

USE OF NUCLEAR MAGNETIC RESONANCE IMAGING TO STUDY ASPHALT

Francis P. Miknis and Daniel A. Netzel
Western Research Institute
365 North 9th Street
Laramie, WY 82070

Keywords: magnetic resonance imaging, asphalt, natural rubber, asphaltenes

INTRODUCTION

Magnetic resonance imaging (MRI) combines the basic principles of magnetic resonance with spatial encoding to obtain images of the distribution of fluids in samples. Because of the sensitivity of the hydrogen nucleus in NMR and because of its favorable relaxation times, water is the fluid most often imaged. This favorable aspect suggests that MRI might be used to obtain valuable information about water susceptibility and moisture damage mechanisms in asphalt. However, it has only been fairly recently that nonmedical applications of MRI have been increasing partly because of improvements in instrumentation and speed of data acquisition. MRI has been used to measure the distribution of fluids in porous rocks [1], ceramics [2], wood [3], other plant materials [4], synthetic polymers [5], solvent diffusion in polymers [6], coals [7,8], and bonding of adhesives [9].

In favorable circumstances, NMR imaging methods can be employed for imaging solid materials such as elastomers. NMR imaging has been used to study the morphology and defects in tire composites and the dispersion of carbon black in sections of tire tread [10] and to detect voids, gaps, and foreign particles in elastomers [11]. NMR imaging has also been used to study aging and phase separation in elastomers and to obtain the kinetics of the aging reaction [12]. In addition, inhomogeneities in natural rubber have been detected and characterized. Komorowski [13] has written a recent review of nonmedical applications of MRI. Little work has been done on the use of MRI in asphalt research.

EXPERIMENTAL

MRI measurements were made using spin echo (SE) or 3 dimensional (3D) imaging techniques. For nonviscous materials, such as water and organic solvents, the spin echo technique provided the best images because the relaxation times of nonviscous liquids were generally long and therefore more favorable for spin echo imaging. For elastomeric and viscous materials, the relaxation times of the protons were generally too short for spin echo imaging. Consequently, the 3D technique was used for these materials.

Magnetic resonance imaging experiments were carried out at a nominal proton resonance frequency of 200 MHz using a Chemagnetics/Otsuka Electronics microimaging probe. Samples for NMR imaging experiments were placed in 23 mm (OD) glass vials, which were then placed in 25 mm(OD) glass tubes. The tubes were inserted into the MRI probe and were positioned in the probe using O rings such that the cross sections to be imaged were contained in the experimental field of views (FOV).

Typical instrument parameters using the spin echo technique were echo times of 10-40 ms, a pulse delay of 1 s, a free induction decay size of 256 data points, 256 phase encodes, and a gradient strength of 34 G/cm. Eight slices, 1 mm thick and separated by 1 mm were obtained. The measuring time was ~ 1 hr. Images using the 3D method were made using an echo time of 2 ms, a pulse delay of 1 s, a free induction decay size of 256 data points, 128 phase encodes, 50 acquisitions and a gradient strength of 69 G/cm. Eight slices were usually obtained. The measuring time was 14.2 hrs for these experiments.

RESULTS AND DISCUSSION

MRI Measurements on Asphalts. MRI measurements cannot be obtained on asphalts at room temperature because the lack of molecular mobility (high viscosity), causes the NMR signal to decay away before any spin echoes can be formed. However,

there are some techniques that can be employed to decrease the viscosity and to increase the relaxation time, T_2 , so that images of asphalt are obtained. One approach is to acquire images at elevated temperatures where the asphalt viscosity is reduced and the relaxation times are lengthened. Cursory MRI experiments of this nature have been performed using a heat gun to melt asphalt and to acquire images as soon as possible while the sample is cooling. Images of asphalt have been obtained in this fashion but are not shown here. The experiments demonstrated that temperature can be used as an aid in imaging asphalts.

The use of solvents to dissolve asphalts is another approach to imaging asphalts. However, this approach poses some problems because the solvent and dissolved asphalt both contain protons so that the respective contributions from each set of protons to the NMR image is not evident. Chemical shift imaging is a possible solution in this situation, albeit a remote one given the present state-of-the-art of NMR imaging. The use of deuterated solvents is another way to circumvent this problem.

