THE VISCOELASTIC BEHAVIOR OF SOLVENT-SWOLLEN COAL

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Introduction

Under conditions typical of most industrial processes, such as liquefaction, coal is subjected to thermal and pressure- driven stresses. Deformation, diffusion, and chemical reaction all occur simultaneously during liquefaction; in order to optimize process conditions, it is important to understand the nature of such internal processes occurring within coal. Details on the time dependences of such processes could reveal much about the architecture of coal's macromolecular network.

Viscoelasticity is an important time-dependent phenomenon in terms of elucidating aspects of coal's structure. Coal's viscoelastic properties in the glassy state have been measured by numerous researchers[1-5]; under such conditions the measurements only detect deformational mechanisms which are rapid and correlate over a very short contour interval, where the contour describes the spatial arrangement of a macromolecular chain. At higher temperatures (T > 250 ·C) deformational mechanisms involving larger scale contour relationships become important. It is these larger scale motions which dominate coal's physical response to process conditions. The thermo-mechanical behavior of coals has also been measured[6]; in addition to viscoelastic behavior at elevated temperatures thermal degradation also accompanies the viscoelastic deformation. The presence of such parallel processes greatly hinders interpretation of macromolecular characteristics, i.e. under conditions of thermal degradation the state of the coal's network structure is also time dependent. The optimum experiment would be to characterize coal in a rubbery state at room temperature. Brenner demonstrated that coals immersed in appropriate solvents, such as pyridine, exhibit rubbery characteristics[7]. He subsequently quantified this observation by measuring coal's elastic modulus while in the swollen state[8]; the magnitude of this was shown to lie in the range of stiff rubber. The experiments of Brenner constituted an important step towards characterizing coal's macromolecular structure. This present paper continues the investigation and focuses on a set of simple experiments designed to highlight aspects of the viscoelastic behavior of solvent swollen coals.

Experimental

The experiments described in this presentation involve monitoring creep (i.e. time-dependent strain) under compressive stress. The two samples used in this study were procured from the Penn State Coal Sample Bank; both coals are high volatile C bituminous in rank from the Illinois No. 6 and the Lower Kittaning seams, respectively. Details on the samples are presented in table 1 under the designation PSOC-1539 and PSOC- 1274, samples 1 and 2, respectively. The sample selection and preparation protocol has been described in detail elsewhere[9]. The crucial characteristics of an optimum sample for such studies are 1) that it be homogeneous, i.e. entirely vitrinite, 2) that it be exhaustively extracted in pyridine, and 3) that it be free of cracks. Using the protocol described in reference 9, these ideal characteristics are very closely approached. The instrument employed to measure strain is a microdilatometer also previously described[9]. In brief, vertical displacement of a piston is measured using a linear variable differential transformer (LVDT); the analog signal is sent to a chart recorder so that strain can be continuously monitored. All measurements reported here are made while the sample is immersed in solvent.

Two different experiments were conducted; in the first, a constant compressive stress was applied to the sample, while the resultant strain was measured as a function of time; a standard creep test. In the second, the sample was subjected to a progressively greater stress up to a maximum on the order of 0.6 MPa. Upon reaching the maximum, the stress was progressively reduced. The stress rates in both loading and unloading are on the order of 0.2 MPa/min. To avoid introducing uncertainties in the position of the piston upon complete unloading, it was necessary to unload only to approximately 0.1 MPa before initiating the next stress cycle. The subsequent stress cycle was begun only after the strain recovery rate reached zero.

The precision of the instrument is such that displacements on the order of 0.5 μm are detectable. The compliance of the instrument is very low; at the maximum stress the LVDT recorded a displacement of less than 5 μm, whereas the typical displacement of a swollen coal sample at stress maximum is on the order of 70 μm in the case of the first experiment and on the order of 300 μm in the second.

