

SOME APPLICATIONS OF NUCLEAR MAGNETIC RESONANCE IMAGING TO RUBBER MODIFIED ASPHALTS

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INTRODUCTION

In 1991, the United States Congress passed the Intermodal Surface Transportation Efficiency Act (ISTEA), which mandated the use of rubber from scrap tires in Federally funded roadway construction projects. The rationale for the mandate is easily understood when considering that the United States discards more than 300 million tires each year and that a large portion of these end up in stockpiles, which may create environmental problems and health hazards. Initially, the mandate called for 5% of scrap tire rubber to be used in 1992, increasing to 20 % by 1997. However, when the mandate was imposed systematic studies concerned with the effects of such variables as asphalt type, rubber type, particle size, mixing time and temperature on the asphalt-rubber rheological properties, as well as handling, safety and health effects of scrap tires had not been carried out. In 1995, the Federal mandate was lifted and States are no longer required by law to utilize scrap tires in paving projects. Nevertheless, between 1991 and 1995 systematic studies of various aspects of crumb rubber modified asphalts were made [1-5], and use of crumb rubber modified asphalts for paving has continued in California, Arizona and Florida.

Crumb rubber generally refers to scrap tires that are ground to a particle size of less than 4 mesh, although in the so-called "dry process" particle sizes of up to 12.5 mm might be used. Regardless of particle size, rubber tires are complex mixtures of elastomers (natural and synthetic rubber), curatives (sulfur, peroxides, etc.), cure-system activators (e.g., stearic acid), fillers and reinforcing agents (carbon black, fibers, etc.), process oils, plasticizer(s), and additives (antioxidants, antiozonants, etc.). Likewise, asphalts are complex mixtures of chemical compounds, consisting functionally of such compound classes as strong and weak acids, strong and weak bases, neutral (aromatic and aliphatic) compounds, and amphoteric. Therefore, questions about what happens when these complex materials are blended at mix temperatures (~170 °C) have not been satisfactorily answered. The influence of crumb rubber on rheology is somewhat understood [2], but the mechanisms of interaction of rubber and asphalt have been difficult to elucidate. For example, does the rubber dissolve in the asphalt, does it swell in the asphalt, do volatile components (extender oils, plasticizers) in the rubber migrate into the asphalt, and how might these reactions influence the rheological properties of the mixture? This work was undertaken to address some of these questions.

Although the crumb rubber mandate of ISTEA has been removed, there are enough successful applications of crumb rubber in asphalt to maintain an interest to more fully understand the compatibility and physicochemical interactions of these materials. This has been a difficult task because of the lack of suitable instrumental techniques to study these interactions. In this paper some preliminary results on the use of NMR imaging to study asphalt-rubber mixtures are presented. The results suggest that NMR imaging may provide a method to obtain information about asphalt-scrap tire rubber interactions. However, applications of NMR imaging to study asphalt behavior are still in their infancy [6,7].

EXPERIMENTAL

Sample Preparation. Natural tire rubber and styrene butadiene rubber samples were obtained from Rouse Rubber Industries, Inc. The natural rubber samples were roughly conical in shape (~8 mm dia x ~10 mm height) and sat on a circular base (16 mm dia x 2 mm height). The styrene-butadiene samples had the shape of a triangular prism (~16 mm base x ~8 mm height x ~10 mm length).

The natural rubber and styrene-butadiene samples were attached to the bottom of 23 mm (OD) glass vials with epoxy glue. This was to prevent their floating and moving during heating in the asphalt and to ensure that images taken after the heating experiments were made of the same sample orientation. The vials were then

placed in 25 mm(OD) flat-bottom 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 view (FOV).

Two sets of samples were made for each rubber. One set was used for heating experiments in the absence of asphalt; the other set was used for heating experiments in the presence of asphalt. The asphalt chosen for study was derived from a crude oil from the San Joaquin valley, California and had a high carboxylic acid content (0.025 mol/l). Carboxylic acids have been shown to dissolve different rubber materials when heated to 200 °C for extended periods of time [2]. The asphalt was heated and then poured into the glass vials such that the rubber samples were several mm below the level of the asphalt.

Each sample was heated in an oven which was set at 170° C for periods of 1, 2, 4, 8, 12, 24 and 48 hours. Between the different heating periods, images were recorded while the sample cooled and after the sample was at room temperature. A temperature of 170 °C corresponds closely to the temperature at which the paving industry produces asphalt-rubber binders [3]. The temperature at which the images were acquired during the cooling phase was not known because the NMRI probe was not capable of variable temperature measurements. By convention, the samples were allowed to set for 3 minutes after they were removed from the oven. Images were then acquired using the same conditions described below, except only 2 acquisitions were obtained.

NMR Imaging Experiments. NMR imaging experiments were carried out at a nominal proton resonance frequency of 200 MHz using a Chemagnetics/Otsuka Electronics microimaging probe. For elastomeric and viscous materials, the relaxation times of the protons are generally too short for spin echo imaging. Consequently, a 3D imaging technique was used.

Images using the 3D method were acquired using an echo time of 2 ms, a pulse delay of 0.5 s, a free induction decay size of 256 data points, 64 phase encodes, 20 acquisitions and a gradient strength of 70 G/cm. Eight 3 mm thick slices were obtained in a FOV of 22 mm. The measuring time was ~1.4 hrs for these experiments. Images taken during cooling were acquired under the same conditions, except that 2 acquisitions were made. These images were acquired in ~8.5 minutes. All images were recorded in the XZ plane, where the z axis is the direction of the magnetic field and also corresponds to the cylindrical axis of the glass vial.

