

MECHANICAL CHARACTERIZATION OF COALS IN THEIR RUBBERY STATE

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INTRODUCTION

The macromolecular structure of a material affects a range of physical characteristics. It affects whether the material is a hard solid or a soft rubber, or whether it is a viscoelastic fluid or a low viscosity liquid. The macromolecular structure affects such properties as solubility, penetration by liquids and gases, and the ease of breaking down the structure. For coals, the macromolecular structures play a significant part in a number of processes. By understanding the macromolecular structure better we may hope to more effectively utilize coals.

Mechanical measurements on a material above its glass transition is one of the most effective means of probing its macromolecular structure (1,2). However, for undegraded coals above their glass transition in their rubbery state, no information has been available. Virtually all of the numerous mechanical measurements on undegraded coals have been below the glass transition temperature where the coals are in a glassy or semicrystalline state. This is to be expected since this is the natural state of coals under ambient conditions. On the other hand, the macromolecular chain segments have very limited mobility below the glass transition temperature, so they can not be probed very effectively. It is desirable to make measurements on coals in their rubbery state where the macromolecules can move and respond to stimuli. Measurements of the degree of swelling (3,4) have given some information on solvent-swollen coal, but the information that can be obtained is limited. Also the interpretation of those results depends on solution thermodynamics, and the need to determine the interaction parameter is a particular problem.

Previously we had been able to demonstrate that high volatile bituminous coals could attain a rubbery state when immersed in an appropriate solvent (5,6). Having established this, it became highly desirable to characterize macromolecular parameters of the rubbery coals using mechanical measurements. Unfortunately, though, satisfactory samples of rubbery coals had never been prepared. The problem which prevented the preparation of adequate samples of rubbery coals was the tendency of the coal to decrepitate when it is immersed in a good swelling solvent (7). In fact, solvent-swelling has been proposed as a beneficiation process to break down coal into particles (8). However, in our earlier work we had shown that coals in the form of thin sections could be swollen without much damage occurring. But such thin samples are not amenable to mechanical measurements. For this reason a program was undertaken to determine whether it was possible to develop new techniques for preparing adequate samples.

EXPERIMENTAL

A procedure has now been developed which for many coals enables the preparation of samples in the rubbery state which are satisfactory for mechanical measurements. The technique involves selecting relatively homogeneous regions of vitrinite which have low mineral matter content. The selected region of the sample is isolated by cutting on a wafering saw or by grinding away the unwanted material using a coarse grit. The isolated region is further ground to remove microcracked or weakened parts. The samples are ground dry on a revolving horizontal grinder using a SiC disk. Prior to swelling, typical samples are from 0.5 to 2.0 mm thick with top and bottom surfaces roughly 20 sq. mm in area. In the final grinding of the samples the top and bottom surfaces are ground parallel on a 600 grit SiC disk.

Sometimes samples can be swollen in the liquid form of the swelling agent without appreciable crack formation; but there has been better success by more slowly swelling the sample in the vapor of the solvent wherein its vapor pressure is well below its saturation value. Usually conditions have been used in which the swelling occurs over about one day. Although after swelling the top and bottom surfaces may no longer be precisely parallel, they are generally sufficiently parallel to be satisfactory for measurements. The effect of the deviation from parallelity can be observed in stress-strain curves as a "foot" or as a lower modulus region at the start of the curve. Once they are swollen, the samples are not allowed to dry. Drying usually causes many more cracks than the swelling does. The fully swollen samples have excellent retention of the original shape, and contain few, if any, cracks.

With the coherent specimens of solvent-swollen coals, physical qualities could be readily observed. The highly solvent-swollen specimens of coal have a distinct rubbery feel when pressed between the fingers -- somewhat firmer than a typical rubber band. However, the coals are poor quality rubbers. They split easily when stretching forces are applied to them so they have low tensile strength. The splits tend to have relatively smooth sides, and once a small split forms only a small force is needed to lengthen the crack. On the other hand, under compression the rubbery coals can generally undergo compressions of 15% or even more without splitting occurring.

