

MICROSCOPIC OBSERVATION AND IMAGE ANALYSIS FOR THE EVALUATION OF TOPOLOGICAL FEATURES OF SINGLE COAL PARTICLES IN PYRIDINE

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ABSTRACT

Time dependent solvent swelling behavior of six different rank coal particles in pyridine was observed by the application of a microscopy combined with a video camera: the time-resolved swelling ratios were evaluated quantitatively by an image analysis system. The topological features of the coal particles with three dimensional macromolecular structure in pyridine are classified into four types among six different rank coals. We also found that the solvent-swelling ratios of single coal particles at quasi-equilibrium state are rank dependent.

INTRODUCTION

Coal is a complex and heterogeneous material. This heterogeneity leads to difficulties in accurately characterizing its structure, so that there is no universally accepted model for the chemical structure of coal. However, it appears to have been generally conceived that coal consists of a small chain substituted aromatic and hydroaromatic units linked by covalent bonds and non-covalent bonds like hydrogen bonding and van der Waals interactions, with entanglements of skeletal chain structure to form a three-dimensional network structure [1-4]. Apart from its three-dimensional cross-linked macromolecular structure, coal is viscoelastic and largely does not dissolve in conventional solvent, but swells when exposed to a solvent. The extent of swelling is thought to be controlled by the cross-link density and the magnitude of its interaction with the solvent [5-7]. In general, the density of cross-link is evaluated in terms of volumetric swelling ratio (Q_v), defined simply as the swollen sample volume divided by the unswollen sample volume. In evaluation of coal swelling, three methods of measurement have been adopted: volumetric measurement based on packed bed [8-10]; gravimetric measurements using solvent sorption from the vapor phase [11]; microscopy coupled with image analysis [12] and Malvern laser diffraction particle sizer [12] based on the measurement of particle distribution.

The important problem existing in volumetric techniques, with which the cross-link density of macromolecular level is evaluated with packed bed, is that the topological features of particles and interactions among the particles in solvent are not yet clear. Another problem of volumetric techniques is that the soluble fractions in polar solvent are present in coal. When the solvent like pyridine is introduced into the tube, a significant amount of dissolution occurs, resulting in the reduction of solvent activity. Therefore, it is clear that there is an enthusiastic need for the more reasonable method on the measurement of coal swelling in solvent on the macromolecular level. The methods based on particle size distribution measurement [12] offers a significant advantage over volumetric method, since the ambiguity of the packing of particle beds is removed, and the method employs a coal solid concentration which is sufficiently low for solubilization of the coals not to markedly affect the solvent activity. However, two implicit assumptions were made in this approach. They are particles of all sizes swell to the same average extent and the particles must not fracture or agglomerate during swelling. In practice, because of heterogeneity of coals, the distribution of equilibrium swelling ratios and the fracture exist in some kinds of coal particles, especially for the high-solvent-swelling coal. It is clear that the systematic investigation on the dynamical behavior and characteristics of single coal particle in solvent are in need for further understanding of the change of macrostructure of coal in solvent at the macromolecule level.

EXPERIMENTAL

Coal Samples. In the present study, six kinds of coal sample with different rank used in this study ranging from low rank to anthracite, were Witbank [weak coking coal, 83.1 C% (daf), Canada], Prima [coking coal, 81.0 C% (daf), Indonesia], Goonyella [coking coal, 84.6 C% (daf), Australia], Blue Creek [coking coal, 80.0 C% (daf), USA], K-9 [coking coal, 90.1 C% (daf), Russia], and Honken [anthracite coal, 93.2 C% (daf), Vietnam].

Swelling measurements on six kinds of coals in pyridine were conducted. Pyridine used in this study was of analytical reagent grade.

Experimental Apparatus and Procedure. As shown in Figure 1, the experimental apparatus consists of a microscope coupled with a TV camera system for observing and recording the behavior of the coals in solvent container. An image analysis system was used for quantitative evaluation of time-resolved swelling ratio of the single coal particles.

The microscope (Japan Olympus Co. Ltd.) fitted with a video camera provides input to an image analysis system (Japan Nireco Co. Ltd., LUZEX-3). A 6.3 \times objective was used with the microscope which, with the other optical components used, gave a magnification, at the analyzer monitor, from 20 to 100 \times objective.

