SOLVENT-INDUCED SWELLING OF THIN SECTIONS OF COAL

D. Brenner

Corporate Research Science Laboratories
Exxon Research and Engineering Company
P.O. Box 45, Linden, New Jersey 07036

Introduction

The swelling of coals in solvents is an important technique for investigating the physicochemical structure of coals. For example, swelling has been used to estimate the solubility parameters of coals (1,2), and to study the relative degrees of cross-linking (3). Swelling expands the coal structure and this can allow faster or more complete penetration of the coal by liquids or by substances dissolved in the swelling liquids. This behavior is potentially of considerable practical utility for chemical treatments of coal prior to processing. Dryden (4,5,6,7) has studied the swelling of coals in numerous solvents, and he categorized a number of liquids which highly swelled coals as "specific solvents." Nelson, Mahajan, and Walker (8) have developed procedures to more accurately compute the volumetric expansion of ground coal by solvents by taking into account the porosity of the coal. In the study described here, instead of using ground coal, the solvent-swelling of uncontaminated thin section samples of coal was observed "in situ." Several important new results were obtained, and implications of these results for understanding the macromolecular structure of coal are discussed.

Experimental

Thin section samples of Illinois #6 coal were prepared by cementing a piece of the coal which had been ground flat to a glass slide with a hydrocarbon-based wax which is soluble in hexane. The flat surface was prepared perpendicular to the bedding plane. The coal on the slide was then ground to a thickness of about 15 micrometers. At this thickness the coal is translucent and red colored. In order to obtain an uncontaminated sample the adhesive was dissolved by soaking in excess hexane and the coal was removed from the slide. The sample was then placed in fresh solvent for several days to insure complete removal of any adhesive remaining on the coal. The solvent was then decanted off and the pieces of thin section were stored under dry nitrogen gas at room temperature until they were used.

A Leitz Ortholux II - Pol BK microscope was used to observe the thin section coal samples during experiments and a Wild Photoautomat MPS 50 system was used for the photomicrography. High speed Kodak Ektachrome film having an ASA rating of 400 daylight was used. For the light source, a CB 12 blue filter was used in front of a 50 watt Leitz tungsten-halogen illuminator.

The procedure for exposing a fragment of coal thin section to liquid pyridine and ethylenediamine swelling agents was as follows. The thin section was placed in the shallow depression of a specially prepared microscope slide and a photomicrograph was taken of this untreated sample. Next the depression containing the thin section was filled with the swelling agent using a hypodermic syringe, and a cover glass was used to seal the enclosure. The time of addition of the liquid was noted, and, if necessary, the sample was relocated and refocused in the microscope. Photomicrographs of the sample were then taken as a function of time. In order to dry the swollen samples, the cover glass over the sample was simply removed to allow drying in air at room temperature. In the case of n-propylamine,

swelling of the thin sections of coal was accomplished by exposure to the vapor of the solvent in a small glass ring enclosure which rested on a microscope slide. The sample was placed in the center of the enclosure and a piece of Teflon sheet was placed next to it. At the start of an experiment a drop of pyropylamine was placed on the Teflon, but not touching the sample, and a #0 cover glass was immediately placed on top of the ring to form a closed system.

Measurements of the linear dimensions or area of the dry or swollen coal thin sections were made on the photomicrographs. The photographs give no information on thickness, but since the samples were prepared with the surface perpendicular to the bedding plane, it was assumed that the degree of swelling perpendicular to the surface is within the range of linear expansions observed parallel to the surface.

Results

"In situ" observations of the dimensional swelling of thin sections of relatively homogeneous vitrinite from Illinois #6 coal were made with four different liquids: pyridine, ethylenediamine, n-propylamine, and water. In addition, the degree of shrinkage which occurred when the liquid was allowed to evaporate was also studied with some of these swelling agents.

