

VISCOELASTIC PROPERTIES OF BITUMINOUS COALS

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INTRODUCTION

The study of the swelling and thermal behavior of coals and the implications these have on possible coal structures are of increasing interest as industrial processes are developed for coal utilization (liquifaction and gasification). Developing accurate structural models and appropriate relations to predict the swelling and thermal behavior of coals would greatly aid plant design by enabling engineers to estimate reaction kinetics and mechanisms for reactions.

It is useful to consider coal as a crosslinked macromolecular network when explaining its swelling and thermal behavior. A crosslinked structure such as that illustrated in Figure 1 has been proposed by Lucht and Peppas [1]. This type of model is in agreement with current experimental findings and is applied in the analysis of experimental results.

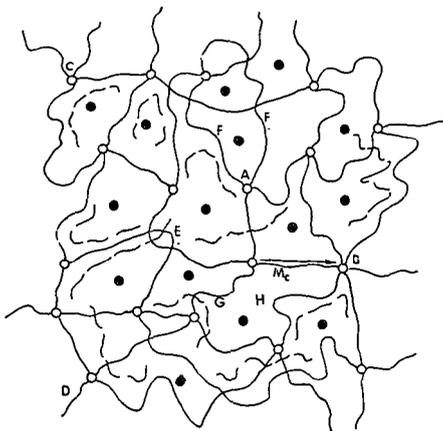


Figure 1. Simplified representation of the crosslinked structure of coal including possible defects. —: Chains participating in network structure; - - - -: extractable (unreacted or degraded) chains; O: crosslinks (junctions); ●: molecules of swelling agent; M_c : molecular weight between crosslinks; A: tetra-functional crosslink; B: multifunctional crosslink; C: unreacted functionalities; D: chain end; E: entanglement; F: chain loop; G: effective network chain; H: mesh size.

Chemical and Physical Structure of Coal

Interpreting the physical structure of macromolecular chains in coal with cross-linked macromolecular network models and theories has become increasingly common in the recent past, although such models have existed for over twenty years [2]. If mineral matter, ash and other impurities naturally occurring in coal are excluded,

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coal structures can be described by two distinct phases. The first phase consists of small and large molecules which are uncrosslinked and occupy a substantial portion of the whole coal sample. These macromolecular chains can be intact uncrosslinked molecules formed during diagenesis [3], or somewhat degraded chains formed by depolymerization reactions during the metamorphic stage of coal development. The primary phase of the coal structure consists of a highly crosslinked macromolecular phase forming a crosslinked three-dimensional network (coal matrix) [1]. This is the structure shown in Figure 1, which depicts several forms of macromolecular chains and possible chain defects.

The crosslinked structure cannot be extracted or dissolved at low temperatures (unless the solvent acts by combined diffusion and reaction, as in depolymerization), and is characterized by both physical and chemical crosslinks. Physical crosslinks are found in highly entangled macromolecular chains that, because of inherent rigidity, have restricted mobility. In this case, disentanglement is not likely. Chemical crosslinks are formed by chemical reactions between two or more coal chains, which lead to multifunctional crosslinks.

Coal researchers have considered models of various "reconstructed" chemical structures of coal as a means to support their theories [3]. But model networks such as those proposed by Wiser and Given are only indicative of the type of chemical crosslinks one would expect in coal, and are not proof of the physical structure of coal or the size of macromolecular chains between crosslinks. Chain ends, unreacted functionalities, chain loops and multifunctional crosslinks are types of defects which make an accurate analysis of the coal network unlikely.

The nature of the crosslinks in coal is a point of scientific dispute. Most of the work on identifying coal crosslinks relies on analysis of the products of depolymerization and degradation reactions. Because the system is complex and strong intermolecular interactions occur, analyzing the results is difficult, often leading only to speculations about chemical structure [3,4].

A promising analytical technique for degradation products (coal liquids) is based on mass-analyzed ion kinetic energy spectrometry. Other techniques have been used including elemental analysis and identification of decomposition and extraction products from coal, IR spectroscopy, high resolution NMR, and GC/mass spectroscopy. These results have given us a clearer understanding of the types of chemical bonds involved in crosslinking.

