

NMR Spin-Lattice Relaxation (T_1) Measurement on Carbon Materials

S. B. Tilden

Union Carbide Corporation, Electrode Systems Division
Parma Technical Center, 12900 Snow Road, Parma, Ohio 44130, U.S.A.

Introduction

The complexity of typical carbonaceous systems (oils, tars, pitches) used in carbon and graphite manufacturing, limit the characterization tools available to the research and/or quality control professional. Bulk physical measurements such as softening point, solvent insolubility tests, flash point, and viscosity, are among those used to characterize these materials. More recently, emphasis has been placed on chemical characterization methods (such as NMR, ESR, DSC, IR, and MS) with the goal being to provide more detailed chemical constitutional and rheological information about these complex carbonaceous systems. The NMR technique is a particularly useful tool which provides direct quantitative information on percent aromaticity and other qualitative constitutional information.

The spin-lattice relaxation time (T_1) measurement is another easily attainable NMR parameter that may be used as a characterization tool useful in the study of complicated carbonaceous systems. The proton T_1 measurement is used to follow and understand the chemistry of heat treated carbonaceous materials.¹ How constitutional and rheological properties and the quantity of unpaired spins influence the spin-lattice relaxation time of model carbonaceous systems will be discussed in this report. Because chemical and physical "manipulations" of carbonaceous systems change the magnitude and, therefore, the relative importance of these factors which influence the T_1 relaxation time, the measurement of T_1 can be a useful monitoring or characterization technique for the study of complex carbonaceous systems.

Experimental

An IBM PC-20 (20 MHz) multispec NMR instrument was used to measure the proton T_1 times of both solid and liquid carbonaceous systems using the standard PC-20 13 mm solid/liquid probe. The temperature-dependent T_1 data was obtained by using the PC-20 7.5 mm variable temperature probe. A specially constructed NMR tube consisting of a fused female T 14/20 ground-glass joint with a companion male T 14/20 ground-glass joint attached to a vacuum valve was used to measure the T_1 of samples under vacuum.

T_1 -Unpaired Spin Interactions

It is well known that unpaired spins contained in the carbonaceous system under study can alter the T_1 relaxation time. Unpaired spins usually exist in all carbonaceous systems to some degree, either as trapped or adsorbed molecular oxygen gas or as free-radicals. The effect of the unpaired spins is manifested as a decrease in the T_1 from the T_1 that would be measured if no unpaired spins were present. Hence, removing molecular oxygen by evacuation resulted in a decrease in the measured T_1 for all carbonaceous systems we studied. In order to meaningfully compare T_1 data, it is necessary to measure the T_1 on samples in which molecular oxygen has been removed.

For a particular carbonaceous system, the T_1 is inversely proportional to the unpaired spin concentration in the sample as shown in Figure 1. The samples were prepared by "spiking" and blending the melted sample with the free-radical DPPH (diphenyl picryl hydrazyl), and then allowing the sample to cool. Free-radicals were generated in the polypropylene sample by gamma irradiation.² The slope of the inverse T_1 versus spin concentration curve can be significantly different for different carbonaceous systems as demonstrated from the data of Figure 1. This difference can be rationalized by considering that the effect of the unpaired spin on the carbonaceous system is also governed by (in solids) a spin diffusion constant and is a function of the sixth power of

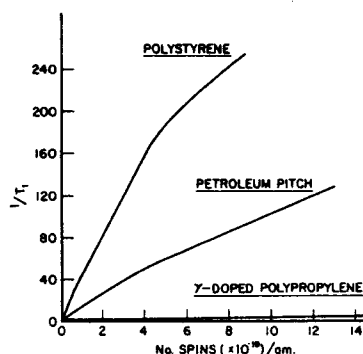


Figure 1. Reciprocal T_1 Versus Spin Concentration of Model Solid Systems. Data of the Eight-Doped Propylene from Reference 2.

the distance between the unpaired spin and the nearest proton layer surrounding the free-radical.² These parameters can vary considerably in different carbonaceous systems.

