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# THROUGH THE LOOKING GLASS: UNRAVELING THE NETWORK STRUCTURE OF COAL*

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# THROUGH THE LOOKING GLASS: UNRAVELING THE NETWORK STRUCTURE OF COAL

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## ABSTRACT

Numerous swelling parameters measured by magnetic resonance microscopy (MRM) are found to correlate with cross-link density of the polymer network under investigation. Use of these parameters to assess the three-dimensional network structure of coal is discussed.

**KEYWORDS:** coal, swelling, network structure, magnetic resonance microscopy

## INTRODUCTION

Since the original idea by Sanada and Honda[1] of treating coal as a three-dimensional cross-linked network, coal structure has been probed by monitoring ingress of solvents using traditional volumetric or gravimetric methods. However, using these techniques has allowed only an indirect observation of the swelling process. More recently, we have developed magnetic resonance microscopy (MRM) approaches for studying solvent ingress in polymeric systems, about which fundamental aspects of the swelling process can be deduced directly and quantitatively[2-5]. The aim of our work is to utilize solvent transport and network response parameters obtained from these methods to assess fundamental properties of the system under investigation. Polymer and coal samples have been studied to date.

Previous work in our laboratory[4,5] had demonstrated that MRM is clearly capable of distinguishing between Fickian and Case II diffusion, which represent two extremes of solvent transport in macromolecular systems. Fickian transport was characterized in rubbery samples as a smooth solvent concentration profile increasing with the square root of time. This process was typical for samples that did not undergo a change in physical state as a result of solvent ingress. By contrast, Case II transport processes were found in glassy polymers and coals that underwent a glass-to-rubber transition during swelling. Transport was characterized by a sharp solvent front moving linearly with time, and network relaxation occurred on a time frame that was fast compared to diffusion of the solvent through the network.

It has long been observed that many polymer systems exhibit what is termed anomalous transport behavior. As in Case II transport, the solvent modifies the physical state of the polymer; however, the transition of state occurs on a time scale comparable to diffusion.

Recent MRM studies have shown direct evidence for the latter process, and has allowed a direct observation of network response with relation to cross link density of the network. To perform these measurements, we took advantage of "contrast" imaging protocols, using protonated and deuterated solvents, and thereby observed physical changes in rubber samples imbibed with solvent. Using contrast-imaging techniques, i.e., employing diffusion weighting or $T_2$ weighting, we were able to obtain additional information on the polymer network directly. We studied four cross-linked isobutylene/*p*-methylstyrene rubber samples and showed that several NMR parameters correlate directly with cross-link density.

## RESULTS AND DISCUSSION

### Imaging of Protonated Solvent

Time-resolved MRM experiments monitoring ingress of cyclohexane in several rubbers has suggested anomalous swelling behavior. Consistent with this, the region in the center of the samples was completely devoid of solvent throughout the swelling process. Although the cyclohexane front retained the original object shape throughout, the solvent front was not completely sharp as would be expected for pure Case II behavior.

The velocity of the solvent front correlated well with cross-link density. The velocity of the front was greatest in samples with lower cross-link density. This result is expected in light of the diffusion coefficient measurements, which showed that cyclohexane diffuses faster in samples with a lower cross-link density.

Although we attained reasonably good fits to the data with a linear function of position of the solvent front (x) vs. time (t), this approach is only completely accurate in those cases where swelling is purely Case II. Instead, the data were fit to a generalized function:

$$x = k + v \bullet t^n, \tag{3}$$

where k = constant and v = front velocity. For the entire suite of rubbers, the average value calculated for exponent n ranged from 0.75 - 0.87, which implied the dynamics of swelling are intermediate between Fickian (n=0.5) and Case II (n=1).

MRM images of cyclohexane swelling of a rubber specimen are shown in Figure 3; a diffusion filter was applied prior to imaging for the images on the right. Because the diffusion coefficient of cyclohexane imbibed in the rubber is substantially less than in the bulk, signal from the faster diffusing bulk solvent is surpressed. In the diffusion-weighted images, however, the intensity of imbibed solvent is greatest immediately behind the solvent front. This is in contrast to the unfiltered images, where the signal intensity is fairly uniform throughout the swollen part of the sample. Thus, there is a direct correlation between intensity of pixels in the diffusion-weighted image and absolute magnitude of the diffusion coefficients. Bright regions indicate solvent with correspondingly lower diffusion coefficients.