Under the conditions of atmospheric pressure and ambient temperature (20 $^{\circ}$ C), pyridine (3 ml) was injected into the cell and then single coal particle was placed into pyridine and the recording was started until to the quasi-equilibrium-state of swelling. The recorded images were directly examined

and analyzed with the image analyzer. The time-resolved swelling ratio of single coal particles were evaluated with an equivalent volume converted from particle projection area under the assumption of spherical coal particle.

RESULTS AND DISCUSSION

As shown in Figure 2, Witbank coal particle (850-1000 μm) swells up to 2.47 times within 28 h. During this period the cracks largely developed, and no change was observed during an additional time exposure both in shape and size. The massive cracks may be caused by any stresses built up from the resultant swelling gradients or uneven swelling of sample. Other cracks may have been due to non-uniform swelling which causes some stresses not being sufficiently relieved. It is also likely that the stresses were caused by heterogeneities in the structure or by differences in the equilibrium swelling of different regions of the specimens. It is clear that transport process of pyridine in the coal macromolecule is greatly enhanced locally by the formation of a large discernible crack for the large specimen. This result suggests the new interface between coal macrostructure and solvent is important for solvent-swelling for high solvent-swollen coals. This phenomenon is consistent with the results of Cody and Botto [13], and Motsegood and Clarkson [28]. It is known that the chemical heterogeneity of coal leads to anisotropic swelling [18]. And coal swelling has been found to be greater in perpendicular direction to the bedding plane than in parallel to it [27]. Cracking at mineral-organic interfaces is also expected due to differential swelling of the organic matrix relative to mineral matter because diffusion of pyridine through areas is different with susceptibility differences, particularly at organic-mineral interfaces and at surface of microfractures.

As shown in Figure 3, the swelling ratio at quasi-equilibrium state of the sample with small size (210-250 μm) is 2.10 which is somewhat smaller than the larger one (2.47). The time required for reaching quasi-equilibrium state is about 10 hours. Moreover, only a few sizable cracks developed during swelling.

The reasons why the smaller sample apparently tended to reduce fracturing of the sample could be interpreted as follows: First, it caused the penetration of the swelling agent into the coal rapid and fairly uniform over the area of the sample so that uneven swelling of the sample was minimized. Second, the smaller sample has limitation of the distance over which liquid concentration gradients could develop perpendicularly to the surface, so any stresses built up from the resultant swelling gradients would be less likely to induce fracture.

For the case of Prima coal, the quasi-equilibrium swelling ratio is 2.34 for the case of smaller coal particle (210-250 μm) and 2.78 for the case of larger particle (850-1000 μm). The times for reaching the equilibrium state were about 5 h for smaller sample (210-250 μm) and 10 h for the larger one (850-1000 μm). During the swelling there is no cracks developed, the shape of the swollen coal particle samples being close to that of the initial specimens. These phenomena were different from the case of Witbank coal.

As described previously, the cracking at mineral-organic interfaces and surface of microfractures is due to differential swelling of the organic matrix relative to mineral matter because the diffusion of pyridine is through areas with susceptibility differences, particularly at organic-mineral interfaces and at surface of microfractures. The difference in solvent-swollen deformation characteristics, therefore, is caused by difference in degree of physical and chemical heterogeneity existing among the coals. The present results suggest that physical and chemical heterogeneity of Witbank coal is much larger than that of Prima coal. On the other hand, it is obvious that energetic interactions between solvent molecules and the coals play an important role in the swelling phenomena. For the coal to expand, the macromolecule chains must be able to reorient. Since the solvent-swollen coal was observed to be substantially more flexible than the dry coal, some bonds among macromolecular chains are apparently broken by solvation. The substantial decrease in modulus which occurs on swelling demonstrates that the bonding is significantly different in the dry and the swollen coal; it indicates that the effective molecule weight between crosslinks in the highly swollen coal is substantially greater than in the original dry coal. This suggests that the elasticity of the swollen sample may have much more of an entropic or rubbery nature than that of the original sample. Therefore, the difference in deformational features between Witbank and Prima is also related to the difference in energetic interactions between solvent molecular and the coal macrostructure. The present results suggest that the interactions of Witbank coal and Prima coal with pyridine are larger than that of other coals or pyridine has sufficient force to destroy the non-covalent bonds existed in Witbank coal and Prima coal.