The coals used in this study were Illinois No. 6, which is of high volatile C rank, and Pittsburgh No. 8, which is of high volatile A rank. The samples were extracted in pyridine prior to the measurements. The measurements were made at room temperature. The apparatus utilized was an Instron mechanical tester Model No. 1122. The measurements were made in the compression mode. Measurements in the tensile mode are disadvantageous because of the difficulty in clamping the rubbery coal and because it is very weak under tensile stresses. The samples were fully immersed in pyridine during testing.

RESULTS and DISCUSSION

Stress-Strain Measurements

Stress-strain measurements involve compressing the sample at a constant rate until the desired degree of deformation is obtained. Then instantaneously the direction of movement of the crosshead is reversed and the sample undergoes decompression. When more than one cycle was taken, there was a one minute waiting period between the end of the previous cycle and the start of the next cycle. This allows for some recovery of the sample between cycles.

Stress-strain results for pyridine-immersed, rubbery Illinois No. 6 coal are shown in Figure 1. The curve actually consists of two compression/expansion cycles. The closeness of the two cycles demonstrates excellent reproducibility. At the maximum strain the compression was about 10%. The stress-strain behavior of the pyridine-swollen coal is characteristic of a rubbery material. The modulus is in the range of conventional rubbers, there is rapid rebound during the decompression, and the curves exhibit good reproducibility over successive cycles.

The stress-strain curve for pyridine-immersed rubbery Pittsburgh No. 8 coal is shown in Figure 2. Two stress-strain cycles are shown. The heavy curves are the first cycle and the light lines are the second cycle. It is seen that the first and second cycles are very close to the same shape, but there is a slight displacement of the second cycle with respect to the first. The displacement is caused by incomplete recovery of the rubbery coal after the first cycle; a slight deformation or "set" was retained in the sample. Some of this "set" relaxes if a longer waiting time between cycles is used.

The shape of the decompression curve in the region of low force for the Pittsburgh No. 8 coal is considerably different from the Illinois No. 6 coal shown in Figure 1. The curve for the Pittsburgh No. 8 coal actually reaches zero force well before the crosshead returns to its initial position. This is a manifestation of incomplete recovery of the Pittsburgh coal at the test rate used. The macromolecular chains in the coal are not able to reorient fast enough to keep up with the crosshead. The point at which the force becomes non zero near the start of the second cycle for the Pittsburgh coal is at a considerably lower strain than where the force became zero during the decompression of the first cycle. This demonstrates that during the one minute waiting period before starting the second cycle, the coal has recovered to near its original height.

The slope of the stress-strain curve gives the dynamic Young's modulus. The dynamic moduli of the Illinois No. 6 and Pittsburgh No. 8 coals determined near the top of the compressional part of their stress-strain curves are given in Figure 3. Both elastic and viscous effects contribute to the dynamic Young's modulus. The elastic component is caused by the instantaneous effective cross-link density in the coal including temporary entanglements. The viscous drag results from the resistance of the macromolecular chain segments sliding past each other. The dynamic Young's modulus of the coals is influenced by how fast the macromolecular chain segments are able to

reorient in response to the applied stresses. If the reorientation is fast compared to the imposed strain rate, then the modulus should show relatively little dependence on the strain rate; whereas, if the reorientation rate is comparable to the strain rate, a large dependence on strain rate would be expected. The dynamic modulus is also affected by some of the solvent being squeezed out of or absorbed into the rubbery coal during portions of the cycle.

Figure 4 shows the effect of deformation rate on the dynamic Young's modulus of the coals. For a change in deformation rate of a factor of 25, the Pittsburgh No. 8 coal shows relatively little change in modulus. For the Illinois No. 6 coal the change in modulus is slightly larger even though the difference in rate is a factor of 10 rather than 25. It is not clear whether this change is related to the higher deformation rates used with the Illinois No. 6 coal (which would suggest that more of the macromolecular relaxation occurs at higher rates) or whether the change is indicative of structural differences between the Illinois No. 6 and Pittsburgh No. 8 coals.