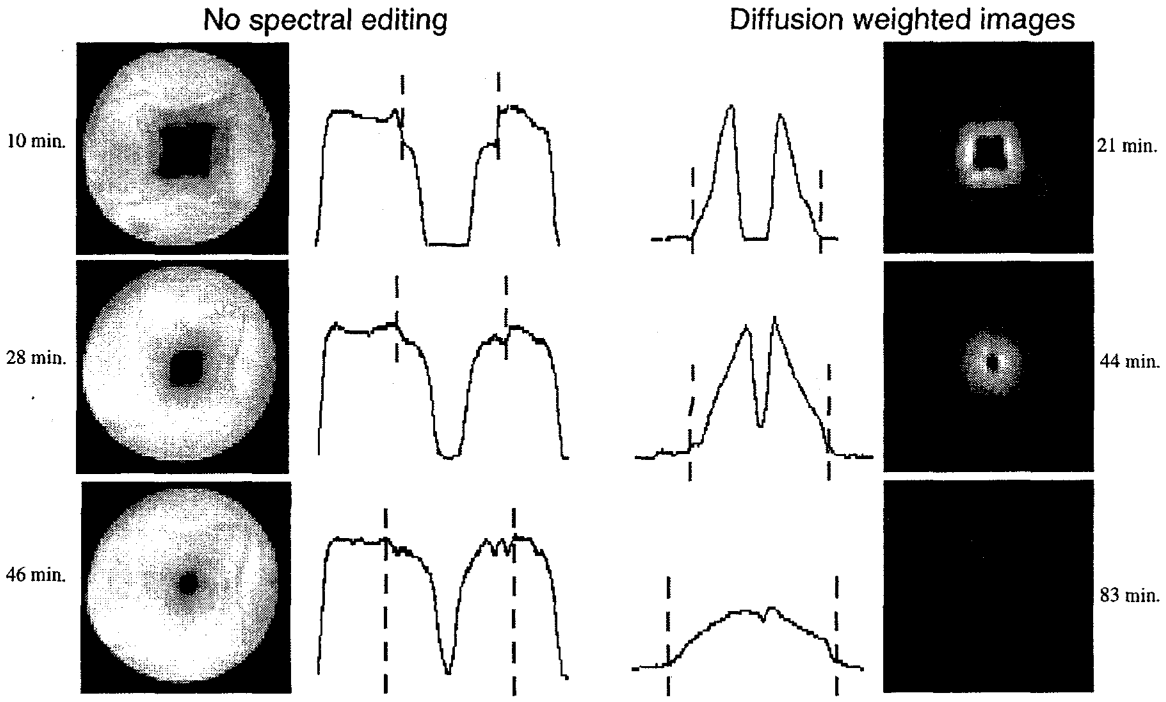

**Figure 3.** Spin-echo (left) and diffusion-weighted (right) MRM images of rubber specimens.

Moreover, gradations in diffusion coefficients across the swollen samples are perceptible in the filtered images. These effects are most clearly seen and measured in the 1D profiles. Because the diffusion coefficient is a measure of mean free path of a solvent molecule, this distance is shortest for solvent molecules near the solvent front and gradually increases with distance behind the front. This implies that the polymer network continues to expand well after its voids have been filled with solvent.

Imaging in Deuterated Solvent

By acquiring proton images of the rubber samples during a swelling experiment with $d_{12}$-cyclohexane, we were able to observe changes in the properties of the polymer directly. During swelling, conventional spin-echo MRM indicated that the greatest density of polymer occurs near the solvent front. Behind the front, the density of polymer gradually falls off, consistent with previous results from diffusion-weighted imaging.

Distributional $T_2$ maps created from the data show a gradation in $T_2$ values, again with the shortest $T_2$'s occurring near the solvent front. This parameter reflects changes in polymer chain motion, i.e. the frequency of motion of the polymer chains increases gradually with increasing distance from the solvent front.