For certain applications, signals from the solvent may not present problems as illustrated by the images in Figure 1. This is a set of images for an asphalt dissolved in an equal volume of toluene and titrated with isooctane to the point at which flocculation occurs and asphaltenes begin to precipitate. After a period of time the asphaltenes settle out to form a layer, the height of which depends on the amount of isooctane used to precipitate the asphaltenes.

Figure 1 is also an example of how the experimental parameters can be chosen to enhance the signal contrast between different components of the system. In Figure 1, the spin echo time was varied from 10 to 40 ms. For the shorter echo time (10 ms), the image shows little contrast because for this echo time the NMR signals from all the components are strong. As the echo time gets longer, the contrast between the asphaltenes and solvent improves. For an echo time of 40 ms, the NMR signal from the asphaltenes has decayed considerably and appears as a dark gray band at the bottom of the vial. The NMR signals from the asphalt/toluene/isooctane components are still strong for this echo time and appear as the bright areas in the figure. If the layer of asphaltenes is of interest, the solvent and dissolved asphalt do not present a problem so long as long echo times are used to form the images. This procedure is referred to as T_2 weighting.

There is a thin black layer between the solvent and asphaltenes which is very noticeable in the images taken at a 40 ms echo time (Figure 1). To obtain some idea of the nature of the black layer, a spatula was inserted to the bottom of the vial and an "X" pattern was scribed to disrupt the asphaltene/solvent interface (Figure 2). The images of the asphaltenes show that the surface was apparently rigid as indicated by the pieces of the black layer that were broken and scattered throughout the asphaltene layer. The nature of this layer is not known at present. This layer could be a part of the asphaltene layer that is becoming more rigid with time at the asphaltene/solvent interface. A more rigid system would have shorter relaxation times and would appear darker in the NMR images. The layer could also be due to oxidation of the maltenes, which are then attracted to the highly polar surface of the asphaltenes and form a distinct layer at the interface. Other possibilities also exist and investigations are continuing to characterize this layer.

Natural Rubber in Asphalt. Although the federal mandate on the use of crumb rubber in paving applications has been removed, there still is sufficient interest to more fully understand the compatibility and physicochemical interactions of asphalt and crumb rubber materials. Preliminary MRI measurements were conducted on the feasibility of observing the presence of natural rubber in asphalt and the possibility of natural rubber dissolution in asphalt after heat treatment. A conical piece of natural rubber was submerged in an asphalt and heated to a temperature of 160 °C for 16 hrs. The asphalt had a high carboxylic acid content and carboxylic acids have been shown to dissolve different rubber materials when heated to 200 °C for extended periods of time (Tauer and Robertson, this symposium)[14]. Images of the asphalt/natural rubber system were acquired before and after heating using the 3D technique (Figure 3). Only the protons in the rubber are imaged using the 3D imaging sequence. Images of the asphalt are not obtained because the proton relaxation times of asphalt are too short. The image of the heated sample (Figure 3b) is not as clear as

that of the unheated sample (Figure 3a). The current interpretation is that the less sharp image of the heated sample is a result of reactions that have taken place at the surface of the natural rubber cone. Reactions between the natural rubber and components in the asphalt could cause the relaxation times of the protons in both materials to be slightly different at the surface than that of the bulk natural rubber leading to less sharp images. Further experiments along these lines are in progress.

Asphalt/Water/Aggregate Systems. Moisture damage in pavements generally leads to stripping, raveling and late rutting. One probable mechanism responsible for these failures is loss of adhesion of the asphalt at the aggregate interface. Water is suspected to play a major role in this damage mechanism. Direct observation of this failure mode has been difficult because of the lack of suitable instrumental techniques. Magnetic resonance imaging (MRI) methods may offer an approach to study this mechanism because of the favorable response of water in MRI experiments. However, little research has been done on the use of MRI to study asphalt/aggregate/water interactions in order to validate whether MRI methods can provide insight into moisture damage mechanisms.