For the case of Goonyella coal, the quasi-equilibrium swelling ratio was 1.11 for the coal particle of 210-250 μm and 1.16 for the coal particle of 850-1000 μm . The times for reaching the equilibrium state are about 16 h for the smaller sample (210-250 μm) and 20 h for the larger sample (850-1000 μm), respectively. Moreover, during swelling there is a few sizable cracks developed with distortion, and in the initial swollen stage there is a shrinking period for both particle size although the appearance of this stage is much faster in the case of small coal particle than the case of large one. These phenomena are different from the cases of Witbank coal and Prima coal. The shrinking phenomena may be caused by transition from glass to rubbery or change in amount of the coal microporosity, although it is unclear how much the change occurs.

For the cases of Blue Creek coal, K-9 coal and Honken coal, there are almost no swelling and deformation in pyridine.

The detailed discussion on above phenomena will be conducted from the view point of non-covalent interaction existed in different rank coals in the following parts.

The physical properties of solvent-swollen coal are related to its three dimensional macromolecular architecture. The dynamic nature of the macromolecular structure of coal governs the time dependence of its response during the solvent-swollen processes. The extent of swelling is thought to be controlled by the cross-link density and magnitude of interaction between coal and solvent [19-21]. The mechanism of coal swelling in polar basic solvents such as pyridine involves the disruption of hydrogen bonding cross-links of the network [29-31]. Pyridine is often used in solvent swelling

experiments on coal and, because of its basic character [5], is capable of reacting with many of the hydrogen bonds in coal to cause swelling, if these hydrogen bonds are cross-links [22]. Brenner [23] demonstrated that swelling of coals in pyridine involves the transformation of the coal from glassy to a rubbery state. In the differential scanning calorimetric investigation on solvent-swollen coals, Hall and Larsen [30] demonstrated the existence of second-order phase transitions well below room temperature. It has been hypothesized that these phase transitions are glass to rubber transitions. Usual state of coal is glassy at room temperature. When hydrogen bonds are disrupted by pyridine, the effective cross-link density decreases. There is an associated change in the viscoelastic properties of the coal as it becomes more rubbery. The degree to which coal becomes rubbery is a function of the density of hydrogen bonds disrupted and hence the solvent swelling. It is reasonable and sufficient to assume that when swollen with pyridine, the coals behave as if some or all of the hydrogen bonds or other non-covalent bonds have been eliminated. The fact that the diffusion mechanism is a strong function of the number of hydrogen bonds disrupted suggests that this in some way limits the extent to which coals can become rubbery. Solvent sorption into glassy polymers contains contributions from both concentration gradient controlled diffusion and relaxation controlled swelling. It was reported that particle size was a factor with case-II [24] behavior being observed for large particles and Fickian diffusion for small particles. Swelling of coal in pyridine involves the disruption of hydrogen bonds in the coal and the formation of bonds between the solvent and functionalities in the coal. It has also been suggested that solvent will disrupt only those coal-coal hydrogen bonds whose bond strengths are lower than those of the coal-solvent hydrogen bonds [25]. It has also been suggested that pyridine, because of its strong basicity, is capable of breaking nearly all hydrogen bonds in coal [26]. Therefore, when coal containing an appreciable amount of hydrogen bonding is exposed to pyridine, it swells to a limitation that is primarily a function of the covalent cross-link density.

As for the present study, the swelling ratio of single coal particles (850-1000 μm) in pyridine at ambient temperature versus time are 2.47 for Witbank coal, 2.34 for Prima coal, 1.12 for Goonyella coal, 1.04 for Blue Creek coal, 0.983 for K-9 coal and 1.04 for Honken coal, respectively. These results suggested that Witbank and Prima coal contain rather more hydrogen bonds, Goonyella coal has small amount of hydrogen bonds, while few hydrogen bond exists in Blue Creek coal, K-9 coal and Honken coal (As for Blue Creek coal, detailed study on oxygen-containing functionalities seems to be needed).