Viscoelastic Properties of Coal

One aspect of the macromolecular coal structure which has been given very little attention upto now is its viscoelastic behavior. It is in general known that coal at high temperatures, close to the liquefaction temperature of 300-350°C, softens and behaves as a highly viscous material. Its viscosity becomes dependent on the conditions of application of stress or strain. For example, Nazem [5] studied the non-Newtonian behavior of carbonaceous mesophase pitch at high temperatures using a Haake viscometer and established the non-Newtonian behavior in terms of the viscosity as a function of the shear rate. Briggs [6] investigated the viscosity of coal tar pitch as a function of temperature. Covey and Stanmore [7] attempted to present a constitutive equation for the rheological behavior of Victorian brown coals of Australia.

An alternative approach of investigation of the viscoelastic behavior of coals is through thermal analysis at high temperatures. The early work of Bangham and Franklin [8] established characteristics of the change and expansion of the coal structure at high temperatures. More recently Sanada and Honda [9] used creep deformation experiments of various Japanese coals to establish their mechanical behavior at high temperatures. Finally, Rovenskii and Melnik [10] were the first and probably the only investigators upto now to investigate the use of thermo-mechanical analysis as a method of characterization of coals.

Here we present new and important information on the results of thermomechanical analysis of some American bituminous coals.

EXPERIMENTAL PART

Previously stored in nitrogen, flat coal samples of the following coals were used in the present studies: PSOC-418 (69.95% C, dmmf basis), PSOC-791 (72.75% C), PSOC-312 (78.33% C), PSOC-853 (80.15% C), PSOC-402 (82.48% C) and PSOC-989 (88.81% C); all obtained from the coal bank of the Pennsylvania State University. All samples had an initial surface area of approximately 2.5 mm². They were tested in a thermo-mechanical analyzer (model TMS-2, Perkin Elmer, Norwalk, Conn.) using the penetration mode of the device, under continuous purging of nitrogen and starting from an initial temperature of 35°C. The tip of the probe was round with a surface area of 0.6207 mm². All samples were tested under the application of loads of 10, 20, 30 and 40 g corresponding to stresses of 0.158, 0.316, 0.474 and 0.632 MPa, respectively. Unless otherwise noted, all studies were performed at a scanning speed of 10°C/min and upto 350°C. The deformation was determined as a function of time and transform to strain by dividing by the original thickness of the flat samples.

RESULTS AND DISCUSSION

Figures 2 and 3 present the strain versus time curves for two of the samples tested, a PSOC-791 sample with 72.75% C on a dmmf basis and a PSOC-312 sample with 78.33% C. It must be remembered that, since the scanning speed is 10°C/min, the same plots represent the deformation, as designated by the strain, as a function of temperature.

All curves show an early induction period which lasts for approximately 5-10 minutes or 50-100 °C and is characteristic of the very slow compressive creep of highly glassy polymeric materials. Indeed for these coals we have determined [11] values of T_g in the range of 300-350°C, much higher than the temperatures at the beginning of these experiments. After about 18 to 25 minutes from the beginning of the experiment, corresponding to temperatures of 215°C to 285°C, a plateau is observed in the strain versus time behavior. Further temperature increase leads to considerable increase of the strain probably due, either to yielding of the macromolecular coal structure at temperatures where enough mobility of the macromolecular chains has been attained, or to thermal degradation at these temperatures. However, the second explanation is probably not valid since thermogravimetric

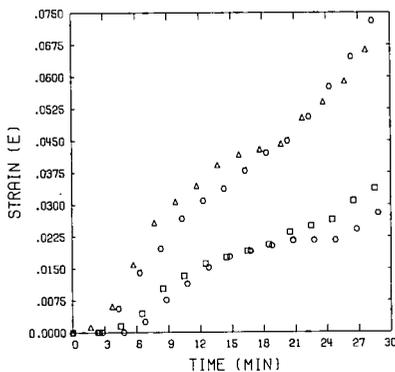


Figure 2: Compressive strain as a function of time for flat coal samples of PSOC-791 (72.75% C, dmmf basis). The results are for applied stresses of 0.158 (○), 0.316 (□), 0.47 (△) and 0.632 (◇) MPa.

