SMALL ANGLE X-RAY SCATTERING STUDIES ON CARBONS DERIVED FROM POLYFURFURYL ALCOHOL AND POLYFURFURYL ALCOHOL–FERROCENE COPOLYMERS

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Abstract—Small angle X-ray scattering techniques have been used to characterize the porous nature of glassy carbons derived from polyfurfuryl alcohol (PFA) and from PFA–ferrocene derivative copolymers. Samples were prepared under controlled heating conditions within the temperature range 970–2500°C. For carbons produced only from PFA it is shown that each contains micropores of a narrow size distribution. As heat treatment temperature increases there is a progressive development of both pore structure and of order within the carbon matrix. A comparison is made of specific surface area results for PFA carbons as measured by small angle X-ray procedures and by CO_2 at −78°C. The small angle X-ray results for the materials produced from the iron-containing precursors indicate the presence of two distinct regions of heterogeneity in the carbon matrix. One is microporous and the other is of larger pores of a much wider size distribution. It is also suggested that these larger pores account for these carbons having lower tensile strength and higher electrical resistivity than a corresponding PFA carbon.

1. INTRODUCTION

Small angle X-ray scattering (*SAXS*) arises from the presence of heterogeneities in solid matrices[1]. In the case of porous carbons heterogeneities stem from the presence of voids within the carbon matrix. *SAXS* studies are ideally suited for characterizing glassy carbons, since although they are known to be porous they are impermeable to gases.

Glassy carbons are prepared by controlled thermal degradation of polymeric precursors at temperatures generally in excess of 1000°C. They are isotropic, non-graphitizing carbons. Reports[2–4] of previous *SAXS* studies on commercially prepared glassy carbons have shown that the total extent and physical size of the pore systems are dependent on the history of thermal degradation.

In these laboratories, attempts have been made to modify the structure and properties of polyfurfuryl alcohol (PFA) glassy carbons by the addition of iron, in the form of ferrocene derivatives, to the polymeric precursors[5, 6]. This study is aimed at investigating the effects of iron on the pore structures of these carbons prepared in the temperature range 970–2500°C.

2. EXPERIMENTAL

2.1 *Sample preparation*

Detailed experimental procedures for the preparation of the carbons are fully described elsewhere[6]. One series of carbons was prepared from pure PFA by heating it in a N_2 atmosphere at 6°C hr^{-1} to a temperature of 700°C. The temperature was then raised at 25°C hr^{-1} to 970°C. Further PFA carbons were prepared by heating some of the 970°C material to 1500, 2000 and 2500°C in a graphite resistance furnace in flowing dry Ar. A second series of carbons was prepared, under the same thermal conditions as above, from copolymers of PFA and fer-rocene derivatives. The ferrocene derivatives used were ferrocene dicarboxylic acid (FDA) and vinylferrocene (VF). All samples were rods of diameters from 1·5 to 3·0 mm.

2.2 *Small angle X-ray measurements*

All small angle X-ray measurements were made with a Kratky camera using monochromatic CuKα radiation. Rods of the samples were selected to ensure that they were as near to the optimum thickness as possible, that is they gave maximum scattering intensities. Small deviations from the optimum thickness were corrected by a method described by Williams[7]. All intensity data were normalized against the scattered intensities of a uniform plate of a commercially prepared glassy carbon (Tokai GC-30) which served as a standard. At comparatively high angles the data were corrected for deviations from Porod's Law[8]. It has been suggested that these deviations are due to anisotropic fluctuations in density within the carbon matrix[3, 9].

2.3 *Porosity*

The density of the carbons in mercury (ρ_{Hg}) was measured using an Aminco mercury porosimeter. The X-ray density (ρ_X) was estimated from the position of the (002) reflection obtained from wide angle X-ray profiles[10]. From these values the pore volume fraction (porosity) was calculated as follows

$$c = 1 - \rho_{Hg}/\rho_X. \qquad (1)$$

3. ANALYSIS AND INTERPRETATION OF *SAXS* DATA

There are several excellent reviews on the theory of the analysis of *SAXS* intensity profiles[1, 11, 12]. In this study four "primary" parameters were used to characterize the carbons. These parameters pertain to the following

methods of analyses:

(i) radius of gyration (R_g) which is calculated from a plot proposed by Guinier, i.e. log intensity $J(s)$ vs s^2 where $s = \sin 2\theta/\lambda$. According to the theory of Guinier such a plot should be linear over a large angular range;

(ii) length of coherence (l_c) which is defined by

$$l_c = \int_0^\infty J(s)\,ds \Big/ \left(\pi \int_0^\infty sJ(s)\,ds\right); \qquad (2)$$

(iii) range of inhomogeneity (l_m) which is defined by

$$l_m = \int_0^\infty sJ(s)\,ds / [2\pi \lim_{s\to\infty} s^3 J(s)]. \qquad (3)$$

The integrations involved in eqns (2) and (3) were performed by planimetry and were corrected for termination effects[13].

