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Swelling and dissolution of the macromolecular structure of bituminous coals

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The disintegration/swelling force of thin samples of bituminous coal was determined in methylene chloride and dimethyl formamide. The results were analysed with a mechanistic model identifying diffusional and relaxational mechanisms. © 1997 Elsevier Science Ltd.

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Introduction

Certain types of coals have a tendency to swell in thermodynamically good solvents and eventually dissolve due to strong forces that first disrupt the three dimensional macromolecular network structure and then solubilize the entangled chains. As previously discussed by Lucht *et al.*[1], the organic phase of certain coals exhibits a highly glassy state that has a glass transition temperature, T_g, in the range of 580–632 K. However, in the presence of compatible swelling agents such as pyridine, the glass transition temperature decreases significantly due to the glassy/rubbery transition. The result is an expansion of the coal network leading to significant solvent swelling. For example, the macromolecular structure of a bituminous coal containing 79.8% C on a dmmf basis showed a decrease of T_g by 179°C down to 50°C after 190 h of swelling in pyridine at 35°C, which leads to 0.819 g of pyridine incorporated per g of coal sample. Coal samples may eventually dissolve due to strong stresses which lead to disruption of crosslinks, chain disentanglement, and extraction and isolation of small molecular weight chains[2,3].

Investigation of the volume expansion (swelling) followed by coal dissolution is of utmost importance in attempting to understand the forces and stresses that may be measured during coal liquefaction. As *Figure 1* indicates, such stresses are created during the early process of swelling and can be compressive in the glassy region and tensile in the rubbery region[2,3].

Penetrant (solvent) transport in macromolecular coal networks may induce structural changes such as swelling, microcavity formation, primary phase transition and secondary phase transition. Obviously, these changes require rearrangement of molecular chains. Therefore, penetrant uptake may be controlled by diffusion, by structural relaxations, or by coupling of the two phenomena. The phenomenon of swelling of polymers has been investigated for more than forty years. In the late sixties, Kuhn[5] offered the first accurate calculations of stresses created during swelling. Yet, experimental techniques for continuous measurement of the kinetics of swelling were not reported until Zasimov *et al.*[6] proposed a simple device for such analysis. A most accurate method of measuring swelling and disintegration stresses was developed by Catellani *et al.*[7] We have reproduced and used this technique in our laboratory to measure swelling and disintegration stresses in the macromolecular structure of coals in the presence of thermodynamically good solvents.

Experimental

Uncontaminated thin sections of coal were prepared using a paraffin-based adhesive which could be completely removed from the sample. Coal samples containing 78.3, 80.1, 82.4, 86.0, and 94.0% C on a dry, mineral matter free basis (dmmf) were obtained from the Pennsylvania State University Coal Bank. A coal chunk was ground flat in a direction parallel to the geographic bedding plane in a horizontal diamond grinding wheel using progressively finer diamond grits. The flat surface of the coal was then heat-cemented to a preconditioned microscope slide. Preparation of the microscope slide consisted of rough grinding to a uniform thickness to provide a textured surface for enhanced adhesion using a hexane-soluble, paraffin-based, thermoplastic compound (Paraplast, American Scientific Products, St. Louis, MO). When the adhesive had hardened, the coal chunk was cut with a diamond saw leaving an approximately 2 mm thick slab of coal mounted on the glass slide. The slab was then ground using a vertical diamond grinding wheel to the desired final thickness.

Thin coal sections were removed from the glass slide by soaking in *n*-hexane (a non-solvent of coal) for several hours. The original *n*-hexane was decanted off and a large excess of additional *n*-hexane was added to insure removal of any residual adhesive from the coal sections. After a few days of immersion, *n*-hexane was removed and the samples were oven-dried at 60°C. The samples were stored in a dry nitrogen atmosphere at room temperature until use. The obtained uncontaminated samples ranged in thickness from 7 to 15 μm. They were cut into thin discs of diameter of 11 mm.