As to the time required for reaching to quasi-equilibrium state, for the case of 850-1000 μm coal particle size, they are 24 h for Witbank coal, 10 h for Prima coal, 16 h for Goonyella coal, respectively. For the case of 210-250 μm coal particle size, the times required for reaching to equilibrium state is almost same each other (10 h) for three kinds of coal (Witbank, Prima, Goonyella). Therefore, it seems that the diffusion velocity of pyridine molecules in the larger coal particles and relaxation velocity of the coals in pyridine are in the order: Prima > Goonyella > Witbank.

As shown in Figure 4, for the case of large particle size (850-1000 μm), the equilibrium swelling ratios are rank-dependent with decrease of carbon content from 77 to 93 wt % (daf). The pattern is consistent generally with the previous analysis on molecular weight between crosslinks [32,33] and network mobility analysis [34-35]. For the case of particle size of 210-250 μm , the change of swelling ratio with rank is similar to the case of large one.

From the observation on the recorded images, as shown in Figures 5-10, the general features of solvent-swelling behavior of the large coal particles (850-1000 μm) in pyridine seem to be classified into four types: (1) high swelling with massive crack deformation (Witbank); (2) high swelling ratio with non cracks deformation that the shape of swollen coal sample was close to that of the initial specimen (Prima); (3) no-crack shrinkage and distortion with low swelling ratio (Goonyella); and (4) no swelling with no deformation (Blue Creek, K-9, and Honken).

For comparison of the results, it should be noted that measured particles differ in size, shape and in mineral and maceral content. We observed that the distribution of equilibrium solvent swelling ratios exists in some kinds of coals. These results suggest that available data measured by conventional volumetric method may be, at most, an average expression on the equilibrium solvent swelling ratio of the coals. The systematic analysis on the distribution of equilibrium solvent swelling ratios of coals with wide range ranks is in progress in our laboratory.

CONCLUSIONS

Solvent swelling behavior of single coal particles of six different rank coals in pyridine was observed with the application of microscopy combined with video camera and the changes of solvent swelling ratio with time were evaluated quantitatively by an image analysis system. The deformation of the large coal particles seems to be classified into four types: (1) high swelling ratio with massive cracking (Witbank); (2) high swelling ratio with non-cracking and the shape of the swollen sample was close to that of the initial specimen (Prima coal); (3) non cracking shrinkage and distortion with low swelling ratio (Goonyella); and (4) non-swelling and non-deformation (Blue Creek, K-9, and Honken). In the case of coal particle size being 850-1000 μm , the quasi-equilibrium swelling ratios were 2.47 for Witbank coal, 2.34 for Prima coal, 1.12 for Goonyella coal, 1.04 for Blue Creek coal, 0.983 for K-9 coal and 1.04 for Honken coal, respectively. In the case that the coal particle size is 210-250 μm , the quasi-equilibrium swelling ratios are 2.10 for Witbank coal and 2.78 for Prima coal, respectively. On the other hand, it seems that the diffusion velocity of pyridine molecules in the larger coal particles and relaxation velocity of large coal particles in pyridine are in the order: Prima > Goonyella > Witbank.

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REFERENCES

- 1 Van Krevelen, D. W., 'Coal', Elsevier, Amsterdam, 1981.