(iv) Correlation distance, a, which has been shown to be similar to l_m [1] but it is calculated by a comparatively simple procedure not involving integration. Williams[7] has devised a method for obtaining a directly from line collimated data. It is a modified form of the Debye approach[14]; a plot of $J(s)^{-2/3}$ vs s^2 is made and the parameter is obtained from the slope and intercept of the resulting straight line.

Secondary parameters, d_{voids} and d_{solid} can be calculated from l_m or a provided the volume fraction of the pores, c, is known. The parameter d_{voids} corresponds to the average dimension of segments in the voids and is given by

$$d_{voids} = l_m/(1 - c). \qquad (4)$$

Similarly d_{solid} is defined as a measure of the average distance between pore walls within the carbon matrix. It is given by

$$d_{solid} = l_m/c. \qquad (5)$$

The third secondary parameter is specific surface area which for these experimental conditions is given by

$$S_p = 4 \times 10^4 c(1 - c)/l_m \rho_{Hg} \, m^2/g. \qquad (6)$$

It has also been stated[9] that surface area and l_m (and, hence, d_{voids} and d_{solid}) can be considered as parameters which are unambiguous for both dense and dilute systems, in contrast to R_g and l_c for which the exact meaning is in question.

4. RESULTS AND DISCUSSION

Typical intensity data obtained in this investigation are plotted in Fig. 1, which shows the profiles for both a PFA glassy carbon (2500 PFA) and a carbon prepared at 2500°C from an iron-containing copolymer precursor (a copolymer of 1 wt% of vinyl ferrocene and PFA).

It was found that all glassy carbons prepared from PFA alone yielded curves of a similar shape to that shown for 2500°C PFA. At extremely small angles there is a slight upward trend of scattered intensity, which is probably due
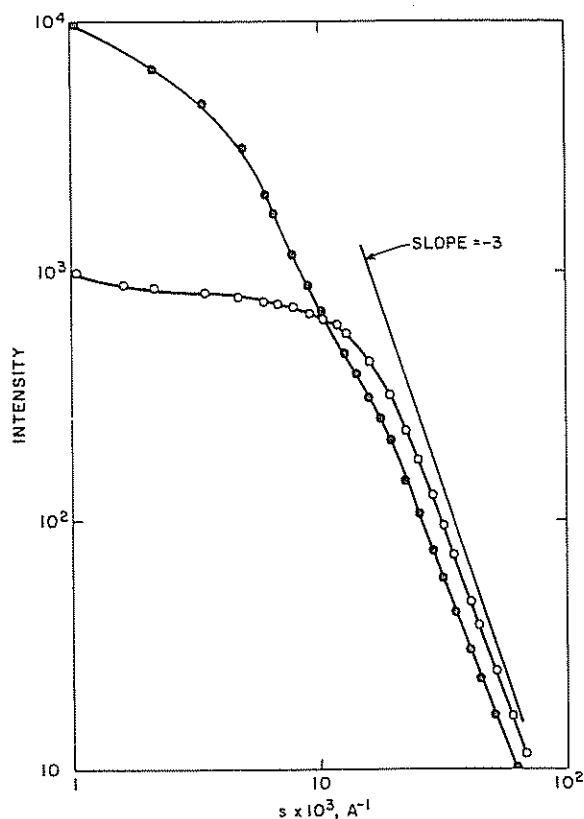

Fig. 1. Scattering curves for 2500°C PFA, O, and 2500°C (PFA + 1% VF), ●.

to the presence of large voids. This region is then followed by a portion of the curve which is plateau-like. Generally data from this region follow the Guinier Law. For the PFA carbons the law held over a large angular region, which indicates that the distribution of pore size for each sample is narrow. At higher angles, where there is a sharp decrease of intensity with increasing angle, Porod's Law is very nearly followed. However, no data exhibited an exact slope of -3. In general, it was observed that the lower the heat treatment temperature (HTT) the greater the deviation from Porod's relationship, that is a slope of -3. This supports the suggestion that the anisotropic density fluctuations decrease with increasing HTT[3]. As stated previously, a correction was made to the diffraction profiles to compensate for these deviations prior to calculation of the structural parameters.

