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Pore morphology in pressurized lignite coal: A small angle x-ray scattering investigation

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The morphological changes in lignite coal at two different pressures, using small angle x-ray scattering, have been investigated. All the scattering profiles are interpreted in terms of surface fractal morphology. It is observed that the surface fractal dimension does not change appreciably under the experimental pressure range, while the volume of micro-cracks and inter-particle pore space is reduced with increasing pressure. By and large, the constant value of the surface fractal dimension of all the specimens, as calculated from the scattering profiles, indicates that the roughness on the pore coal interface remains almost unaffected under the experimental pressure range. The validity of single scattering approximation for this experiment has also been confirmed by the observation of the identical nature of the small angle scattering profiles with respect to change of wave lengths, namely, 0.154 nm. (Cu K_α) and 0.072 nm (Mo K_α), of the probing radiation.

1. Introduction

Among the naturally occurring disordered materials, coals are particularly interesting because of their applications in thermal power plants and in other industries. The rank of a coal depends on various factors such as the carbon content vis-a vis the contents of oxygen and hydrogen and also on the pore morphology and on the pore-coal interface [1]. Small angle x-ray scattering (SAXS) is one of the useful nondestructive techniques to characterize the pore morphology of different porous materials as well as to characterize the fractal nature of different pore matrix interfaces [2–7]. The pioneering work on coal structure by Bale *et al*. [4] first indicated the surface fractal morphology in Beullah lignite coal. After that, number of SAXS studies have been carried out to characterize coal structure. Nemmers *et al*. [7] have studied the *in situ* SAXS from coal during fluid extraction and interpreted the results in terms of the micro pores and porosity. Kalliat *et al*. [2] measured the SAXS intensities of natural coals in an attempt of correlating the rank of a coal with the shape of the corresponding scattering profile as well as with the relative fractions of micro, meso and macro-pores [2]. Bendetti *et al*. [1] have investigated coal rank with the help of the shape of the SAXS profiles.

The effect of external parameters on fractal system is of current interest. Recently Sorensen *et al*. [8] have studied the scaling behavior of the structure factor of fractal soot composites under compression. However, effect of compression/pressure, on the microstructure of a fractal system like coal, is yet to be investigated and the present work is a step in that direction. In this paper, we report the small angle x-ray scattering investigations performed on as-received and pressurized (at two different pressures) lignite coal.

2. Experimental procedure

2.1. Samples

Lignite coal specimens were collected from Neyveli lignite Corp. (N.L.C), Tamilnadu, India. As-received specimen was in powder form (sample 1). Pellets of thickness ∼1.2 mm, and 1.4 cm diameter were made after pressuring at 54.7 Mpa (sample 2) and 164.0 Mpa (sample 3) from the powder samples for performing SAXS experiments.

2.2. SAXS experiment

SAXS experiments were performed using a rotating anode based Rigaku (Japan) machine, which is a three slit system. Intensities were measured by a scintillation counter with a pulse height analyzer. Nickel filtered Cu K_α ($\lambda = 0.1541$ nm.) and Zirconium filtered Mo K_α ($\lambda = 0.072$ nm.) were used as the incident x-ray source. The scattered intensities, $I(q)$, were recorded as a function of scattering vector length, q ($= 4\pi \sin\theta/\lambda$, 2θ being the scattering angle and λ being the x-ray wavelength.). The absorption corrected SAXS data are shown in Fig. 1. Fig. 2 depicts the

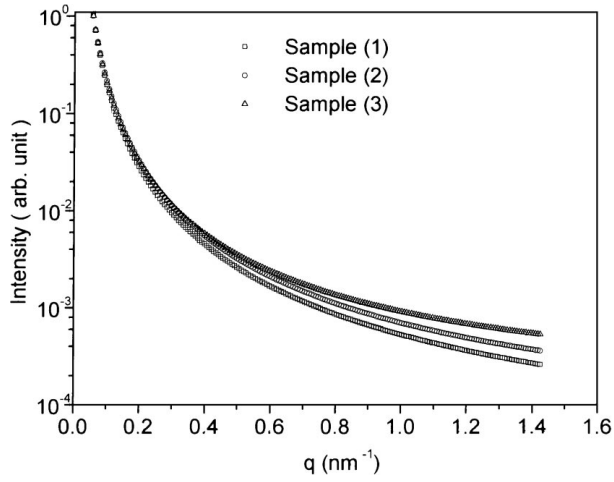

Figure 1 Absorption Corrected SAXS data for as received and pressurized samples. The profiles are normalized to unity at $q \sim 0.05\ \mathrm{nm}^{-1}$ to indicate the difference in the functionality in the profiles for the three samples.