- 2 Lucht, L. M.; Peppas, N. A. *Fuel* 1989, 66, 803.
- 3 M. Vahrman, *Fuel* 1970, 49, 5.
- 4 Spence, J. A.; Vahrman, M. *Fuel* 1970, 49, 395.
- 5 Sanada Y.; Honda, H. *Fuel* 1966, 45, 295.
- 6 Marzec, A.; Kisielow, W. *Fuel* 1983, 62, 971.
- 7 Mastral, A. N.; Izquierdo, M.; Rubio, T., B. *Fuel* 1990, 69, 892.
- 8 Liotta R.; Brons, G.; Isaacs, J. *Fuel* 1983, 62, 781.
- 9 Larsen, J. W.; Green, T. K. *Fuel* 1984, 63, 1538.
- 10 Ndaji, F. E.; Thomas, K. M. *Fuel* 1993, 72, 1525.
- 11 Hsieh, S. T.; Duda, J. L. *Fuel* 1987, 66, 170.
- 12 Turpin, M.; Rand, B.; Ellis, B. *Fuel* 1996, 57, 107.
- 13 Cody, G. D.; Botto, R. E. *Energy Fuels* 1993, 7, 561.
- 14 Lynch, L. J.; Peppas, N. A. *Fuel* 1987, 66, 803.
- 15 Ritger, P. L.; Peppas, N. A. *Fuel* 1987, 66, 1379.
- 16 Barton, W. A.; Lynch, L. J. *Energy Fuels* 1989, 3, 402.
- 17 Barton, W. A.; Lynch, L. J. In 'Proceedings of 1989 International Conference on Coal Science' Tokyo, 1989, pp. 13-16.
- 18 Brenner, D. *Fuel* 1984, 63, 1324-1328.
- 19 Suuberg, E. M.; Otake, Y.; Langner, M. J.; Leung, K. T.; Milosavljevic, I. *Energy Fuels* 1994, 8, 1247-1262.
- 20 Ndaji, F. E.; Thomas, K. M. *Fuel* 1995, 74, 842-845.
- 21 Cody, G. D.; Davis, A.; Hatcher, P. G. *Energy Fuels* 1993, 7, 455
- 22 Marzec, A.; Kisielow, W. *Fuel* 1983, 62, 971.
- 23 Hall, P. J.; Marsh, H.; Thomas, K. M. *Fuel* 1988, 67, 863.
- 24 Nishioka, M.; Larsen, J. W. *Energy Fuels* 1988, 2, 351
- 25 Larsen, J. W.; Green, T. K.; Kovac, J. J. *Org. Chem.* 1985, 50, 4729.
- 26 Brenner, D. *Fuel* 1985, 64, 167.
- 27 Cody, G. D.; Larsen, J. W.; Siskin, M. *Energy Fuels* 1988, 2, 340
- 28 Mosegood, A. G. W.; Clarkson, R. B. *Fuel* 1993, 72, 1235-1237.
- 29 Green, T. K.; Kovac, J.; Brenner, D.; Larsen, J. W., in 'Coal Structure' (Ed. R. A. Meyer), Academic Press, New York, 1982
- 30 Cody, G. D.; Larsen, J. W.; Siskin, M. *Energy Fuels* 1988, 2, 342
- 31 Hall, P. J.; Thomas, K. M.; Marsh, H. *Fuel* 1988, 67, 863
- 32 Lynch, L. J.; Peppas, Nikolaos A. *Fuel* 1987, 66, 803-809.
- 33 Ritger, Philip L.; Peppas, Nikolaos A. *Fuel* 1987, 66, 1379-1388.
- 34 Barton, W. A.; Lynch, L. J. *Energy Fuels* 1989, 3, 402
- 35 Sakurovs, R.; Lynch, L. J.; Barton, W. A., In 'Coal Science II', Symposium Series 461 (Eds Schobert, H. H.; Bartle, K. D.; Lynch, L. J.), American Chemical Society, Washington, DC, 1991, pp. 111-126.

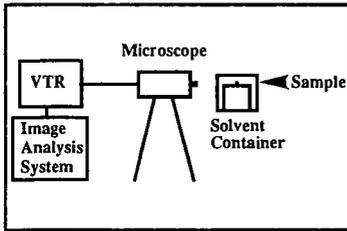


Figure 1. Schematic diagram of the apparatus for the observation and measurement of solvent swelling of single coal particles.

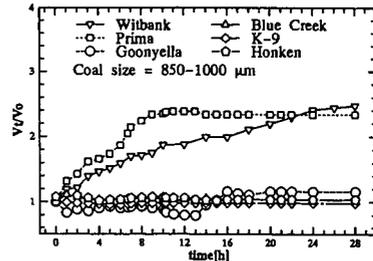


Figure 2. Changes of solvent swelling ratio with time in pyridine at ambient temperature.

