

SOLVENT SWELLING OF COAL AND COAL MACERALS

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INTRODUCTION

Coal is composed of organic macerals, inorganic mineral matter, pores and pore-filling fluids. Coal normally displays the properties of an amorphous solid, but under appropriate conditions, coal displays both plastic and elastic behavior(1-3). A model to describe the structure of the organic constituents of bituminous coal is that of a branched/crosslinked polymer. There is no repeating monomer unit, but a unit structure which is covalently bonded by bridging groups. The unit structures are composed of condensed-ring aromatic groups of from 2-4 rings, with molecular weights of around 300. The aromatic rings are substituted by naphthenic rings, alkyl groups and phenolic groups. The bridging groups contain C-O and C-C bonds which are broken during depolymerization and other liquefaction processes. The unit structures cluster in groups which give rise to X-ray diffraction patterns similar to those observed for graphite. The three-dimensional arrangement of the structural units produces a significant micropore volume. In addition to the covalent bridges, polar interactions also serve as crosslinks.

The condensed-ring aromatic units are rigid, but the covalent bridges should provide some flexibility. However, the bonding within clusters of unit structures and the polar interactions reduce the mobility of the coal units and under normal conditions, coal is a glass. At temperatures in the softening range, covalent bonds in the bridging groups are broken and the polar interactions disrupted, providing fluidity to the coal mass. When contacted at room temperature with a suitable polar solvent, coals swell and exhibit plastic and elastic properties(1-3). Under these conditions, the polar bonds are broken and the solvent acts as a plasticizer for the macromolecular network of the coal. Coal passes through a similar state in both carbonization and liquefaction processes, with the solvent being either added vehicle oil or decomposition products of the coal itself. Solvents with Hildebrand solubility parameters in the range of 9-15 (cal/cm³)^{1/2} are effective in swelling coals and, in some cases, inducing spontaneous fracturing(4). The interaction of coal with organic solvents is of interest because of the potential for reacting swollen coals under relatively mild conditions and because of the potential for chemical comminution and chemical cleaning of coals. Changes in the physical properties of coals in the presence of organic solvents are discussed in this paper.

EXPERIMENTAL

Four coals from the Pennsylvania State University Coal Sample Bank and five bituminous coals from Utah were studied. The coals included one anthracite and samples rich in sporinite, resinite, vitrinite and semifusinite. The Utah coals cover a range of response in flotation experiments from easily and quickly floated to difficult to float.

The method of Green et al.(5) was used to measure the swelling properties of the coals. The coal sample was centrifuged in a narrow tube. Solvent is added and the coal is allowed to swell. After

equilibrium is achieved, the coal and solvent are again centrifuged. The increase in height of the column of coal is taken as the volumetric swelling of the coal. This method is reported to be more reliable than gravimetric methods and does not require corrections for pores.

Surface areas of coals and solvent-treated and heat-treated coals were measured by carbon dioxide adsorption at -77°C . The samples were placed in a vacuum system and any solvent was removed. The amount of CO_2 adsorbed was determined as a function of the pressure and the Dubinin-Polanyi equation was used to determine the surface area/pore volume⁶. X-ray diffraction measurements were performed at room temperature after solvents were removed at lower temperatures. The assignment of the 002 peak in the diffraction pattern was by comparison with the diffraction pattern of graphite.

Maceral fractions were prepared by the density gradient centrifugation method of Dyrkacz and Horwitz(7). The coal was ground in a fluid energy mill to an average particle diameter of several microns. The sample was then introduced into a density gradient of CsCl in water in a centrifuge and dispersed throughout the gradient. The gradient is displaced from the centrifuge and fractions of different density collected. The sample is recovered and a plot of yield versus density provides a density distribution for the sample. Fractions of similar density were combined for further measurements.

RESULTS AND DISCUSSION

The swelling ratio for coal PSOC-297 is shown in figure 1 as a function of the solubility parameter of the solvent used to cause swelling. This coal is 63% vitrinite and 16% sporinite. The swelling behavior is similar to that observed for the other bituminous coals, although the magnitude of the swelling varies from sample to sample. The swelling is expected to be a maximum for solvents that have solubility parameters similar to that of the coal. The curve shows two maxima. Pyridine causes the most swelling of the solvents tested. The effectiveness of pyridine in swelling the coals is thought to be due to the disruption of polar bonds between segments of the coal molecule, replacing them with H-bonds between the pyridine and the coal. The second maximum in the swelling curve is observed for THF as the solvent. The solubility parameter for coals is expected to be closer to that for THF than for pyridine. The less polar solvents may be causing the coal to swell within the constraints of the hydrogen bond crosslinks, without appreciably breaking the crosslinks.

The swelling is greatest for coals with higher vitrinite content among coals of similar rank. The coals with high inertinite and exinite contents show reduced swelling, although the behavior with regard to solubility parameter is qualitatively the same. The inertinite fraction is not expected to swell appreciably. The anthracite sample did not show any swelling in any of the solvents. The behavior of the anthracite and the inertinite fractions is expected to be similar. A separated sample of resinite showed high solubility in the more polar solvents. It is not certain whether a true solution was formed or if it was a gel or colloidal suspension. Swelling measurements could not be made on the resinite.