The scattering curve for the carbon produced from the vinyl ferrocene–PFA copolymer (Fig. 1) is typical of all those obtained for carbons produced from the iron-containing precursors. The curve is not wholly smooth. At small angles $(s < 1\cdot0 \times 10^{-2} \, A^{-1})$ the scattered intensity is always large for this type of carbon, much larger than for the corresponding PFA carbon. However, there was no correlation between the magnitude of the intensity and HTT or the nature of the ferrocene derivative precursor. It is suggested that these phenomena are the result of the presence of irregular heterogenities. Guinier plots for these carbons are comparatively poor; the law only held over a very small angular region, suggesting again that the pore distribution is somewhat broad. At higher angles, where Porod's Law is approximated, the slope of the scattering profile is the same as the corresponding PFA

carbon. This suggests the presence of small, more regular, heterogeneities of a size similar to those in the PFA carbon.

Kammereck *et al.*[6] have shown that at temperatures below 1000°C these iron-doped carbons contain large domains of iron and iron compounds. On heating to higher temperatures these domains migrate from the carbon matrix giving rise to comparatively large discontinuities. In addition, there is evidence that this "doping" treatment leads to catalyzed graphitization and presumably to further structural reorganization[6, 15, 16].

Table 1 lists the small angle structural parameters evaluated for the PFA carbons and Tokai GC-30. The values found for this latter carbon are similar to those found for other commercially produced glassy carbon[3]. Since the Guinier plots for all these materials are linear over a wide angular region, it can be assumed that they contain micropores of a comparatively narrow size distribution. The values of a and l_m, which should be the same; both show the same trend but a is always larger than l_m and its use to estimate the secondary parameter leads to slightly larger values of d_{voids} and d_{solid} and smaller values of surface area. We found that this modified Debye method, which involves only one plot, can be used successfully to characterize glassy carbons.

All these primary parameters increase with increasing *HTT*, suggesting a development of the pore structure. The changes are most marked between 970 and 1500°C which must be due, in part, to the final stages of chemical degradation of the carbonized polymer. It is interesting to note that the 1500 and 2000°C samples are very similar and

only on subsequent heating to 2500°C is the structure markedly changed.

Table 2 shows the effect of *HTT* on the porosity and the secondary structural parameters calculated for these carbons.

The average void size and the intervoid distance show large increases accompanied by a large decrease in specific surface area. The reordering of the carbon matrix in this temperature range is also reflected in the results reported in Table 3. The d_{002} spacing decreases from 3·83 to 3·51A and L_c [the apparent crystallite size normal to the (002) planes] increases from 12 to 20A. Heating to 2000°C results in very small changes in the small angle parameters and the d_{002} spacing. However, some reordering takes place since there is an increase in L_c. Changes in the (*SAXS*) parameters are once again significant on further heating to 2500°C.

A comparison can be made with surface areas of PFA carbons determined from CO_2 adsorption isotherms measured at −78°C. Surface areas were calculated using the BET equation and a molecular area for CO_2 of $20·7A^2$[17]. As is seen in Table 4, surface area goes through a maximum at about 800°C. Samples prepared at 1500°C and above have little or no area available to CO_2 at −78°C. These results are in contrast to those obtained by *SAXS*. It shows the cavity-aperture nature of the PFA carbons. *SAXS* results confirm that large surface areas continue to be present in the cavities for *HTT* up to 3000°C. On the other hand, the aperture opening decreases in size such that CO_2 at −78°C cannot penetrate. It is estimated that the size must be less than about 5A for this to occur[18]. On the basis of the structural model of glassy carbon proposed by Perret and Ruland[3], it is suggested that the cavity-aperture system is a result of the entanglement of stacks of ribbon-shaped carbon layers. Points of close approach of the ribbons create the apertures in the system.

It was previously shown that from the shape of the scattering curves the iron-containing carbons are quite different from those derived from pure PFA. There is evidence for at least two modes of heterogeneities within the carbon matrix, one consisting of small pores similar to those found for PFA carbons and another of large irregular heterogeneities of a wide size distribution. However,

Table 1. Small angle parameters for PFA glassy carbons and Tokai GC-30

Parameter in A	Heat Treatment Temperature, °C				Tokai GC-30
	970	1500	2000	2500	
l_m	6	10	11	14	18
a	7	13	15	17	19
l_c	8	17	18	20	19
R_g	5	12	13	15	20

Table 2. Porosity and structural parameters for PFA carbons and Tokai GC-30

Parameter	Heat Treatment Temperature, °C				Tokai GC-30
	970	1500	2000	2500	
Porosity	0.196	0.200	0.219	0.236	0.342
d_{voids}, A	8	14	14	18	27
d_{solid}, A	31	50	51	60	52
Surface Area, $m^2 g^{-1}$	660	400	380	310	350

Table 4. Equivalent surface areas of PFA carbons measured by CO_2 adsorption at −78°C

Surface Area	Heat Treatment Temperature, °C				
	700	800	900	1500	2000
$m^2 gm^{-1}$	475	505	465	14	<1

Table 3. Wide angle X-ray diffraction data of PFA and iron-doped carbons (from [6])