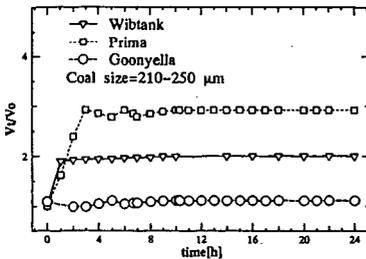


Figure 3. Changes of solvent-swelling ratio with time in pyridine at ambient temperature.

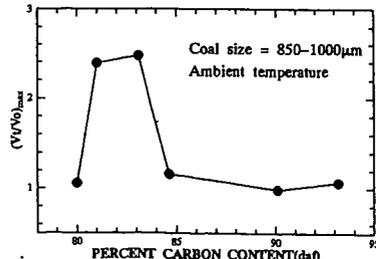


Figure 4. Relationship between maximum solvent swelling ratio in pyridine and carbon content.



Figure 5. Frame photographs of swelling of Witbank coal particle (850-1000 μm) in pyridine at ambient temperature (a: 0 h, b: 1 h, c: 2 h, d: 3 h, e: 4 h, f: 5 h, g: 6 h, h: 7 h, i: 8 h, j: 9 h, k: 10 h, l: 11 h, m: 11.25 h, n: 12 h, o: 13 h, p: 14 h, q: 14.5 h, r: 24 h).

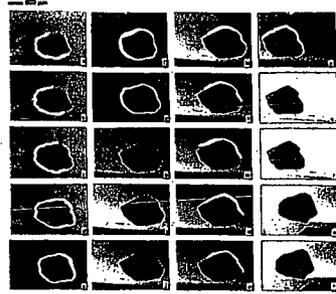


Figure 6. Frame photographs of swelling of Prima coal particle (850-1000 μm) in pyridine at ambient temperature (a: 0 h, b: 1 h, c: 2 h, d: 3 h, e: 4 h, f: 5 h, g: 6 h, h: 7 h, i: 8 h, j: 9 h, k: 10 h, l: 11 h, m: 12 h, n: 13 h, o: 14 h, p: 15 h, q: 16 h, r: 17 h, u: 18 h, v: 20 h, w: 21 h, x: 24 h).

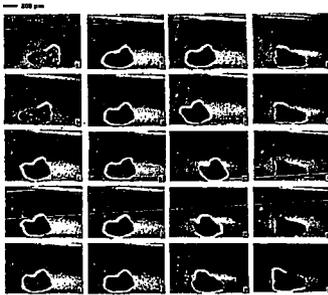


Figure 7. Frame photographs of swelling of Goonyella coal particle (850-1000 μm) in pyridine at ambient temperature (a: 0 h, b: 1 h, c: 2 h, d: 3 h, e: 4 h, f: 5 h, g: 6 h, h: 7 h, i: 8 h, j: 10 h, k: 12 h, l: 14 h, m: 14.25 h, n: 14.5 h, o: 15 h, p: 16 h, q: 18 h, r: 20 h, u: 22 h, v: 24 h).

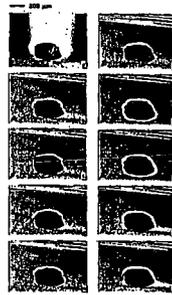


Figure 8. Frame photographs of swelling of Blue Creek coal particle (850-1000 μm) in pyridine at ambient temperature (a: 0 h, b: 1 h, c: 2 h, d: 3 h, e: 4 h, f: 6 h, g: 8 h, h: 10 h, i: 18 h, j: 24 h).



Figure 9. Frame photographs of swelling of K-9 coal particle (850-1000 μm) in pyridine at ambient temperature (a: 0 h, b: 2 h, c: 4 h, d: 6 h, e: 8 h, f: 10 h, g: 12 h, h: 24 h).

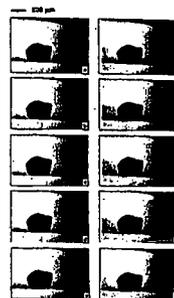


Figure 10. Frame photographs of swelling of Honken coal particle (850-1000 μm) in pyridine at ambient temperature (a: 0 h, b: 2 h, c: 4 h, d: 6 h, e: 8 h, f: 10 h, g: 12 h, h: 16 h, i: 18 h, j: 24 h).