Results and Discussion

The time dependent compressive strain of solvent-swollen coal while under a constant stress can be separated into three fundamental deformational modes. These have been illustrated schematically in figure 1. The first is an instantaneous (time-independent) element (Eo in figure 1, which here appears Hookean, but is, in fact, nonlinear, see below). The second mode is a time-dependent, reversible viscoelastic element (K-V in figure 1; signifying that the strain response in this region can be described with a Kelvin-Voigt model). The third mode is a time- dependent, irreversible element (N in figure 1; indicating that strain in this region is largely viscous in nature and thus can considered as a Newtonian fluid with a coefficient of viscosity, η).

The time-dependent strain behavior of sample 2 is presented in figure 2 (the strain presented in this figure is compressive, strain = $-(\Delta L/L)$). The applied stress is on the order of 0.1 MPa; the instantaneous elastic strain component has been factored out and only the time-dependent deformation is presented. Therefore, the magnitude of the strain is calculated from height of the instantaneously compressed sample. The magnitude of the instantaneous deformation, under a small stress applied in this manner, accounted for approximately 50 percent of the strain. As will be discussed below, however, the instantaneous strain is nonlinear and its contribution to the total strain diminishes with progressively increased stress.

The first part of figure 2 corresponds to viscoelastic deformation which can be described with a generalized Kelvin-Voigt element model (i.e a model in which elements composed of a Hookean solid spring in parallel with a Newtonian fluid dashpot are arranged in a series). At longer times ($t > 30$ minutes) the deformation is essentially linear and can be modeled using a single Newtonian fluid dashpot. The viscosity of the "fluid" in this case is calculated to be approximately 3×10^{8} centipoise.

The behavior of this coal at small strains (figure 2) suggests that linear viscoelastic models could be applied to parameterize sample 2's strain behavior. Investigations at higher stresses, however, indicate that the overall viscoelastic behavior is significantly non-linear. Non-linearity in the instantaneous reversible strain component is demonstrated in figure 3 (sample 1), where the incremental displacement accompanying incremental stress clearly decreases. A noteworthy point is that magnitude of the incremental displacement for a given stress is apparently independent of the other deformational mechanisms.

The viscoelastic behavior of sample 1 with cyclic stress loading is presented in figure 4. In this figure, the strain is presented as the ratio of the height to the original height. Several interesting features are evident. First, there is a progressive shift to greater strains with each subsequent cycle, the result of superposition of viscous irreversible deformation on the reversible viscoelastic deformation. Second, upon compression, the stress-strain slope remains essentially constant, i.e. the time-dependent compliance remains the same for each cycle. Third, the magnitude of energy dissipation evident upon stress reduction is also nearly constant. The implication is that the same retardational strain mechanisms are being utilized upon each cycle. Also, it appears that these modes are independent of the viscous strain superposed on the entire strain process.

Conclusions

Solvent swollen coals, exhibit three apparently independent strain modes. The first is reversible and time-independent; although it exhibits regular reproducible behavior it is nonlinear, i.e. non-Hookean. The second mode is reversible and time-dependent; it is reproducible, hence predictable. The third strain mode is entirely viscous and appears to be independent of the previous two and is readily treated using a Newtonian fluid model. These results indicate that swollen coal's viscoelastic behavior can be described through a constitutive equation where the individual elements, e.g, Maxwell or Kelvin-Voigt elements, are nonlinear with respect to stress. Coal's viscoelastic behavior, therefore, can be parameterized, e.g. in terms of a retardation spectrum; this has the potential to yield fundamental information on the nature of coal's macromolecular structure.

Acknowlegement

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TABLE 1- SAMPLES

SAMPLE	%C*	%H*	%O*	H/C*	O/C*	$\%R_M$**	%Q***
1539 (1)	81.0	5.5	9.4	0.8	0.1	0.58	2.3
1274 (2)	82.1	5.9	8.0	0.9	0.1	0.63	2.1