The area enclosed by the stress-strain curve is the integral of force times distance over the cycle, so it is the net work done by the apparatus on the rubbery coal. This energy is dissipated in the sample as heat. The energy dissipation arises from the viscous movements of the macromolecular chain segments and also from some solvent being released from or absorbed by the rubbery sample during the cycle. The ratio of the net energy dissipated over the cycle to the maximum energy stored in the sample during the cycle is commonly used as a figure of merit to quantify the energy dissipation of a rubbery substance. A table showing the energy dissipations of the Illinois No. 6 and Pittsburgh No. 8 coals is given in Figure 5. The Pittsburgh coal exhibits a particularly high energy dissipation. Both coals show high energy dissipation as compared to most conventional rubbers, such as the rubber band.

Stress-Relaxation Measurements

The stress-relaxation behavior of macromolecular materials is an important probe of the rates of segmental motion of the substance. In a stress-relaxation measurement the sample is rapidly compressed by a selected amount, after which the deformation is held fixed. The stress on the sample is then measured as a function of time.

A stress-relaxation curve for Illinois No. 6 coal in its pyridine-swollen rubbery state is shown in Figure 6. The observed behavior can be explained as follows. As the sample is rapidly compressed, the structure deforms and the stress increases. When the sample first attains the selected deformation after the rapid compression, the macromolecular chains have not yet reached their equilibrium state. With time the macromolecular chain segments rearrange (within the constraints of the cross-links) to more probable configurations. As the macromolecular chain segments move past each other and the reorganization proceeds to a more entropically favorable state, the stress exerted by the rubber on the fixed constraining plates decreases. This is seen as a downward slope in a plot of stress versus time, such as is seen in Figure 6. Some degree of stress relaxation is characteristic of most rubbery materials. Slow

stress-relaxation indicates low mobility of some of the macromolecular chain segments, or high internal viscosity.

For liquid-saturated rubbers some of the liquid is squeezed out under compressive stress. This loss of liquid contributes to the stress-relaxation, though, it is a diffusional process involving small solvent molecules as contrasted to the segmental rearrangement of the macromolecular structure. For most swollen polymers this loss of fluid is small. For the pyridine-immersed coal samples there will also be loss of some liquid as a result of compression and it will contribute to the stress-relaxation. The extent of fluid loss under compression for coals has not been established. It is thought that the slower relaxation at longer times is caused primarily by this diffusion of solvent out of the rubbery coal.

SUMMARY

The first mechanical measurements on satisfactory samples of rubbery coals have been made. The rubbery character of highly solvent-swollen coals has now been substantiated by direct mechanical measurements. The techniques developed allow us to apply many of the methods and approaches of polymer science to the understanding and characterization of macromolecular properties of coals.

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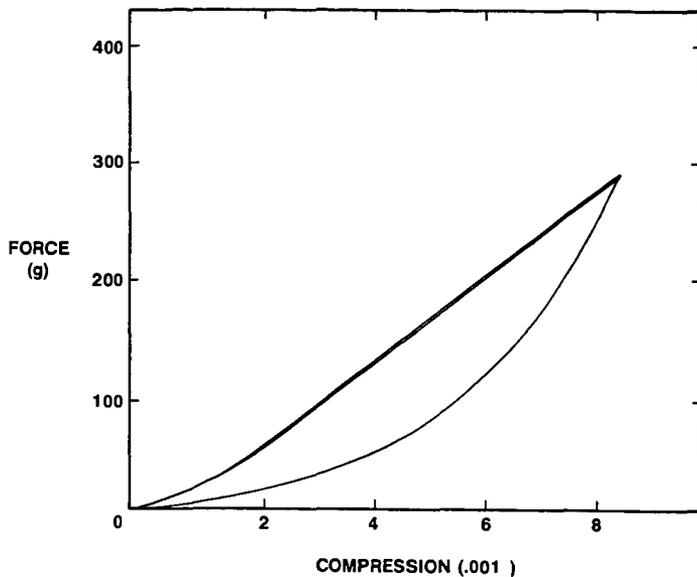