We also monitored changes in $T_2$ vs. swelling time for an area of polymer at a constant distance from the outside edge of the sample. The data fit well to a simple exponential function. The 'rate' of change in $T_2$ for protons in the polymer correlates with cross-link density of the rubber; the rate is slower for samples with higher cross-link density. Final $T_2$ values show the same trend; samples with a higher degree of cross linking exhibit a lower final $T_2$ value.

## Relation to Mechanical Models

As we have shown, diffusion coefficients of the solvent and polymer $T_2$ values parallel one another and reflect the segmental motions of the polymer chains. These changes take place on a time scale comparable to the diffusion process and are characterized by a single rate constant. At this point it is tempting to try to find analogies between the swelling process that we observe and the mechanical processes commonly measured in polymer systems[4]. We draw an analogy between changes in the motional correlation times of the network and strain relaxation in stress-strain experiments.

In a stress-strain experiment, a constant mechanical stress is applied, and the strain required is measured. In a swelling experiment, a constant osmotic stress is exerted by the solvent at and beyond the solvent front. In this case, segmental motion of the polymer chains is measured. In both cases, the strain decreases, or relaxes, over time. In the simple Maxwell model, the relaxation rate is given by a single exponential function. As shown in Figure 4, network relaxation rates, as represented by the experimental $T_2$ relaxation times and solvent diffusion coefficients, decrease with higher cross-link density of the polymer network.

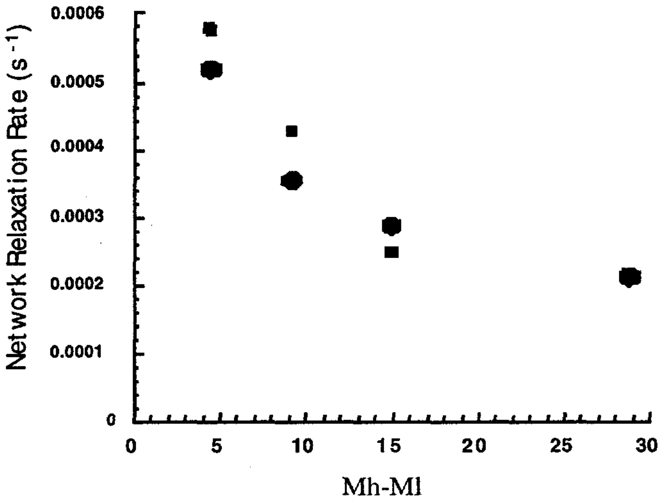

**Figure 4.** Changes in strain rate from $T_2$ (circles) and diffusion-weighted (squares) images with cross-link density (Mh-Ml) from rheometry torque measurements.

## Preliminary Studies on Coal

MRM images depicting *in situ* swelling of a selected specimen of Pittsburgh No. 8 (APCS 4) vitrain with pyridine are shown in Figure 5. The swelling behavior of this coal is highly anisotropic, and is characterized by the solvent moving fastest in a direction perpendicular to the bedding plane. Diffusion of pryidine in this coal is purely Case II: the solvent front is extremely sharp, moves at a constant velocity, is linear with time, and has an exponential factor close to unity. Furthermore, bright regions are not observed near the solvent front in diffusion-weighted images, suggesting that network relaxation occurs on a time scale that is considerably faster than solvent diffusion.

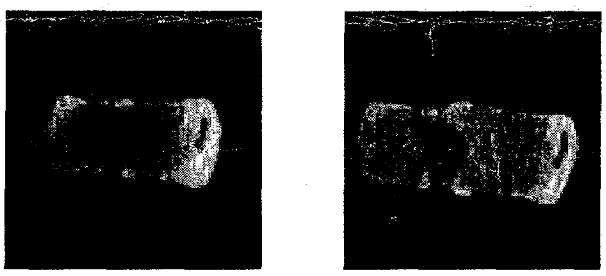

**Figure 5.** Time-resolved MRM of swelling of Pittsburgh No. 8 vitrain in pyridine.

## Back to the Future

It is without question that unraveling the three-dimensional architecture of coal will be key in advancing our understanding of coal behavior and reactivity. In attempts to realize this objective, many researchers in the past have performed systematic swelling studies on coals of different rank. Recently, Suuberg and coworkers[6] have explored thermodynamic aspects of solvent-coal interactions by monitoring swelling kinetics as a function of solvent type and temperature. Trends in the observed activation energies were consistent with those expected on the basis of size effects of the solvent molecules and by disruption of donor-acceptor and/or hydrogen bonding interactions. Painter and his coworkers[7,8] also have explored the intricate balance of thermodynamic forces in various hydrogen bonded systems and have developed good mathematical approaches to model the influence of strong intermolecular interactions on polymer properties. There is little question that theoretical treatment of solvent/solute thermodynamics holds the answer to understanding coal behavior, albeit heretofore difficult to realize.