The sample used for the swelling in pyridine is shown in Figure 1; it was about 0.5 mm across. The sample was placed in the depression of the special microscope slide, covered with a cover slip and immersed in pyridine. Within 60 seconds the sample was fully swollen. There was no noticable change in size after 14 additional minutes. Figure 2 shows a photomicrograph of the sample after 15 minutes exposure to pyridine. Comparing Figures 1 and 2, it is seen that the sample has expanded appreciably. (The darker region on the left side is where a small part of the sample folded over during realignment). A few cracks have developed in the sample. The cracks are probably the result of stresses caused by nonuniform swelling. In this case it is unlikely that the stresses were caused by differences in equilibrium swellability of different areas because the sample was relatively homogeneous. The shape of the swelled sample is close to the initial specimen; though, there was slightly more expansion in the direction perpendicular to the bedding plane. This is seen more clearly in Figure 3 where the initial and swelled samples are superimposed. The increase in area of the swelled sample is roughly 70 percent which corresponds to a volume increase of about 125 percent.

Ethylenediamine was used to treat a different thin section sample of Illinois #6 vitrinite. The initial sample is shown in Figure 4. It is about 0.7 mm across. When immersed in ethylenediamine the specimen fully swelled within 100 seconds. No change was observed during an additional 11 minutes exposure. The last photomicrograph shown in Figure 5, was taken after 12.5 minutes exposure to the ethylenediamine. For this sample the total area expansion is roughly 60%. If the increase in the volume is approximated as being equal to the 3/2 power of the area, then the volume expansion is about 100%.

Another thin section sample was fully swelled in ethylenediamine. Then the cover glass was removed and additional ethylenediamine was placed on the sample. The immersed sample was manipulated with microprobes while being observed under the microscope. The sample could be bent considerably and was observed to be substantially more flexible than the original sample.

Normal propylamine vapor was used to swell another thin section sample of Illinois #6 vitrinite. The piece was about 0.5 mm across. The initial sample is shown in Figure 6. The sample was fully swollen after less than 30 seconds contact with the vapors. In Figure 7 a superposition of the original sample and the sample

swelled in n-propylamine vapor is shown. It is seen that the sample has expanded substantially. Relatively little cracking occurred during the expansion, and the shape of the expanded sample is very close to that of the original sample.

After leaving this sample exposed to the n-propylamine vapors in the closed system for a total of roughly 2 minutes, the propylamine was removed and the sample was allowed to dry in the ambient air. The shrinkage occurred rapidly. Most of the shrinkage occurred within a few seconds and in less than 30 seconds the sample had shrunken fully. During shrinkage a few cracks formed in the sample. Figure 8 is a superposition of the initial sample and the shrunken sample after drying. The larger sample in Figure 8 is the redried sample. The shape of the shrunken sample is quite close to that of the initial sample.

The shrunken sample was swelled in the n-propylamine vapor a second time. The resultant swollen specimen was a very close replica of the first swollen sample. This sample was then allowed to dry again. This second shrunken sample was almost identical to the first shrunken sample.

A measurement of the swelling in water of a piece of thin section was also made. No changes in the dimensions of the sample were evident.

Discussion

The swelling of chunks of bituminous and subbituminous coals in highly effective swelling agents such as ethylenediamine, pyridine, or propylamine is ordinarily accompanied by massive cracking and distortion of the coal structure. Figure 9 shows an example of such swelling in propylamine. There is little resemblance between the original sample and the swollen sample. These before and after pictures are dramatically different from the results of our study. The occurrence of only a few large cracks and the good retention of shape in the swollen thin sections in this study had not been anticipated. The thinness of the samples in this study apparently tended to reduce fracturing of the samples in several ways: (a) it caused the penetration of the swelling agent into the coal to be rapid and fairly uniform over the area of the sample so that uneven swelling of the sample was minimized; (b) the thinness of the samples limited the distance over which liquid concentration gradients could develop perpendicular to the surface so any stresses built up from swelling gradients perpendicular to the surface would be less likely to induce fracture; and (c) during swelling the very thin samples could flex appreciably without fracturing--especially the regions of the sample which had already swelled. Therefore, if stresses were generated during swelling, parts of the thin section could deform out of the plane of the sample and thereby prevent excessive stresses from developing.