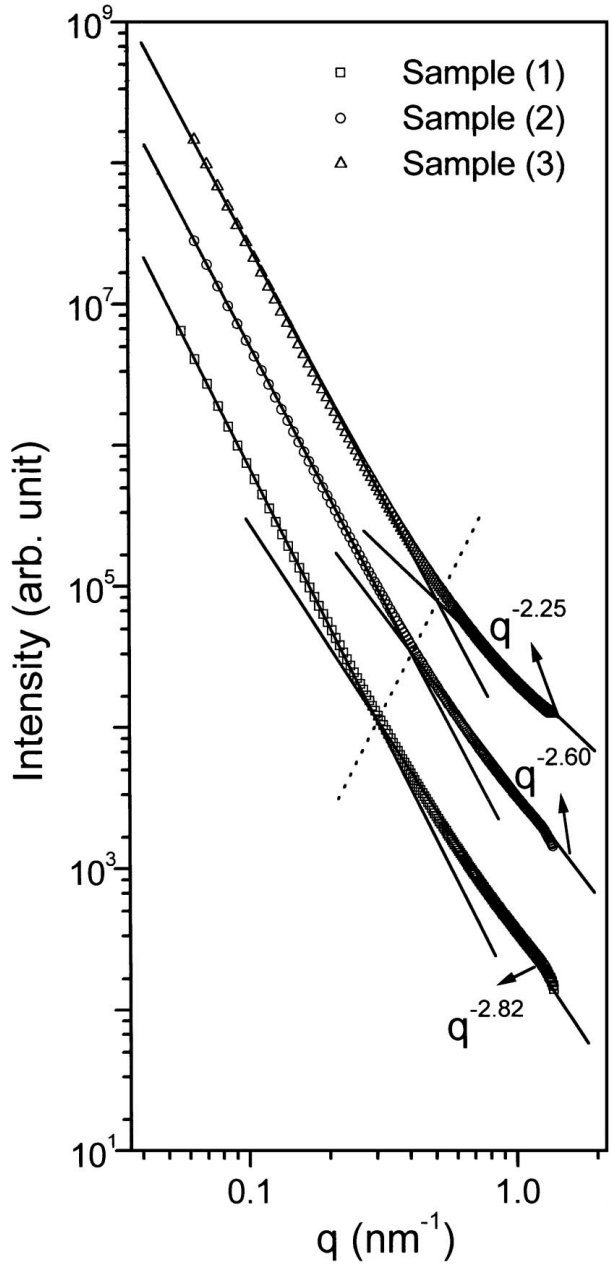

Figure 2 Collimation and absorption corrected SAXS data in log-log scale. The profiles of samples 2 and 3 are shifted vertically to avoid overlapping.

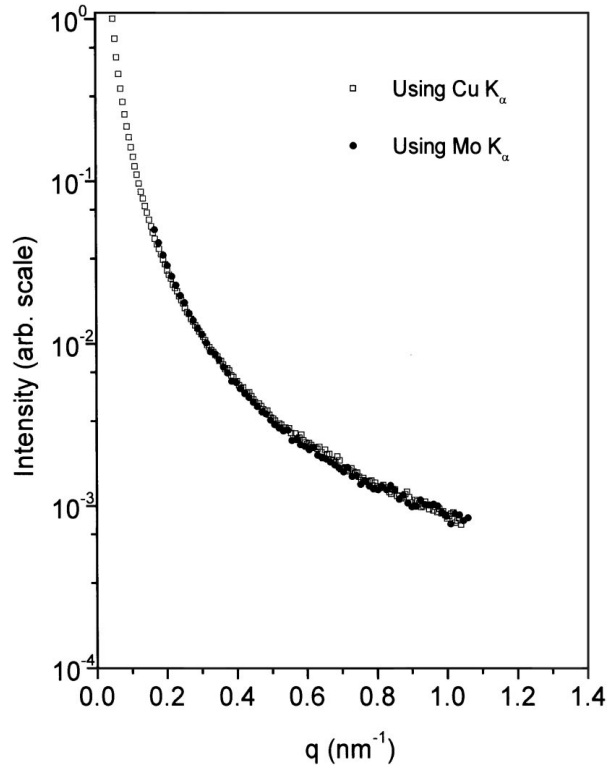

Figure 3 The comparison of the functionality of the SAXS profiles for sample 1, one using Cu K_α and the other using Mo K_α as incident radiation.