• DAF basis
** Mean-Max Reflectance in oil
*** Volumetric Swelling Ratio

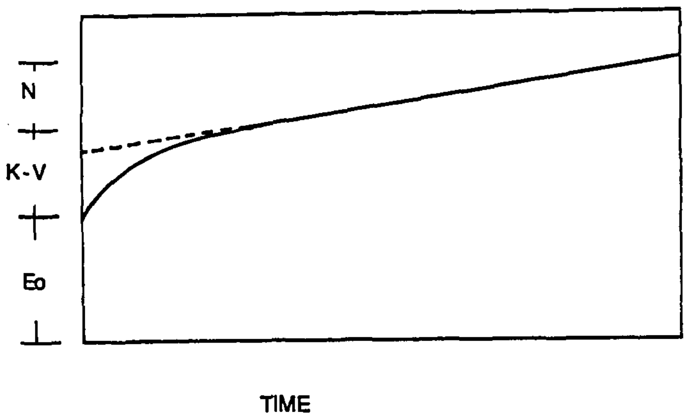

Figure 1: Typical strain vs time curve for a constant applied stress. Eo = instantaneous elastic strain, K-V = reversible viscoelastic strain, N = irreversible viscous strain.

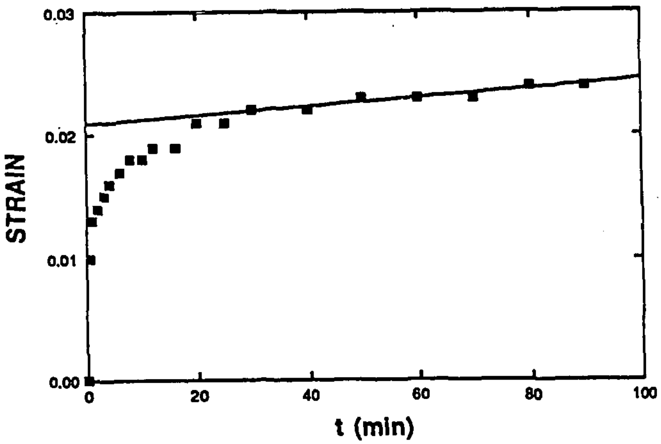

Figure 2: Characteristic Creep curve, sample 2, stress = 0.1 Mpa

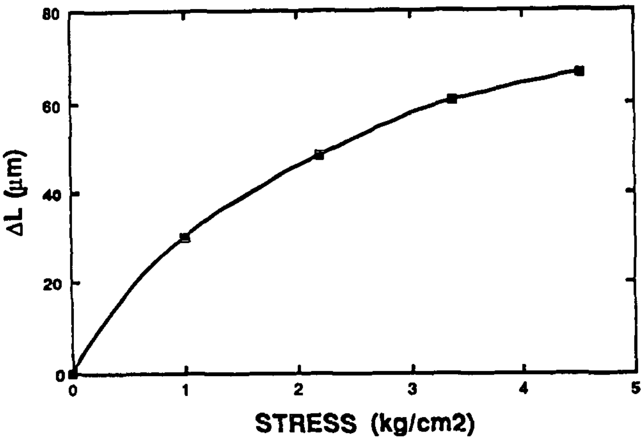

Figure 3: Incremental displacement due to instantaneous strain vs. stress, sample 1.

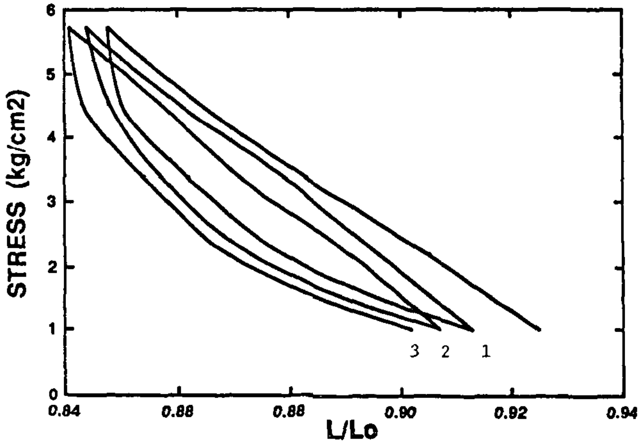

Figure 4: Compressive stress - strain cycles, sample 1. The stress rate is 0.2 Mpa/min