In the experiment in propylamine vapor the sample obtained when the first swollen sample was dried was slightly larger than the initial sample. This increase in size was probably caused by propylamine retained in the dried specimen. This result is consistent with the work of Collins et. al. (9) who found that 10 to 15 percent of various amines remained in coals even after exposure to vacuum at room temperature for many hours.

After the initial swelling and shrinking of the Illinois #6 coal in propylamine vapor, subsequent swelling and shrinkings were close replicas of the previously swollen or shrunken states respectively. The high degree of reversibility is an important result of this study; reversibility is required for the thermodynamic treatment of solvent-swelling.

The rapidness with which the shrinkage occurred in the thin sections expanded with n-propylamine gives an important clue to the interaction of the

solvent with the coal. Most of the shrinkage takes place less than 5 seconds after removal of the cover glass. During this short drying time at room temperature in air not only did the propylamine evaporate from the sample, but also the excess liquid around and under the sample evaporated. This rapid shrinkage indicates that the liquid which causes most of the swelling is mobile and is not strongly bound to the coal.

Although most of the imbibed propylamine solvent is mobile, it is likely that energetic interactions between at least some of the solvent molecules and the coal play an important role in the swelling phenomenon. In order for the coal to expand, the macromolecular chains must be able to reorient. However, coal has a very rigid structure. Earlier it was noted that the swollen coal is more flexible than dried coal. Some bonds which are present in the dry coal are apparently solvated by the swelling agent and this enables the swelling to take place by reorientation of macromolecular chains.

The substantial decrease in modulus which occurs upon swelling of the coal indicates that the bonding is significantly different in the dry and the swollen coal. The effective molecular weight between cross-links for the highly swollen coal samples is therefore substantially greater than for the original dry sample. This suggests that the undirectional elasticity of the swollen sample may have much more of an entropic nature than that of the original sample. Indeed, if the swelling involves primarily an extension of macromolecular chains, then the elasticity of the swollen coal should be substantially entropic. It may therefore be possible to estimate the cross-link density for highly swollen coal from a measurement of its modulus. Results of modulus measurements on swollen coals will be reported in a future paper.

Conclusions

Thin section samples of relatively homogeneous vitrinite from a high volatile C bituminous coal have been found to swell with good shape retention and without substantial fracturing in several good swelling agents. The swelling in propylamine has a high degree of reversibility and rapid shrinkage of the sample occurs when the volatile propylamine is allowed to evaporate in air. The samples swollen in the specific solvents are substantially more flexible than either the original samples or the dried samples (after swelling). The lack of fracturing and distortion probably results from the homogeneity and thinness of the samples.

Thin section samples of coal can be repeatedly and reversibly swollen by exposure to a swelling agent and shrunken by drying. The successive swollen samples (or dried samples) are close replicas of each other. The rapidness with which the shrinkage of the n-propylamine swelled samples occurred indicates that most of the liquid causing swelling has only a weak interaction with the coal. However, the good swelling agents weaken the secondary bonding in the coal and enable a high degree of swelling. This may involve a strong interaction of part of the solvent with some of the functionalities of the coal.

The increase in the flexibility of the coal thin sections when they are swollen suggests that the elasticity of highly swollen coal may be substantially entropic even if the elasticity of the (higher modulus) dry coal is not.