MRI measurements were made on pieces of aggregates that were embedded in asphalt and covered with a layer of water. A spin echo pulse sequence was used to image the cross-sections of the asphalt/aggregate/water system in the XZ plane, before and after freeze thaw cycling, to determine whether water had any effect on the asphalt/aggregate interface. Three asphalts of differing stiffness and three different aggregate systems were studied. However, preliminary MRI measurements indicated that a limestone aggregate would be the easiest to observe changes as a result of the freeze thaw cycling. The other aggregates had varying amounts of magnetic components and therefore could not be imaged.

Of the three asphalts studied, only one showed displacement of asphalt from the aggregate after freeze thaws. This is shown in Figure 4. Comparison of the boundary at the water/aggregate/asphalt interface in the lower left center of each panel, before and after freeze thawing, shows an increase in the amount of water extending downward into the asphalt along the aggregate. The penetration began after 4 freeze thaws and increased slightly with successive freeze thaws, although there was not much difference after 6 freeze thaws.

SUMMARY

Applications of magnetic resonance imaging to study various aspects of asphalts are in their infancy. Consequently, a number of imaging methods and instrumental parameters need to be investigated to determine the feasibility of MRI to study asphalts. In this study, exploratory MRI measurements were made on the precipitation of asphaltenes from asphalt, observation of natural rubber in asphalt, and the possible interaction of water with asphalt at an aggregate interface. The MRI experiments showed that image contrast between asphaltenes and the precipitating solvent can be improved by varying the echo time used to form the images. Natural rubber in the presence of asphalt can be observed using 3D imaging methods, leading to the possibility of studying solvent swelling and possible dissolution of crumb rubber by components of the asphalt. MRI measurements of asphalt/water/aggregate systems showed evidence of water penetration at the aggregate interface. In all cases, the results were sufficiently encouraging to warrant additional investigations.

DISCLAIMER

This document is disseminated under the sponsorship of the Department of Transportation in the interest of information exchange. The United States Government assumes no liability for its contents or use thereof.

The contents of this report reflect the views of WRI which is responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views of the policy of the Department of Transportation.

Mention of specific brand names or models of equipment is for information only and does not imply endorsement of any particular brand to the exclusion of others that may be suitable.

ACKNOWLEDGMENTS

The authors gratefully acknowledge support of this work by the Federal Highway Administration under Contract No. DTFH61-92-C-00170. Technical discussion with Dr. Joseph Ford of Chemagnetics/Otsuka Electronics was also appreciated.

REFERENCES

1. Sarkar S.N., E.W. Wooten, and R.A. Komoroski, *Appl. Spec.*, 1991, 45, 619.
2. Ackerman J.L., L. Garido, J.E. Moore, and W.A. Ellingson, *Polymer Prepr.*, 1990, 31, 145.
3. Chang S.J., J.R. Olsen, and P.C. Wang, *For. Prod. J.*, 1989, 39, 43.
4. Cofer G.P., J.M. Brown and G.A. Johnson, *J. Magn. Reson.*, 1989, 83, 608.
5. Rothwell, W.P.; Holocek, D.R.; Kershaw, J.A.
6. Weisenberger L.A., and J.L. Koenig, *NMR Investigations of Case II Diffusion in Polymers*, in *Solid State NMR of Polymers*, L.J. Mathias, ed., Plenum Press, New York, 1991, 377-386.
7. Webb A.G., K. Motsegood, and R.B. Clarkson, *Fuel*, 1993, 72, 1235.
8. Hou L.; Cody, G.D.; French, D.C.; Botto, R.E.; Hatcher, P.G. *Energy Fuels*, 1995, 9, 84.
9. Koenig J.L., *Application of NMR Imaging to Polymers*, in *Solid State NMR of Polymers*, L.J. Mathias, ed., Plenum Press, New York, 1991, 61-79.
10. Sarkar S.N. and Komoroski R.A., *Macromolecules*, 1992, 25, 1420.
11. Chang C. and Komoroski R.A., *Macromolecules*, 1989, 22, 600.
12. Blumler P. and B. Blumich, *Macromolecules*, 1991, 24, 2183.
13. Komoroski R.A., *Anal. Chem.*, 1993, 65, 1068A.
14. Tauer, J.E.; Robertson, R.E. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.*, 1996, 41, *Symp. on Modified Asphalts*.