Sample Precursor	Heat Treatment Temperature, °C							
	970		1500		2000		2500	
	d_{002}(A)	L_c(A)	d(A)	L_c(A)	d(A)	L_c(A)	d(A)	L_c(A)
PFA	3.83	12	3.51	20	3.50	28	3.46	38
PFA-1% VF	3.43	86	3.43	100	3.42	100	3.39	123
PFA-10% VF	3.37	166	3.38	170	3.38	181	3.37	201
PFA-3% FDA	3.40	92	3.41	104	3.39	111	3.39	134

Table 5. Small angle parameters for PFA and iron-doped carbons prepared at 2000 and 2500°C

Parameter in Å	PFA		1% VF		3% FDA		10% VF	
	2000	2500	2000	2500	2000	2500	2000	2500
a_1	15	17	16	17	17	17	21	26
a_2	NA	NA	42	40	36	58	36	75
l_m	11	14	19	22	19	37	20	49
l_c	18	20	65	65	53	90	53	112
R_g	13	15	25	26	22	31	24	33

there are problems in the quantitative interpretation of *SAXS* profiles of multiphase systems. Carbons prepared from iron-containing copolymers can have at least four phases: iron compounds, turbostratic carbon, graphitic carbon and voids. The graphitic phase is present because these carbons have undergone catalyzed graphitization[6, 15, 16]. To remove the possibility of iron compounds confusing the interpretation, only those samples which contain negligible iron have been used for the quantitative analysis, that is those prepared at 2000 and 2500°C.

It can be shown for these carbons that the scattering is derived almost totally from carbon-void interfaces and very little from carbon–carbon interfaces. That is, for a multiphase system[19]

$$\lim_{s \to \infty} s^3 J(s) \alpha S_{12}(Q_1 - Q_2)^2 + S_{23}(Q_2 - Q_3)^2 + S_{13}(Q_3 - Q_1)^2$$

(7)

where S_{ij} is the interface area between phases i and j and $Q_{1,2,3}$ are the densities of the three phases: voids, graphitic carbon and turbostratic carbon. Now since Q_2 and Q_3 must be very nearly equal then $(Q_2 - Q_3)$ must be very small and $(Q_1 - Q_2)^2$ is very nearly equal to $(Q_3 - Q_1)^2$. Hence, eqn (7) reduces to

$$\lim_{s \to \infty} s^3 J(s) \alpha K(S_{12} + S_{31}).$$

(8)

Therefore, the greater part of the scattering comes from the combined carbon-void interfaces.

Table 5 lists the small angle parameters evaluated for the 2000 and 2500°C carbons prepared from the iron-doped polymer precursors. It is noted that there are two values of a for each sample. This arises from the observation of two distinct slopes in the modified Debye plots. Although the absolute values quoted may be questionable, this observation suggests the presence of two distinct void-carbon distances. There is similarity between the a values computed for 2000 and 2500°C PFA and the a_1 values found for the 1% VF and 3% FDA carbons, which suggests that the iron has had little effect on the micropore system. However, for the 10% VF carbons there is a marked difference. Further, as heat treatment is increased from 2000 to 2500°C the mean micropore size for this material is significantly enlarged. It is interesting to note that the a_2 value for 1% VF at 2000°C is larger than that found for the 3% FDA and 10% VF samples. On further heat treatment to 2500°C the mean size of these large pores is almost unaltered for 1%VF; yet it is very much

increased for 3% FDA and 10%VF. This shows that the composition of the precursor does have a large effect on the structure of the carbon subsequently produced.

It is somewhat difficult to give a definitive interpretation for the other *SAXS* parameters listed in Table 5. Since l_m and l_c are estimated by procedures involving integration [eqns (2) and (3)], they can only be considered as some measure of an overall mean pore size which is of limited value for analysis of such bimodal pore systems. It also means that any secondary parameters calculated from l_c would be meaningless. In addition, it was stated earlier that the R_g values found for these carbons are not reliable because their Guinier plots are linear only over a short angular range. However, these results do reflect the general observations made previously. For example, carbons from iron-doped precursors contain much larger pores than those from pure PFA. In addition, whereas heat treatment from 2000 to 2500°C has comparatively little effect on the pore structure of the 1% VF carbon, there are marked increases in pore sizes for 3% FDA and 10% VF carbons.

Kammereck *et al.*[6] have observed that the iron-containing carbons prepared at elevated temperatures are more brittle and have lower tensile strengths than the glassy carbons produced from pure PFA under the same conditions. The presence of the large irregular voids suggested by this study would explain to some extent this reduction in tensile strength. Also, the larger voids would be a contributing factor to the higher electrical resistivities reported for the carbons produced from the iron-doped copolymers at higher *HTT*.

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