absorption and the slit collimation corrected [9] data in log-log scale. Fig. 3 shows the comparison of the scattering profiles of sample 1 by using Cu K_α and Mo K_α radiation.

3. SAXS data analysis

Coal is a three-dimensional porous solid with almost uniform electron density inside the particle and with fractal surfaces at the pore matrix interfaces [4] and can be regarded as a two-phase system consisting of a coal matrix of uniform density and the void space. Roughness on the void surfaces are such that the surfaces can be viewed as a system of surface fractals. The small angle scattering intensity $I_s(q)$ from a surface fractal system is given by [10]

$$I_s(q) = C_s q^{-1}\left[1 + (q\xi_s)^2\right]^{(d_s-5)/2} \times \sin[(d_s - 1)\arctan(q\xi_s)] \qquad (1)$$

where ξ_s is the upper cut off length for surface fractal, i.e., the length scale above which the system does not show the fractal nature , C_s is a scale factor and does not depend on q. For $q\xi \gg 1.0$, the above equation reduces to

$$I_s(q) \sim q^{-(6-d_s)} \qquad (2)$$

The value of d_s, the surface fractal dimension of the system, determines quantitatively the fractal nature of a surface and its value lies between 2.0 and 3.0 and hence the exponent of q in Equation 2 can take value between 3.0 and 4.0. For a ideally smooth surface $d_s = 2$

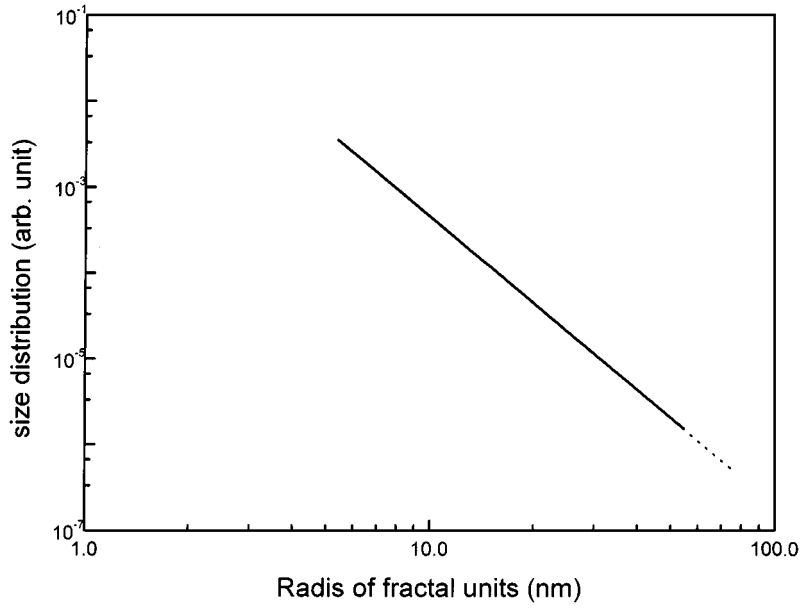

Figure 4 Size distribution of the fractal units in the coal specimen-3.

and then the scattering intensity tends to Porod limit i.e. $I(q) \sim q^{-4}$.

In contrast to surface fractal object, for or a mass fractal object (which are often aggregates of sub-units) also the scattering profile shows a power law behavior as Equation 2 but with an exponent which is less than 3. Hence the scattering intensity for a mass fractal system can be written as [11]

$$I_{\mathrm{m}}(q) \sim q^{-d_{\mathrm{m}}} \tag{3}$$

where d_{m} is the mass fractal dimension and is less than 3.0.