Swelling for the less-polar solvents does not appear to be the equilibrium swelling since the structure is constrained by the crosslinks and the less polar solvents are not strong enough to break these crosslinks. Samples were swollen with mixtures of THF and

cyclohexane. Swelling for the mixtures was intermediate between the values observed for the pure solvents. When the sample was swollen with THF and diluted with cyclohexane, the swelling remained near that of pure THF for dilutions up to 75% cyclohexane. Once the macromolecular network is expanded by the good solvent, the poorer solvent will maintain the swelling. Swelling would be expected to increase the pores in the coal structure. Surface areas for coals and swollen coals are shown in figure 2. The surface area is related to the pore volume. The surface area for non-swollen coals is 230-250 m²/g. as measured at -77°C, for samples that are heat-treated up to 400°C. If the heat-treated samples are swollen in methanol and the solvent removed at low temperatures, the surface areas increase to 300-350 m²/g. The polar solvent is more effective than temperature in causing the network to swell. If the sample is swollen and then heated to 100°C the macromolecular network relaxes and the surface area is similar to that for non-swollen coals. The coals with enhanced porosity show the same x-ray diffraction patterns as non-swollen coals. The solvent apparently does not disrupt the stacking of the condensed-ring aromatic structures in the coal.

CONCLUSIONS

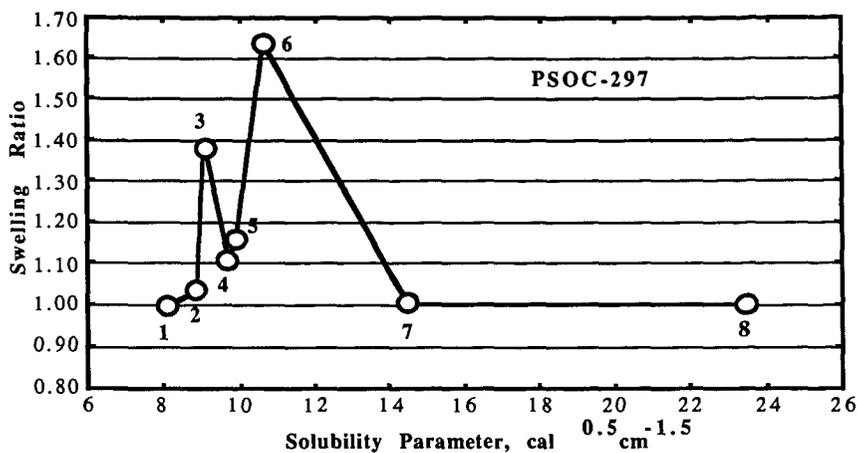
The swelling of bituminous coals as a function of solubility parameter of the solvent shows two maxima. One is attributed to the solvation of the macromolecular network by a solvent with solubility parameter similar to the coal, increasing the hydrodynamic volume of the network. The other maxima is attributed to the breaking of hydrogen bonds that serve as crosslinks by polar solvents. The coal appears to be held in a constrained state by the polar crosslinks. Solvents are more effective in breaking these restraints than temperature. Porosity can be increased by swelling coals and removing the solvent at low temperatures. The coal network has considerable flexibility below 100°C, as evidenced by the relaxation of the induced porosity upon thermal treatment. Inertinite macerals and anthracites show little swelling. Vitrinites show high swelling and exinites show enhanced solubility.

ACKNOWLEDGMENTS

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REFERENCES

1. Green, T., Kovac, J., Brenner, D., and Larson, J., "The Macromolecular Structure of Coals", Coal Science, R. A. Meyers, ed., Academic Press, N. Y., 1982, p. 199.
2. Brenner, D., Fuel, 1985, 64, 167.
3. Larson, J. W., Preprints, Fuel Chem. Div., Am. Chem. Soc., 1985, 30(4), 444.
4. Keller, D. V., Jr., and Smith, C. D., Fuel, 1976, 55, 273.
5. Green, T. K., Kovac, J., and Larsen, J. W., Fuel, 1984, 63, 935.
6. Marsh, M., and Seimeniewska, T., Fuel, 1965, 44, 355.
7. Dyrkacz, G. R., and Horwitz, P., Fuel, 1982, 62, 3.



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| 1 Cyclohexane | 4 Dichloromethane | 7 Methanol |
| 2 Toluene | 5 Acetone | 8 Water |
| 3 Tetrahydrofuran | 6 Pyridine | |

Figure 1 Coal Swelling in Different Solvents

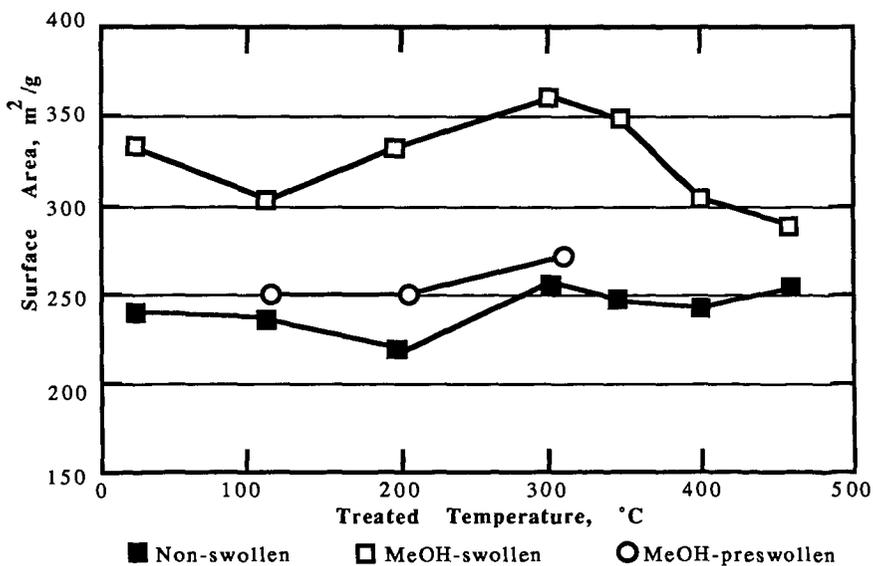


Figure 2 Surface Area of Treated Coal