

Coal Structure Resolved on the Nanoscale

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Exploring chemistry and materials' properties on the nanometer scale presents significant challenges. Characterization methods such as neutron and x-ray scattering, diffuse-reflectance infrared spectroscopy and nuclear magnetic resonance (NMR) spectroscopy are being applied to probe chemistry on the nanoscale; however, many challenges remain when studying extremely complex, heterogeneous substances. Several obstacles are not easily overcome when applying these modern techniques to structurally complex fossil resources that are vital to our national energy needs.

Recent work has focused on identifying the nanoscale variation in the chemistry of complex carbonaceous solids; in particular, our work has focused on a study of coals from the Argonne Premium Coal Sample Program. Coal can be described as being an "organic rock" comprised of different plant remains that have been geologically altered over time. They are considered to be extremely heterogeneous in nature. We addressed the following question: "At what length scale does the chemical heterogeneity prevail in these materials?" Earlier experiments have provided some insight into this question. Magnetic resonance imaging (MRI) and synchrotron-based scanning transmission x-ray microscopy (STXM) studies carried out at ANL provided detailed, two- and three-dimensional pictographs showing the chemical variation of the organic phases of coal. While the images obtained were impressive, showing a definitive, sharp separation in chemistry along maceral (metamorphosed plant organic matter) boundaries, the maximum image resolution that could be achieved was 50-100 nm at best, on the upper boundary of the nanoscale.

Spin-diffusion NMR techniques are capable of probing chemical heterogeneity on a scale of 2-50 nm. These methods have been applied successfully to the study of phase-separated polymer blends whose components have sufficient chemical distinction. The concept behind the experiment is to establish a magnetization gradient, or non-equilibrium magnetization condition, between the chemically different protons that reside in different domains, and then to allow the magnetization to equilibrate, or to 'diffuse' through domains. From the time dependence of the diffusion process, one can estimate the size of the domains. In this manner, the scale of chemical heterogeneity of the system may be assessed. The challenge has been to apply the method to a substance as complex as coal.

Proton NMR experiments, both inversion-recovery and spin-diffusion types, employing CRAMPS (combined rotation and multiple pulse spectroscopy) methods were performed on a sample of Utah Blind Canyon coal (Argonne Premium Coal Sample No. 6), which is largely a bimaceral coal composed of vitrinite with about 7% resinite. Pure maceral fractions were obtained by physical separation methods in order to measure proton NMR spectra and proton relaxation times on the pure macerals, information which is needed to perform the analyses. Inversion-recovery data for measuring the longitudinal proton relaxation time, T_{1H} , is shown in Figure 1. The T_{1H} relaxation

time decays of the resinite and vitrinite polarizations are distinct and the resinite line shape is extracted from this data based on two characteristics, namely, a) that line width for resinite is significantly narrower than for vitrinite and b) that T_{1H} 's of the vitrinite and resinite are distinct and quantifiable. Thus, knowing the general aliphatic line shape from the CRAMPS spectrum of each maceral, one can separate the resinite spectrum appropriate to this mixed sample from the inversion recovery data. The resinite spectrum is isolated when the broader aliphatic vitrinite component passes through the null condition. Note in Figure 1 that the resinite polarization does not decay exponentially for all time. Nevertheless, the fact that the T_{1H} decays are separable and, in particular, that the resinite component, representing about 20% of the total protons, has an upward rather than a downward deviation from exponentiality, implies that most of the resinite domains exceed 100 nm in size.

We were also interested in the possibility that there might be some resinite domains, which were significantly smaller and within spin diffusion (SD) distances. The CRAMPS preparation chosen produces a modestly negative aromatic and a more strongly positive aliphatic proton polarization. An initial gradient of proton polarization is established between the two maceral phases, thereby allowing the use of the CRAMPS line shape to monitor any subsequent SD between those components. Changes in relative polarization levels of resinite and vitrinite domains with diffusion time are shown in Figure 2 with P_0 representing the polarization at Boltzmann equilibrium. Only data for > 4 ms are included, because intra-phase equilibration dominates at earlier times. There is a reproducible, slightly accelerated rate of decay for the resinite polarization and a correspondingly, hardly perceptible rise in the vitrinite polarization in the 4 ms to 12 ms range. The deduction from Figure 2 in terms of mixing is that a maximum of 20% of the resinite protons are in domains small enough (< 6 nm) to undergo SD on the timescale of 12 ms or less. However, the majority of the protons of resinite are isolated from those of the vitrinite so that the resinite decay rate seen is indistinguishable from the resinite T_{1H} observed in the inversion-recovery experiment. From the similarity of slope for the SD and inversion recovery data for resinite, it is clear that most of the resinite is found in domains large enough (> 100 nm) so that SD on a time scale of 250 to 1000 ms has insignificant effect on the rate of decay.

