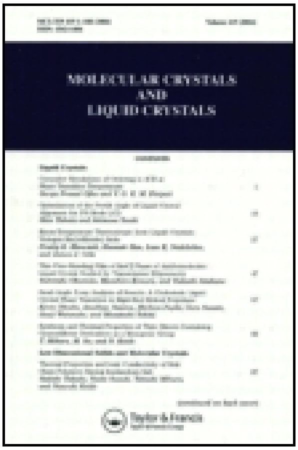

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Pore Structure in Carbon Fibers Prepared from Polymer Blend

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PORE STRUCTURE IN CARBON FIBERS PREPARED FROM POLYMER BLEND

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Pore structure in carbon fibers prepared from a polymer blend has been investigated by measurements of small-angle X-ray scattering (SAXS). Generally, an application of the SAXS method to analyze the pore structure of carbon materials is not so easy, because that in carbon materials is complex and structure correlation between pores cannot be neglected. The polymer blend method does not use the activation process and makes it possible to control the size and concentration of pores dependent on the pore forming resin. It can be said that the present result is positioned as one of the most successful results among pore structure determinations by SAXS, and that the result will become a standard for the study of pore structure in carbon materials.

Keywords: porous carbon; pore structure; small-angle X-ray scattering

INTRODUCTION

Most of specific properties of carbon materials are closely connected with the existence of pores and their form. Consideration of the pore structure in carbon materials is important and interesting from scientific and practical viewpoints. In order to investigate the pore structure in carbon materials, we have carried out small-angle X-ray scattering (SAXS) measurements. However, an application of the SAXS method to analyze the structure of carbon materials is not so easy, because the pore structure in carbon materials is complex and the structural correlation between pores cannot be neglected. It is an ideal condition for SAXS measurements that the size and shape of pores are uniform and the concentration of pores is dilute so that the structural correlation can be neglected. In the present study, we used carbon fibers prepared from a polymer blend which consists of carbon precursor resin and pore forming resin. The polymer blend method is a novel technique to make porous carbon fibers without an activation process [1], and it is possible to control the size and concentration of the pores depending on the pore forming resin.

Because SAXS occurs by inhomogeneity of the local electron density in the sample, it is necessary to consider the influence of adsorbed molecules when the pores are open. Samples with closed pores are convenient to discuss definitively the pore structure, because the experimental operations become easy, and the interpretation of the results is expected to be easy. Hence, it is a favorable condition that pores made by this method are closed. This carbon material has a possibility to be used as a standard sample for the determination of the pore structure by SAXS measurements.

EXPERIMENTAL

Samples

The polymer blend of the present study was made of a mixture of novolac-type phenol-formaldehyde resin (Gun-ei Chemical Co. Ltd.) as the carbon precursor and polystyrene microbeads (JSR Corporation) as the pore forming resin. The content of the polystyrene was 10% in weight, and the grain size was 30 nm. This polymer blend was spun, stabilized and carbonized. Details of the preparation of the fibers are reported elsewhere [2]. Three kinds of samples, non-carbonized and heat-treated at 500 and 1000°C, were used for the SAXS measurements. The diameter of these fibers is about 0.1 mm, whose size does not affect the small-angle X-ray scattering intensities in the present measurable region.

SAXS Measurements

The SAXS intensities were measured by using an apparatus that had been designed and constructed in our laboratory [3]. A point-focused X-ray beam was adopted in the diffractometer. To prevent scattering and absorption of X-rays by air, all X-ray paths were kept in vacuum of about 10^{-1} Pa. The wavelength of the incident X-rays was 0.15406 nm ($\mathrm{CuK}\alpha_1$). A position-sensitive proportional counter (PSPC) was used as the detector. The distance from a sample to the detector was 1170.5 mm and the accumulation time for the intensity measurement was 1800 seconds. Fiber samples were cut short in the direction perpendicular to the fiber axis. For SAXS measurements, the cut-samples were filled in a sample-cell with mylar films for the windows. The thickness of the cell was 1.5 mm.

RESULTS AND DISCUSSION

We tried first to analyze the pore structure by the Guinier method for their SAXS intensities. From the inclination of the Guinier plot, we can estimate the gyration radius value (R_g) of the pores. The Guinier plots are shown in Figure 1. However, we should take care of the fact that the Guinier analysis is effective in the region of $s = 0 - (1/R_g)\,\mathrm{nm}^{-1}$ [4]. The s^2-values corresponding to $(1/R_g)^2$ are shown by broken lines in the figure. We obtained the values of 7.1 nm for HTT500°C and 6.9 nm for HTT1000°C, respectively.