Acknowledgement

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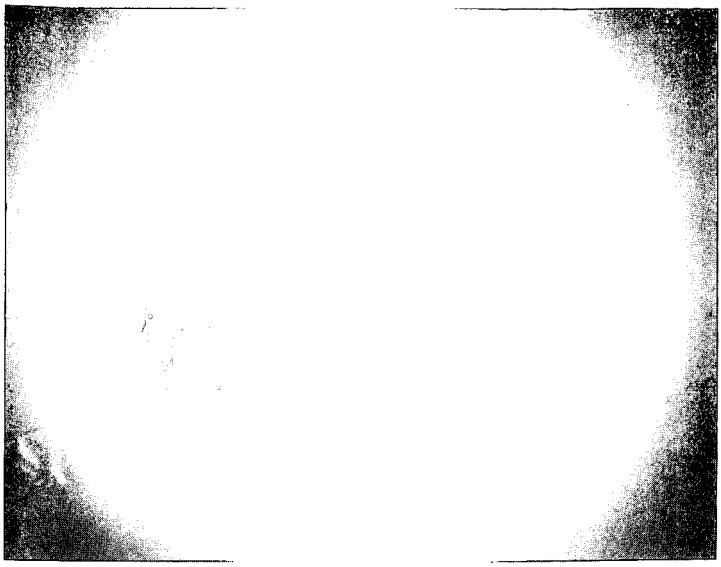

Fig. 1. Thin section sample of Illinois #6 coal about 0.5mm across

Fig. 2. Thin section after 15 min. immersion in liquid pyridine

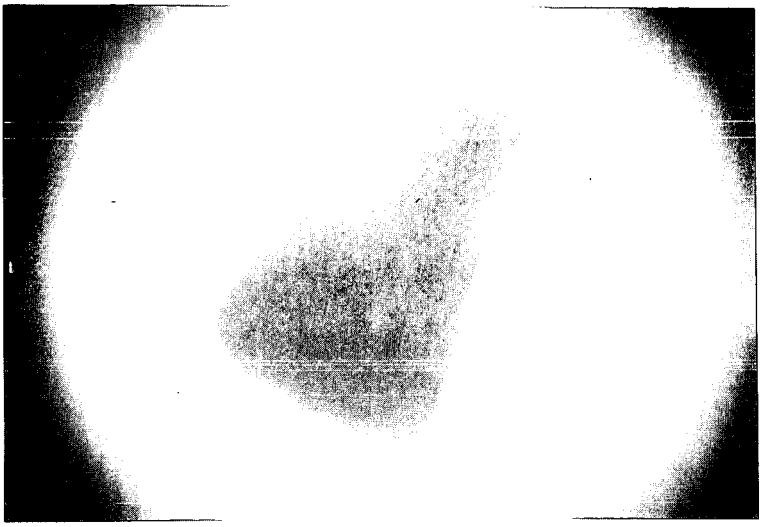

Fig. 3. Superposition of untreated sample and after immersion in pyridine for 15 min.