Fig. 1. Stress-strain curve for pyridine-immersed rubbery Illinois No.6 coal

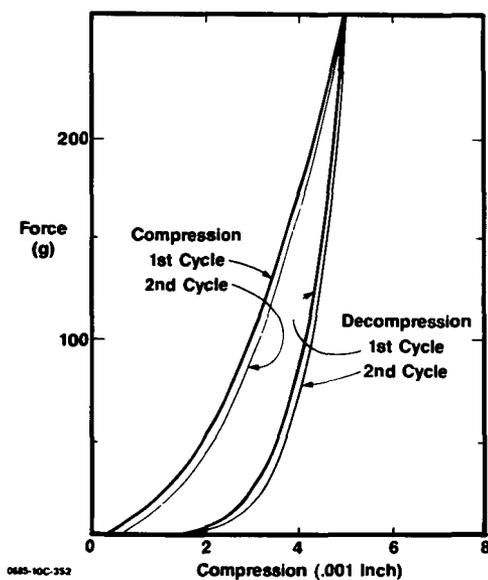


Fig. 2. Stress-strain curve for pyridine-immersed rubbery Pittsburgh No.8 coal

Fig. 3. RUBBERY MODULI OF COALS FROM STRESS-STRAIN CURVES

| <u>COAL</u> | <u>%C (dmmf)</u> | <u>MODULUS (psi)</u> |
|------------------|------------------|----------------------|
| Illinois No. 6 | 80 | 600 |
| Pittsburgh No. 8 | 85 | 300 |

Fig. 4. EFFECT OF DEFORMATION RATE ON MODULUS

| <u>COAL</u> | <u>%C</u> | <u>HIGH Deformation Rate (inch/min.)</u> | <u>LOW Deformation Rate (inch/min.)</u> | <u>Ratio of Moduli Low Rate High Rate</u> |
|------------------|-----------|--|---|---|
| ILLINOIS No. 6 | 80 | .2 | .02 | .7 |
| PITTSBURGH No. 8 | 85 | .05 | .002 | .8 |

Fig. 5. ENERGY DISSIPATION BY COALS IN THEIR RUBBERY STATE

| <u>COAL</u> | <u>%C</u> | <u>RATIO OF ENERGY DISSIPATED PER CYCLE TO MAXIMUM WORK OF DEFORMATION</u> |
|------------------|-----------|--|
| ILLINOIS No. 6 | 80 | .30 |
| PITTSBURGH No. 8 | 85 | .50 |

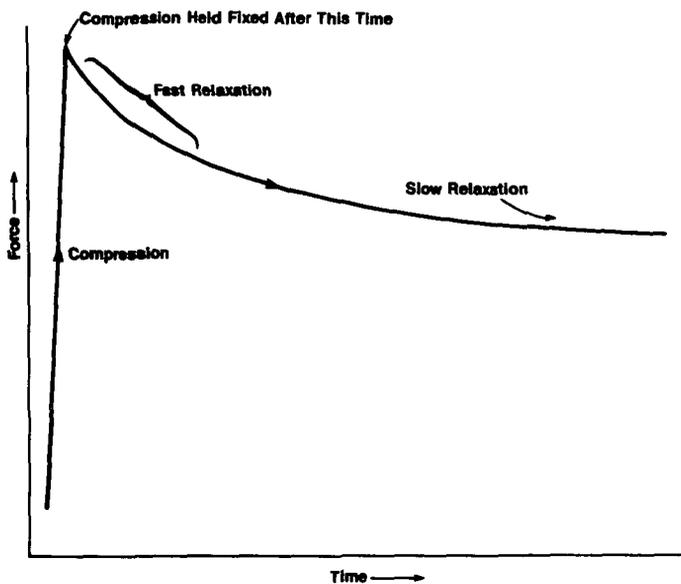


Fig. 6. Stress relaxation of pyridine-immersed rubbery Illinois No.6 coal