metal heated at 400°C and produced hydrogen was analysed[3]. The amount of distilled low molecular weight substance was obtained from the difference of weight decrease measured by thermobalance and the weight of evolved gases analysed by gaschromatography mentioned above.

The infrared spectra was measured by KBr pellet with the sample concentration of about 1%.

Fig.1 Gas evolution curves



NMR was measured in D-pyridine employing TMS as reference. Mesophase was observed by microscope using polarized light with the magnification of 250 times.

(Results and discussion)

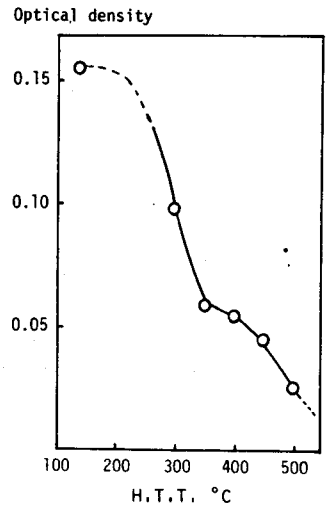
The gas evolution during carbonization is illustrated in fig.1 in the differential curve (ml volume or mg weight of evolved gases/1gr sample/1°C). All the amount is corrected for the loss of low molecular weight substance under the assumption that the low molecular weight substance has the same elemental composition as the original sample.

Firstly dewater reaction starts from 200°C, then methane evolves from 300°C making first peak at about 450°C and second peak at about 520°C. From 400°C second dewater reaction starts and a little later hydrogen begins to evolve reaching to maximum at about 700°C. Third dewater starts from 600°C making a maximum at about 750°C. Evolution of CO makes the maxima at 450°C, 600°C and 750°C.

The decreasing curve of OH absorption intensity in IR spectrum shows two steps divided at about 350°C (fig.2) which corresponds very well to the evolution curve of water. Moreover the absorption at 1200cm^{-1} which means diphenyl ether type oxygen shows a maximum at about 350°C (fig.3). From these results it is concluded that the first dewater reaction should be dewater from two OH groups leaving ether linkages.

The first peak of demethanation may result from the evolution of methane from two neighbouring methyl groups forming naphthene ring between two benzene nuclei, because phenol-formaldehyde resin which has not methyl groups shows a peak of demethanation at the temperature exactly corresponding to the second demethanation peak of 3.5-dimethylphenol-

Fig.2 Change of OH absorption at 3400 cm^{-1}



formaldehyde resin[3].

The sample carbonized at 400°C can dissolve into pyridine up to 92.2% and its molecular weight measured by VPO was 1380. Structural indices of this soluble part calculated from NMR chart are shown in table 1. In this calculation the following procedure was taken. Namely one-third of oxygen is calculated as OH group (from fig.2) and the others ether type between two benzene nuclei. The number of hydrogen substituted as methylene bridges were corrected as to the polymeric type of this resin, that is to say twice of the value was used for the calculation of Hau.

From these results the change of chemical structure when carbonized at 400°C may be estimated as shown in fig.4.

At 400°C mesophase doesn't appear yet, but at 430°C fine mosaic structure suddenly develops over all the faces. The evolution of gases from 400°C to 430°C was as follows. H_2O:0.52mol/MW, CH_4:0.55mol/MW, H_2:0.02mol/MW, CO:0.04mol/MW (MW is assumed to be 1380). That is to say only a very small amount of evolved gases could be observed, indicating that total feature of the molecular structure of 430°C carbonized sample is nearly same as that carbonized at 400°C except a little increase of ether linkage and of ring formation with demethanation. The large aromatic condensed ring structure does not develop at all at 430°C, nevertheless mesophase develops all over the sample. Namely the formation of mesophase doesn't necessitate the existance of large aromatic condensed ring structure, but it can be formed from rather planer large molecules.

(References)

1) Brooks, J.D., Taylor, G.H., Chem. and Phys. of Carbon, vol.4, 243 (1968)
2) White, J.L., AirForce Report, No.SAMSO-TR-74-93 (1974)
3) Yamashita, Y., Ouchi, K., Nenryokyokaishi (J. Fuel Soc. Japan), 53, 1064 (1974)

Fig.3 Change of diphenylether type oxygen at 1200 cm^{-1}

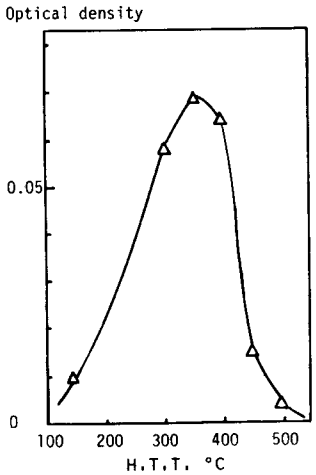


Fig.4 Model of carbonization up to 400°C

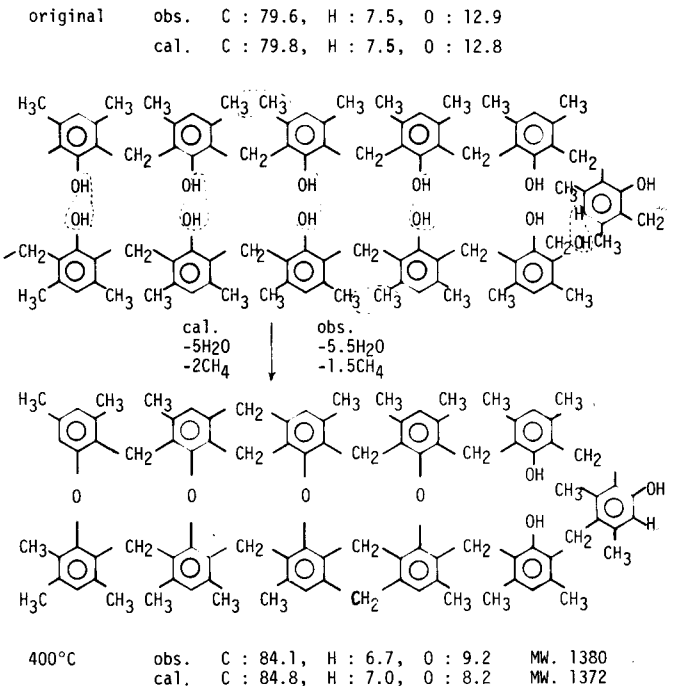


Table 1 Structural indices of pyridine soluble part of carbonized sample at 400°C

	C	H	O	MW	fa	Hau/Ca	σ
Observed	96.8	91.9	7.9	1372	0.71	0.94	0.78
Model	97	96	7	1380	0.67	1.00	0.83

	Ca	Cal	Ca (us)	Cal (us)	polym. degree	Ra	R_T	R_h
Observed	68.9	27.9	6.9	2.8	10.0	9.2	17.4	8.1
Model	66	31	6	2.9	11	11	17	6

fa : Ca/C
Hau/Ca : ring condensation index
σ : substitution index
Ca : aromatic carbon number
Cal : aliphatic carbon number
Ca(us) : aromatic carbon number per unit structure
Cal(us) : aliphatic carbon number per unit structure
Ra : aromatic ring number
R_T : total ring number
R_h : ring number except aromatic one