The findings suggest that the resinite inclusions found in the Utah coal are relatively large in size, consistent with the previous images obtained by STXM, or submicroscopic. These submicroscopic inclusions of 6 nm or less, representing about 20% of the resinite in the Utah coal, have not been identified previously. Their existence implies a process whereby small molecular weight resins produced by the plant epithelial cells percolated through the woody micropores, and subsequent burial and diagenesis led to their ultimate polymerization to form resinite inclusions intimate with the vitrinite matrix. These findings are entirely in accord with the known paleobotany and geochemistry of resins in coal bearing formations, and explain some of the unusual properties of the vitrinite in the Utah coal.

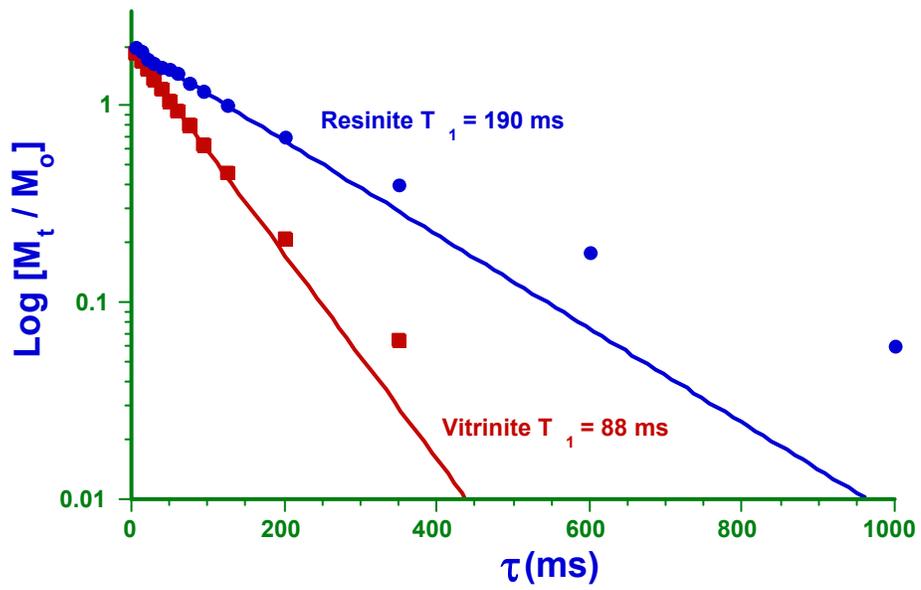


Figure 1. T_1^H of Utah Coal.

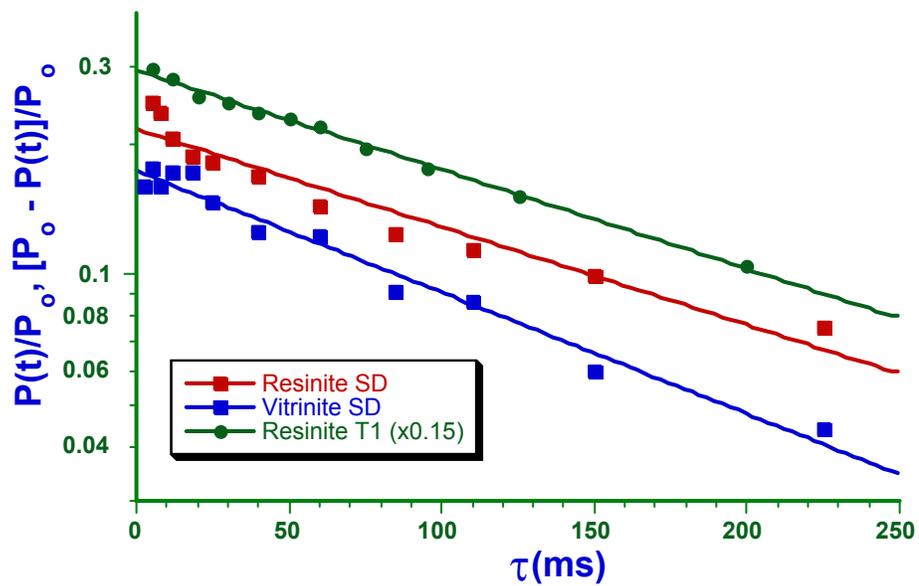


Figure 2. Spin Diffusion in Utah Coal.