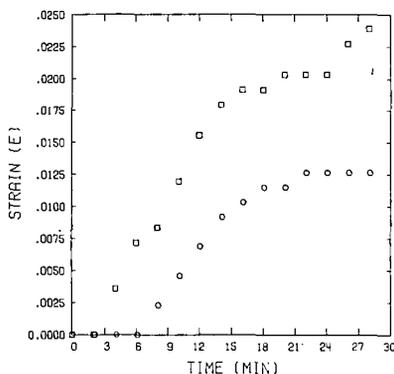


Figure 3: Compressive strain as a function of time for flat coal samples of PSOC-312 (78.33% C). The results are for applied stresses of 0.474 (o) and 0.632 (□) MPa.

analysis experiments under the same scanning speed using a thermogravimetric analyzer (TGS-2, Perkin Elmer, Norwalk, Conn.) showed little measurable weight change of the coal samples up to 250°C.

Figure 2 shows also the general dependence of the strain on stress. Indeed, as the stress increases, the strain is higher and the point of deviation from the original plateau is at lower temperatures (or times), which is characteristic and typical of similar behavior in polymer networks.

Finally, comparison of the data of Figures 2 and 3 at the same stress shows that for the coal samples with the lower carbon content, at the same scanning time the strain is much higher than that of the samples with higher carbon content. This is a clear indication that PSOC-791 is less crosslinked than PSOC-312, a notion which is clearly supported by our recent data on the determination of M_c of these and other coals [12]. Samples PSOC-402 (with 82.48% C) and PSOC-989 (with 88.81% C) were tested not only at these stresses but also at 0.790 and 0.948 MPa. In no cases was any deformation observed, an observation characteristic of very highly crosslinked structures.

Further analysis of these data was achieved by using the Nutting theory, which when applied to creep data, suggests that the creep compliance is logarithmically dependent on time according to equation (1).

$$J = \psi t^n \quad (1)$$

Here J is the coal structure compliance, which is calculated from the previous graphs by dividing the strain by the applied stress, t is the creep time and ψ and n are two constants characteristic of the coal structure.

Figure 4 shows a plot of $\ln J$ versus $\ln t$ for the samples of PSOC-791 plotted earlier. Although one would expect a linear relationship between these two parameters there are some important deviations. For example, the initial portion of the graph, characteristic of the slowly changing induction period could not be represented by the Nutting equation, because of the highly "frozen" structure of the macromolecular network of coal. The region between $\ln t$ of 2 and 3.2 can be reasonably represented by straight lines, which in accordance with Nutting's equation, are parallel for different stresses.

An interesting aspect of these studies is also shown in Figure 5 which presents the insignificant effect of the scanning speed rate on the strain-time behavior. The same figure shows that a continuous increase of the strain is observed even

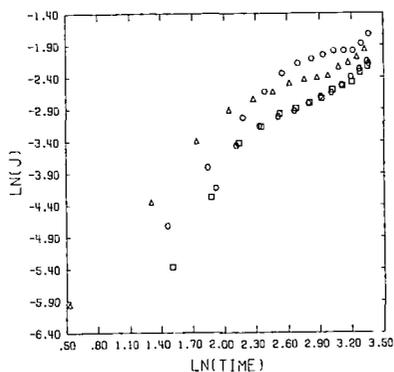


Figure 4: Nutting plot of the compliance of coal structures as a function of time for PSOC-791 (72.75% C). The data are for the same stresses as in Figure 2.

after 60 minutes (at 5°C/min), corresponding to a temperature of 335°C, where the coal "flows" since it is above its T_g.

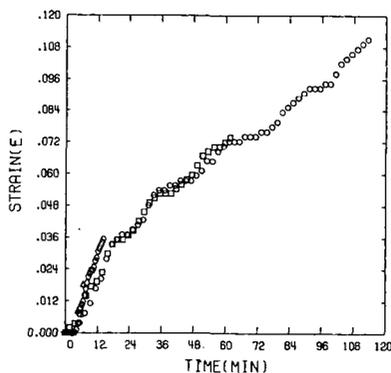


Figure 5: Effect of scanning speed on the strain-time curve. Results for coal PSOC-418 (69.95% C) with 2.5 (○), 5(□), 10 (Δ) and 20 (◇) °C/min.

CONCLUSIONS

These results further support the idea of a highly crosslinked, macromolecular coal network [1], and are indicative of the difficulty by which the thermal degradation occurs.

Aknowledgements

This work was supported by research grant D0E-F6-22-83PC60792 of the Department of Energy, Pittsburgh Energy Technology Center. Helpful discussions with Dr. L.M. Lucht are kindly acknowledged.

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