Constitutional Effects in T_1

The measured T_1 of a carbonaceous system can also be related to the constitution of the solid. Table 1 contains the T_1 values of a representative number of pure solid polyaromatic compounds, the T_1 of a "synthetic pitch" containing equal proportions of eight of these compounds is also given. Two general trends are evident. The hydroaromatic 1,2,6,7-tetrahydropyrene has an abnormally short T_1 , a trend we have observed to be generally true for all the hydroaromatic materials which we have studied. Wilson has reported similar conclusions.³ Another trend which we have observed is that the T_1 of a mixture of pure compounds can have a T_1 , which is less than the T_1 of any of the pure compounds from which it was made. This fact may be rationalized by considering crystalline order which should be largely disrupted by the mutual "plasticizing" effect of the various components in the mixture. Therefore, motion of individual molecules in the solid are increased relative to the pure crystalline material.

Table 1. T_1 Values of Various Solid PAH's

Substance	T_1 (Sec)
Chrysene	24.4
Decacyclene	8.0
Pyrene	5.7
p-quaterphenyl	19.4
Acenaphthene	13.4
Truxene	29.8
Anthracene	> 60
Phenanthrene	> 60
1,2,6,7-Tetrahydropyrene	0.12
Mixture - First Eight Compounds	4.2

The Rheological Effect on T_1

As mentioned in the section above, molecular motion can affect the T_1 value. Therefore, it should not be surprising that there can be a large dependence of T_1 with temperature. In Figure 2 is shown the T_1 temperature dependencies for several types of carbonaceous materials for the temperature range of -5 to +60°C. For a pure material such as hexadecane, a very sharp drop of T_1 is experienced at the melting point (18°C). The paraffin wax sample shows a sharp increase in T_1 at the melting point (35°C).

The temperature-dependent behavior of the T_1 for a coal tar pitch shows that dramatic changes in T_1 can also be caused by a material experiencing a glass transition (T_g is approximately 60°C for this coal tar pitch). For the coal tar pitch studied, a decrease in T_1 at the glass transition is experienced. Other carbonaceous materials such as mineral oil, light hydrocarbons, and mesophase pitch, show little T_1 -temperature dependence over the temperature range studied. The phase transition temperatures for these materials are far removed from the temperature range studied, therefore minimal change in molecular motion with temperature is experienced.

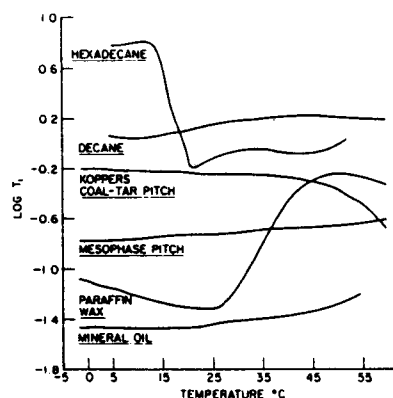


Figure 2. Temperature Dependent T_1 Behavior of Model Carbonaceous Systems.

The data presented in Figure 2 demonstrates a significant difference (one to two orders of magnitude) in T_1 for seemingly closely related materials (i.e., mineral oil and decane). Clearly these differences must be largely due to molecular motion, but it is not clear why motion of a pure decane solvent should be radically different than in a mineral oil. We have postulated that this difference can be explained by the possibility of "coherent concerted" motion in pure materials like decane. This postulate assumes that molecular motion takes place by several molecules in concert, effectively slowing down the frequency of molecular motion. A mineral oil, because of the mutual plasticizing tendencies due to its many components, experiences relatively fast motion.

Conclusion

We have shown that the T_1 parameter is a function of constitutional, rheological (motional) and unpaired spin concentration parameters. Which effect will dominate or be operative in defining the T_1 value at any given measurement temperature is, a priori, almost impossible to predict. However, it has been argued that systems containing large numbers (greater than 10^{19} spins per gram) of unpaired spins (radicals), such as certain coal species, will have a T_1 dominated by the free-radical effect.² We believe this to be the case; we also believe that the T_1 of uncalcined cokes is controlled by the free-radicals contained in the coke. However, for materials with less severe thermal treatment histories, such as oils, tars, pitches, etc., it is believed that the three effects (constitutional, rheological, and unpaired spin) are important. In any case, we feel that the T_1 parameter can be very useful as a monitoring tool when a particular carbonaceous system is undergoing physical or chemical change. The T_1 parameter might also be useful as a screening tool to detect gross lot-to-lot differences in raw materials.

References

1. D. S. Webster and L. J. Lynch, *Fuel*, **60**, 1981, p. 549.
2. T. Yokono, K. Miyazawa, Y. Sanada, and H. Marsh, *Fuel*, **58**, 1979, p. 896.
3. M. A. Wilson, Data Presented at Rocky Mountain Conference, Denver, Colorado, August 5-9, 1984.