The size distribution of the fractal units also can be expressed as a power law [4]

$$\rho(R) \sim R^{-(d_{\mathrm{s}}+1)} \tag{4}$$

where R is the radius of a sphere inscribing a fractal unit. Fig. 4 presents the size distribution of the fractal units in the coal specimen-3 as calculated using the estimated fractal dimension. The distributions for the other specimens are not shown because of their almost identical nature.

4. Results and discussion

From Fig. 2, it is evident that for all the samples, the scattering profiles show linear regions (region I) at low q value ($\sim$0.05 nm^{-1} to $\sim$0.5 nm^{-1}) and a region (region II) ($\sim$0.5 to $\sim$1.4 nm^{-1}) with a slight deviation from linearity and with relatively smaller slope value. The value of the slopes of the two regions for the samples 1, 2 and 3 are shown in the Table I. The region (I) of the profiles being a linear region with slope value between 3 and 4 and being extended over a wide q range ($\sim$0.05 nm^{-1} to $\sim$0.5 nm^{-1}), reflects the surface fractal morphology of the pore coal interface with surface fractal dimension $d_{\mathrm{s}} \sim 2.4$. It is interesting to note here that the slope of the region I for all the specimens remain almost unchanged at different pressures which indicates that the surface fractal dimension vis-a-vis the roughness on the pore coal interface remain unchanged under the experimental pressure range. The slope being nearly equal to -3.6 indicates a surface fractal dimension $\sim$2.4 of the pore coal interface. The cross over from region (I) to region (II) occurs in the vicinity of $q \sim 0.5\,\mathrm{nm}^{-1}$. The cross over point shifts (as shown by the broken line in Fig. 2) towards higher q value, from $\sim$0.30 nm^{-1} to $\sim$0.55 nm^{-1} (i.e. from a length scale of $\sim$20.9 nm. to $\sim$11.5 nm.) with increasing pressure which indicates that the basic unit of the surface fractals becomes smaller with increasing applied pressure. Although the slope of the region (I) remains unaffected by compression, the sharpness of the region (II) of the scattering profiles is reduced with increasing pressure. A linear fit of the profile, in the double-logarithmic scale, in the region (II) shows that for the specimen 1, the tail follows a $q^{-2.82}$ behavior while that for the specimens 2 and 3 show $q^{-2.60}$ and $q^{-2.25}$ variation respectively. These observations can be interpreted as follows.

As the pressure increases, the volume of the inter-particle pore and interconnected micro-cracks in a coal sample decreases, which in turn decreases the sharpness of the region (II). Here it is interesting to note that for all the scattering profiles, the crossover occurs from a slope value which is less than -3.0 to a slope value which is greater than -3.0, crossing the border value of -3.0. But it is not possible to conclude whether the inter-particle pore and the micro-cracks also form a pore fractal (i.e., a mass fractal object where mass is replaced by pore) morphology inspite of the signature of linearity of the region (II) because of the limited q-range of region (II).

TABLE I The slopes of the two regions of Fig. 2

Specimen	Slope of region (I)	Slope of region (II)
Specimen 1	-3.65 ± 0.10 ($d_s \sim 2.35$)	-2.85 ± 0.10
Specimen 2	-3.59 ± 0.10 ($d_s \sim 2.41$)	-2.60 ± 0.11
Specimen 3	-3.60 ± 0.10 ($d_s \sim 2.40$)	-2.25 ± 0.11

To check the validity of single scattering approximation and the effect of multiple scattering [12] for the present case, SAXS experiment was carried out at two different wavelengths 0.154 nm (Cu K_α) and 0.072 nm (Mo K_α) for sample 1. The close similarity in the functionality of the two profiles recorded at the above two different wavelengths indicates the validity of the single scattering approximation for this present experiment.

5. Conclusion

The effect of external pressure on pore morphology in lignite coal has been investigated by small angle x-ray scattering that reveals the surface fractal nature of the pore-coal interface. The fractal dimension does not change appreciably under the experimental pressure range though the size of the interconnected microcracks decreases with increasing pressure. This investigation will help in understanding the various physical properties like adsorption, which affect the moisture retention capacity, of coal which depends on the pore morphology and the fractal dimension. As pressure is an important parameter to determine the quality of coal inside a coal mine, the present investigation may help in correlating the quality of coal and with its pore structure.

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