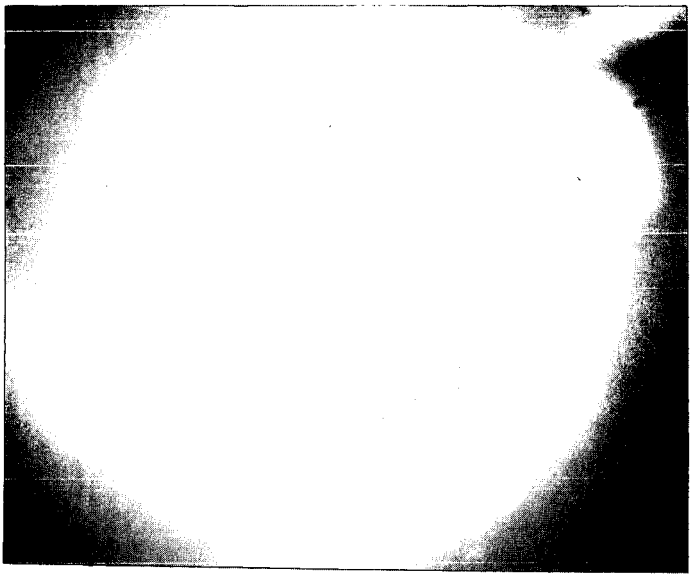

Fig. 4. Thin section sample of Illinois #6 coal about 0.7mm across

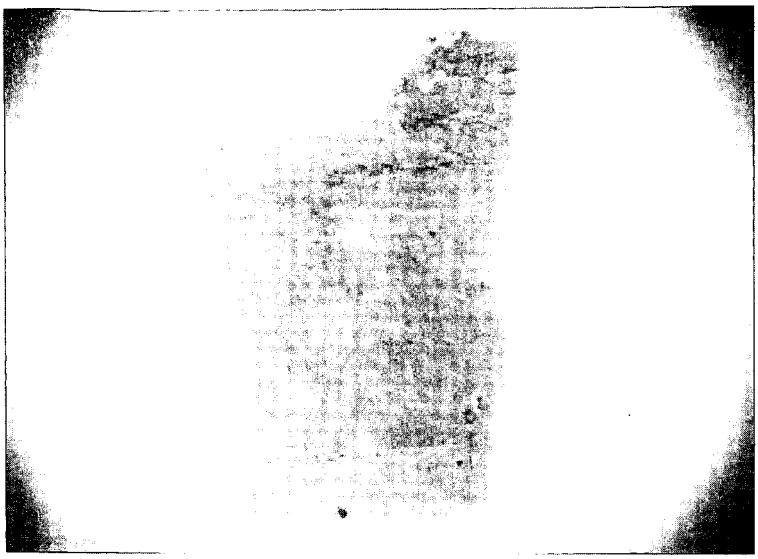

Fig. 5. Thin section after 12.5 min. immersion in liquid ethylenediamine

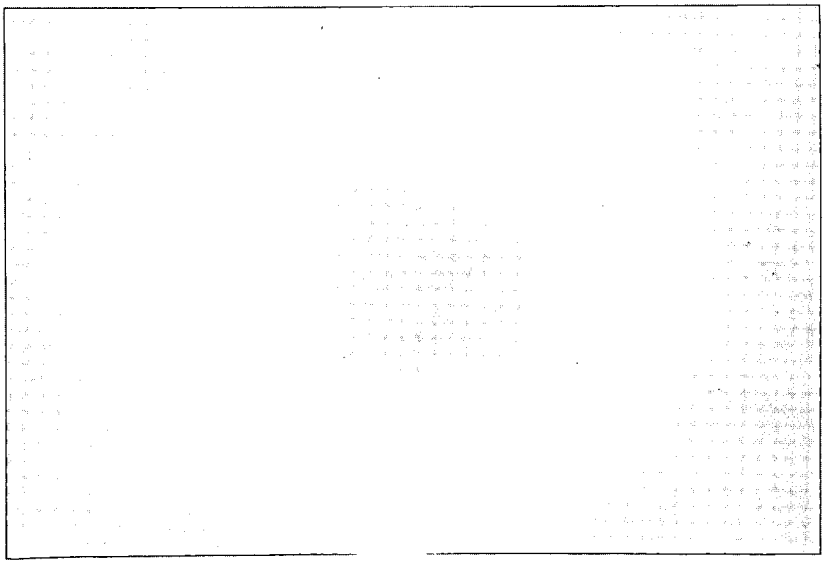

Fig. 6. Thin section sample of Illinois #6 coal about 0.5mm across

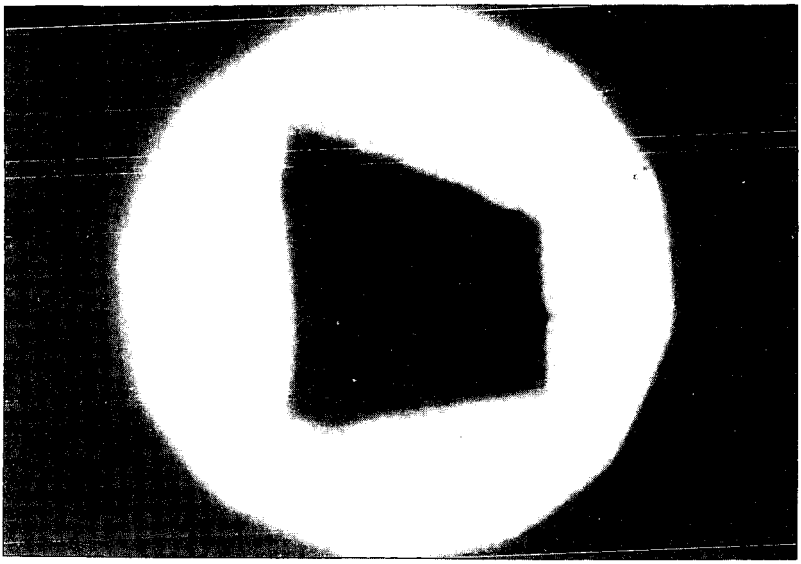