A disintegrating force–solvent uptake apparatus (see *Figure 2*) was used for these studies[8]. The coal samples were placed between two sintered glass disks and positioned into a steel cage. Solvent entered into the coal through these sintered glasses. An extensiometric

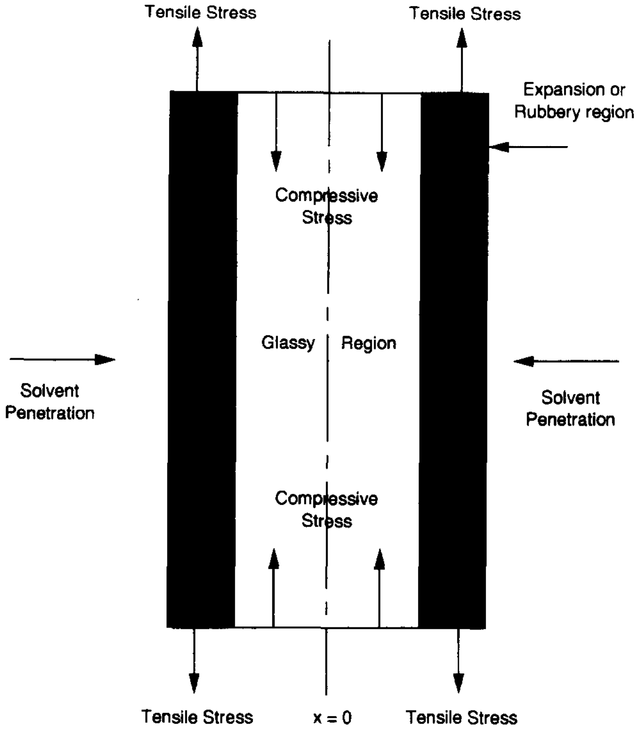

Figure 1 Tensile and compressive stresses during coal slab swelling/dissolution in thermodynamically good solvents

load cell was located directly above the cage and was used to measure the force exerted by the coal sample when the latter was placed in contact with the solvent. Solvents used in these studies were methylene chloride and dimethyl formamide.

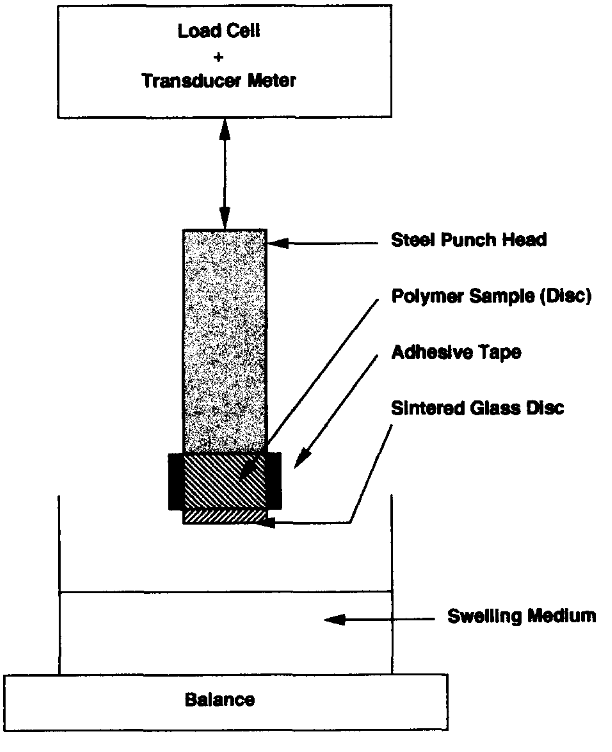

Figure 2 Apparatus for measurement of swelling force

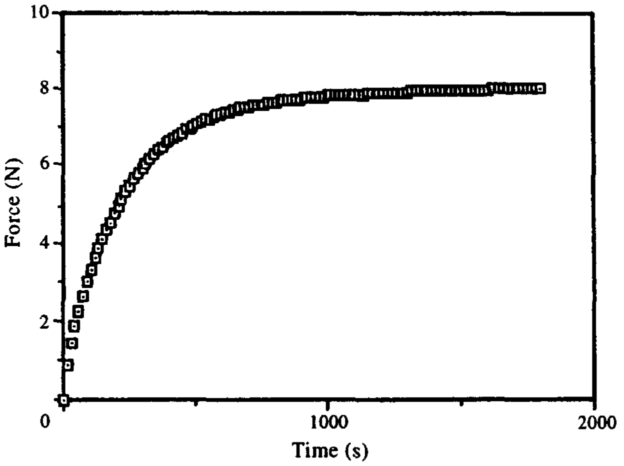

Figure 3 Swelling force as a function of time for a coal slab (thickness of 4.57 mm) containing 78.3% C (dmmf) and swollen in methylene chloride at 25°C

Results and discussion

To describe the physical situation in coal samples we propose a model which can present the step-wise development of the swelling/disintegration/dissolution model. As the swelling studies were done using thin discs of coal, and the swelling process proceeded in layers parallel to the surface of largest area, the overall process could be analysed by two rate-limiting steps. The first one, henceforth called a *swelling-controlled mechanism*, is the detachment of the first layer from the coal/solvent interface. The second process which will be called a *dissolution-controlled mechanism* is the transfer of coal chains from the interface.