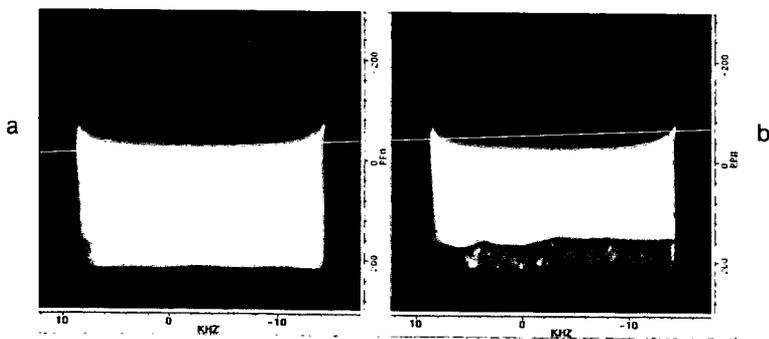


Figure 1. Spin echo images of asphaltene settling illustrating T_2 weighting to enhance image contrast: (a) 10, and (b) 40 ms echo time.

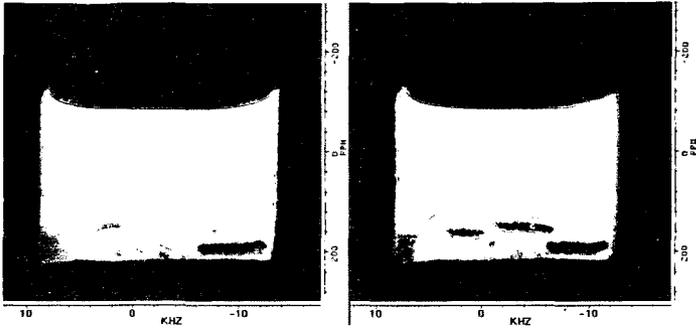


Figure 2. Spin echo images of asphaltene layer after stirring.

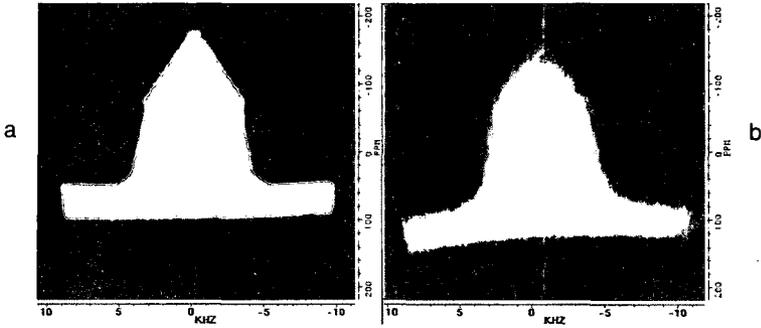


Figure 3. 3D images of natural rubber submerged in asphalt: (a) unheated, (b) heated for 16 hrs at 160 °C.

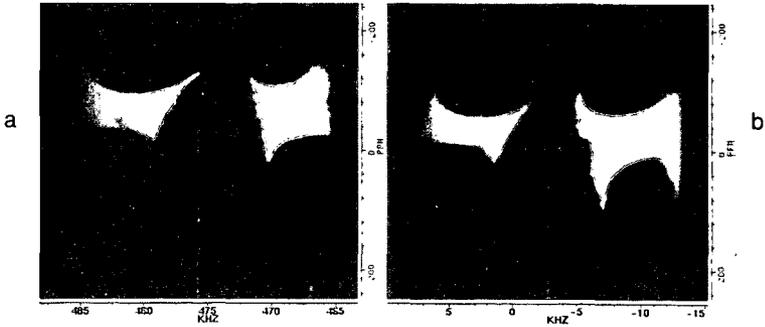


Figure 4. Spin echo images of SHRP asphalt AAM-1 and MRL aggregate RE in water after: (a) 0, and (b) 6 freeze thaws.