Our previous work[4] has allowed an estimate of strain rates from solvent front velocities and network relaxation rates, assuming coal/solvent systems exhibit pure Newtonian viscous behavior. To a first-order approximation, the strain rate can be related to the osmotic stress imparted by the solvent, i.e., the chemical potential of the solvent in equilibrium with the polymer. By applying Flory-Rehner (F-R) theory, parameters such as the number-averaged molecular weight between cross links may be estimated.

Assuming stress is purely osmotic in nature, $\sigma = \Pi$, it follows that for a Newtonian fluid the strain rate

$$d\varepsilon/dt = RT/\nu_s\eta \bullet \ln a_s \qquad (4)$$

Using classical F-R theory, we can determine $\Pi$ at $\nu_2^*$, by defining the chemical potential of a solvent in equilibrium with the polymer

$$\ln a_s = [\ln(1-\nu_2) + \nu_2 + \chi\,\nu_2] + [Z(\nu_2^{1/3} + \nu_2/2)] \qquad (5)$$

solvent terms entropic constraint

where $Z = \rho\,\nu_s / \langle M_c \rangle$, $\rho$ is the dry density of the polymer, $\nu_s$ is the molar volume of the solvent, and $\langle M_c \rangle$ is the number-averaged molecular weight between cross links. In the past, numerous simplifying assumptions had to be made in order to apply F-R theory to coal systems, e.g. ignoring the non-Gaussian behavioir of dense coal networks, hydrogen bonding effects and changing solvent affinities during swelling.

The problem with applying a statistical mechanics treatment to coals as densely cross-linked networks has now been solved using Painter's recently published approach.[9] Furthermore, any contributions from hydrogen-bonding equilibria to the chemical potential can be dealt with by considering hydrogen bonding effects globally as part of the interaction enthapy term, and a resolution of this issue soon will be at hand[7,8] for coal systems. Moreover, in order to compute the osmotic pressure at $\nu_2^*$, one must assume that solvent $\chi$ parameter is independent of concentration. Although this is certainly not true, it is unlikely that $\chi$ will vary significantly with concentration (the 3rd term in equation 5).

Moreover, MRM is now capable of providing us with a number of key parameters which can be related to cross-link density of the network. We are able to accurately monitor propagation of the solvent through the network, and can obtain important parameters such as the rate of solvent transport, the kinetic order of transport (from Fickian, through anomalous, to Case II), spatial distributuions of the solvent diffusion coefficients, and are capable of determining the concentration profile of the solvent front. We have been able to relate these solvent properties to strain rate. Employing deuterated solvents, we additionally are able to monitor changes of the macromolecular network *in situ* during the swelling process. We are able to observe directly mechanical relaxation of the network on the time scale of the swelling experiment, and to determine concomitant changes in microscopic expansion and mobility of the polymer chains.

There are however several relevant issues that need to be resolved first regarding treatment of the MRM data. Can we infer intrinsic strain rates from swelling experiments, in which the stress forces are exerted by solvent at the front under non-equilibrium solvent-solute conditions? Furthermore, is it possible to derive strict relationships of experimental data that are free of assumption yet adequately define fundamental thermodynamic properties of the system? Can parameters such as the $T_2$ and $T_{1\rho}$ relaxation times and the NMR second moments be used to evaluate cross-link densities directly? Finally, would it be possible to systematically vary solvent and temperature conditions of swelling measurements (cf.

Otake and Suuberg[6]) in such a way that influences the kinetic order of transport, thus allowing a direct observation of network relaxation on a time scale appropriate for imaging?

Although the treatment and analysis of MRM data has until now been only approximate, linking network parameters from MRM with new statistical modeling approaches holds exceptional promise in the future for assessing the three-dimensional structure of coal.

## ACKNOWLEDGMENTS

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