Though R_g values of both samples were almost the same, the Guinier plots differ from each other as shown in Figure 1. The dots for HTT500°C deviate from the regression line in relatively small s^2-region, while those for HTT1000°C remain on the regression line over a wider range. This fact shows that the shapes of the pores for the two samples are different and that the shapes of the pores in HTT1000°C are relatively long and more slender than the ones for HTT500°C. The information on the shape of the pores is included over a lager region of the scattering curve than the

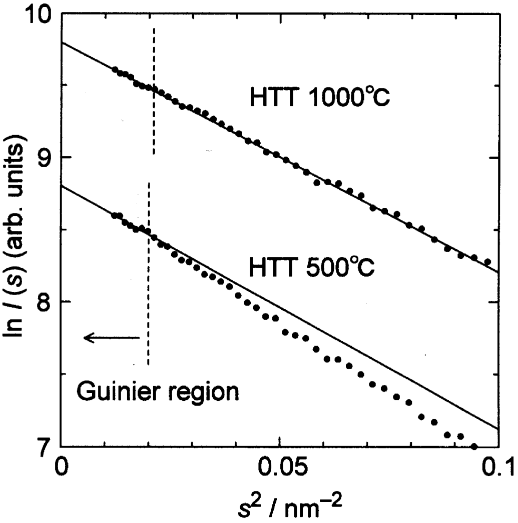


FIGURE 1 Guinier plots. The plot for HTT 1000°C is displaced by +1 unit for clarity.

Guinier one [4]. One useful analysis for the slender shapes is the cross-section plot [5,6]. We can estimate the gyration radius (R_c) of the bottom of the cylinder from the plot. From the results, we obtained 5.0 and 4.1 nm as the R_c values and we also obtained 7.1 and 5.8 nm as the radius r of the column bottom for HTT500 and 1000°C, respectively. By using the values of R_g and r, we can determine the value of the length of cylinder (L) as 17.4 and 19.2 nm for HTT500 and 1000°C, respectively. In the case of HTT 1000°C, the ratio of the diameter ($2r$) and the length (L) becomes about 1:1.66. It is known that in the case of the column with the ratio of 1:1.65 the Guinier plot shows the linearity over a wide region [4]. Therefore, it shows a reasonable result.

Secondly, we obtained R_g values by use of the distance distribution function (DDF), because the Guinier regions are narrow in the present measurable region. The DDFs for HTT500 and 1000°C are shown in Figure 2. The R_g values become 7.2 and 6.7 nm for the both samples, which agree well with the ones obtained by the Guinier analysis. The D values at which the *P(r)* curve crosses the 0 line corresponds to the longest distance of the pore. The distances refer to 22.6 and 23.0 nm for both samples. The results from the analysis of the DDF are consistent with the Guinier plots and cross-section plots.

As the main reason why the shape of the pores becomes slender in spite of being spherical in their starting shape, we expected that the grains of the pore-forming resin, polystyrene, will be deformed in shape by spinning.

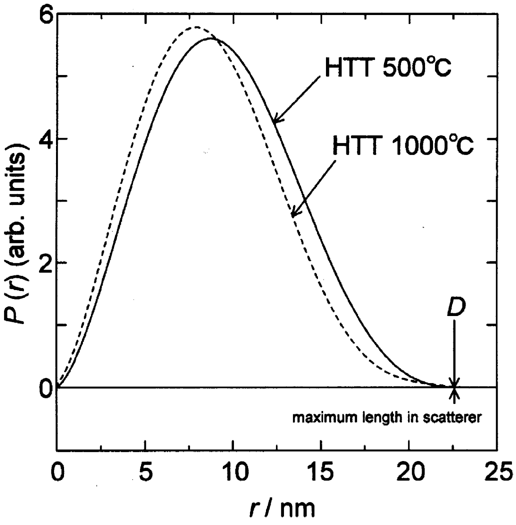
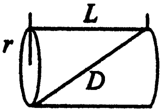


FIGURE 2 The distance distribution functions $P(r)$.

TABLE 1 Structure Parameters of Carbonized and Non-carbonized Fibers

Sample	R_g by G.P.*	R_g by DDF	r	L	D
non-carbonized	—	14	—	—	47
HTT 500°C	7.1	7.2	7.1	17.4	22.6
HTT 1000°C	6.9	6.7	5.8	19.2	23.0

*G.P. means the Guinier plot. (unit: nm)



We have also measured the SAXS intensity for the non-carbonized fiber. From the analysis, we obtained the value of 14 nm as the R_g and the value of 47 nm as the longest distance for the pore forming resin. It was found that the pore-forming resin is changed at the spinning process; the deformation, of course, is caused by heat-treatment. The structure parameters of the three samples are summarized in Table 1.

To the best of our knowledge, there has been no investigation of the pore structure in carbon materials by use of SAXS methods which is more comprehensive than the present study. The sample made by the polymer blend method is expected to become a standard sample for study of the pore structure in various carbon materials.

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