Fig. 7. Superposition of untreated sample and expanded sample after swelling in n-propylamine vapor

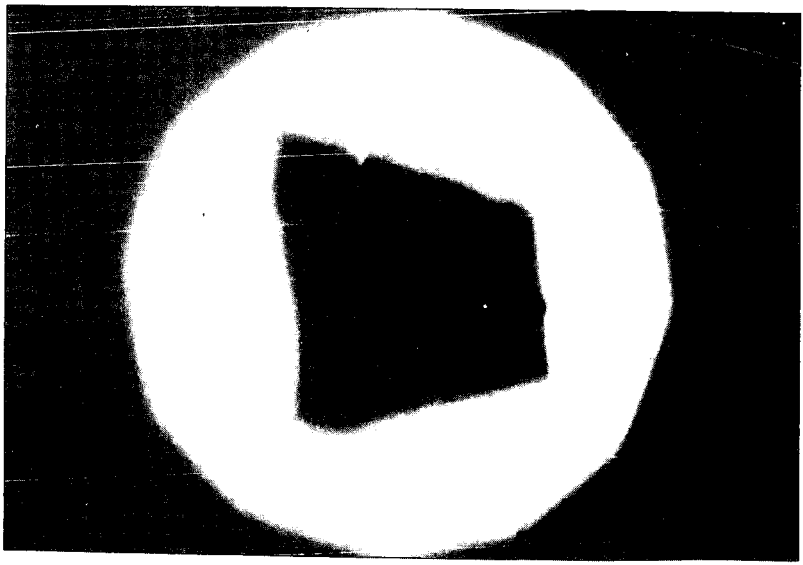

Fig. 8. Superposition of untreated sample and dried sample

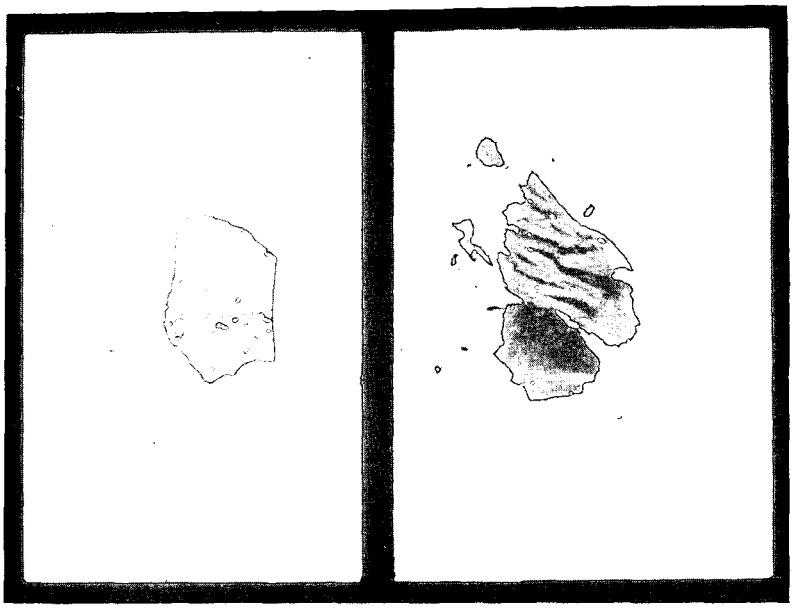

Fig. 9. Chunk of Illinois #6 coal about 10mm across before and after overnight immersion in propylamine