During the overall coal swelling/dissolution process, the controlling step may be either the ease of swelling of coal layers or their ability to dissolve outward. The disintegration/swelling force could be measured because of the resulting volume expansion of the disc. Indeed, if the expanding surface were prevented from moving, it would exert a force, F, which could be related to the expanding core.

We have previously shown[8] that the disintegration force can be written as

$$\frac{F}{F_\infty} = 1 - \exp(-kt^n) \qquad (1)$$

where n is indicative of the rate-controlling mechanism of dissolution, either interfacial or diffusional.

In the present studies, the swelling force of bituminous coal samples was recorded as a function of time up to its maximum value. *Figure 3* shows a typical graph of the force development for a coal containing 78.3% C on a dmmf basis and swollen in methylene chloride. The swelling force developed relatively fast, and 90% of its maximum value was achieved in less than 5 min. The maximum swelling force developed, F_∞, was 8.35 N, significantly lower than for any other 'swellable' synthetic polymer system that has been reported in the literature up to now[8].

Table 1 summarizes the results for a number of coal samples of increasing carbon content. Clearly, as the degree of coalification increased, the maximum swelling force developed was decreased. For coals containing 94% C the swelling force measured was at the limit of the apparatus ($F_\infty \sim 0.01$ N). These results are in general agreement with the studies of Olivares and Peppas[9] who determined that methylene chloride transport in a coal containing 80.1% C (dmmf) proceeded with an average velocity of 206 μm min^{-1} at room temperature. This

Table 1 Swelling force analysis of thin coal slabs

		Swelling/dissolution in methylene chloride		Swelling/dissolution in dimethyl formamide	
Coal (dmmf)	Thickness (mm)	Max. force, F_∞ (N)	Exponent (n)	Max. force, F_∞ (N)	Exponent (n)
78.3	4.57	8.35	0.92	2.10	0.90
80.1	3.56	5.40	0.90	1.10	0.85
82.4	4.26	3.20	0.88	0.60	—
86.0	4.35	0.38	—	<0.01	—
94.0	4.60	<0.01	—	<0.01	—

would correspond to approximately 8.5 min for complete transition of the thin coal sample tested here, which is similar to the dynamic study observed here.

The swelling/dissolution mechanism was analysed using equation (1) by calculating the exponent n for each dynamic process. All values determined were of the order of 1, indicating[8] a diffusion-controlled dissolution process whereby 'layers' of coal could disintegrate and dissolve. This would be in agreement with very early studies by Hsieh and Duda[4] concerning the swelling/dissolution of coals.

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References

1. Lucht, L. M., Larson, J. M. and Peppas, N. A., *Energy & Fuels*, 1987, **1**, 56.
2. Ritger, P. L., and Peppas, N. A., *Fuel*, 1987, **66**, 1379.
3. Alfrey, T., Gurnee, E. F. and Lloyd, W. G., *J. Polym. Sci.*, 1966, **C12**, 249.
4. Hsieh, S. T. and Duda, J. L., *Polym. Mater. Sci. Eng.*, 1984, **51**, 703.
5. Kuhn, H. J., *J. Polym. Sci.*, 1967, **C16**, 859.
6. Zasimov, V. M., Golubera, M. G. and Chepupin, A. N., *Zavodsk. Laborat.*, 1978, **44**, 989.
7. Catellani, P. I., Predella, P., Bellotti, A. and Colombo, P., *Int. J. Pharmac.*, 1989, **51**, 63.
8. am Ende, M. T., Bell, C. L., Peppas, N. A., Massimo, G. and Colombo, P., *Int. J. Pharmac.*, 1995 **120**, 33.
9. Olivares, J. M. and Peppas, N. A., *Chem. Eng. Commun.*, 1995, **132**, 91.