RESULTS AND DISCUSSION

Images of natural tire rubber (Figure 1) and styrene butadiene tire rubber (Figure 2) in the absence and presence of asphalt were acquired before and after heating, and during cooling using the 3D technique. NMR images of the protons in asphalt are not obtained at room temperature because the lack of molecular mobility (high viscosity) shortens the NMR relaxation times such that the NMR signal decays away before any spin echoes can be formed. Only the protons in the rubber are imaged at room temperature. However, at higher temperature the NMR relaxation times are lengthened so that asphalt protons that do not image at room temperature might be imaged at the higher temperature. In the lower sets of images in Figures 1 and 2, signals from the heated asphalt can be seen as the light contrast surrounding the rubber samples. In the bottom set of images in Figure 2 b- d, the signal (light area) below the triangularly shaped styrene-butadiene is an artefact. In reality, this signal is the top of the asphalt covering the rubber, but has been folded into the image because the positioning of the sample in the image probe was such that the field of view (FOV) was not large enough to encompass the sample. In all cases, the 5th slice of an image set of 8 slices is shown. This slice is a 3 mm thick slice through the approximate center of the sample in the XZ plane.

In Figure 1, the set of 4 images at the top are for the natural tire rubber heated at 170 °C for 0 (unheated), 2, 8, and 24 hrs in the absence of asphalt. The middle set of 4 images are for another natural tire rubber sample heated for the same time periods, but in the presence of asphalt. These images were recorded when the sample returned to room temperature after having been heated at 170 °C for the different periods of time. The bottom set of 4 images was acquired while the sample was cooling to room temperature. Analogous sets of images were acquired for styrene-butadiene crumb rubber heated in the same manner and are shown in Figure 2.

The intensity of the NMR images decreases with increased time of heating. This is true for both the natural tire rubber and styrene-butadiene tire rubber, heated in the presence and absence of asphalt (Figures 1 and 2, top and middle). The loss of signal

is more evident for the rubber pieces that were heated in asphalt, and more so for styrene-butadiene compared to natural rubber.

From an NMR perspective, the loss of signal intensity could have different origins: The rubber could have become more rigid in the asphalt and as a result, the relaxation times would have become shorter. This could happen, for example, if oils and plasticizers were driven from the rubber and/or cross linking reactions occurred as a result of heating.

Another reason for the loss of signal intensity could be that the rubber had dissolved in the asphalt, and the only signal remaining was due to the undissolved material. Others [2,3] have shown that, depending on asphalt crude oil source, crumb rubber particles dissolve in asphalt when heated at elevated temperatures (170 - 200 °C) for extended periods of time.

Natural rubber and styrene-butadiene rubber samples that were heated in the absence of asphalt had undergone changes in structure and became more rigid. This was apparent both from the hardness of the rubber samples after heating, and the fact that the rubber samples were impervious to solvents, such as chloroform, after heating (i.e., did not swell). The apparent change in the physical state of the rubber could be due to oxidation at the rubber surface and/or devolatilization and cross linking reactions in the rubber. Loss of the extender oils could also account for some of the rigidity and brittleness exhibited by the rubber samples after heating in the absence of asphalt. Thermal gravimetric analysis data show that loss of volatile matter in elastomers begins at temperatures around 100 °C [8]. Thus, heating the samples at 170 °C for extended periods of time, as was done in this study, could lead to loss of volatile matter.

The real effect on the tire rubber samples when heated in the presence of asphalt is betrayed by the lower sets of 4 images in Figures 1 and 2. These images were acquired during cooling and clearly show that the rubber had swelled substantially with no evidence of dissolution. However, because the experiments were conducted using large pieces of rubber to enhance the NMR image signal intensity, observation of the swelling behavior would be enhanced over any dissolution that may have taken place. In fact, the cross-section of the natural tire rubber had swelled to about 1.6 times its normal size and the edges did not show any discernible deterioration as would be expected if dissolution had occurred. The images of the swollen rubber could be reproduced by simply reheating the sample for 10 minutes after it had been at room temperature and re-imaging the sample. These images indicate that the loss of signal in the middle sets of images is not due to dissolution of the rubber. However, these images were acquired on rubber pieces that are large compared to crumb rubber particles used in paving, which are typically 4 mesh or less. Therefore, whether dissolution would occur for finer rubber particles mixed in asphalt cannot be ruled out based on these results. Others [2,3] have observed dissolution of fine particles of rubber when heated in asphalt. The images of the swollen rubber also negate the notion that the rubber had crosslinked and became more rigid when heated in the asphalt.

There was little or no swelling of the rubber samples when heated in the absence of asphalt. This is seen by the top set of images in Figures 1 and 2. The lack of swelling was also verified visually immediately after the samples were removed from the oven. Thus, the swelling of the rubber in asphalt appears to have been caused by solvent penetration of components in the asphalt, possibly maltenes. Valkering et al. [9] have shown that maltenes from asphalt cause considerable swelling in styrene-butadiene-styrene block copolymer/asphalt blends. In addition, oils used in tire manufacture are similar to compounds found in neat asphalts. During heating, interaction and/or exchange of these oils with oils in the asphalt could account for the swelling of the rubber. This exchange might also account for the loss of signal at room temperature if the relaxation times of the rubbers took on those of the asphalt components.

SUMMARY

Applications of NMR imaging to study polymer modified asphalts are in their infancy. In this study, exploratory NMR images were acquired on large pieces of natural and styrene-butadiene tire rubbers soaked in asphalt. These measurements demonstrated the feasibility of using NMR imaging to study different interactions between tire rubbers and asphalt, such as swelling by asphalt molecules, possible dissolution of rubber components in asphalt, and devolatilization and cross-linking in rubber when heated at mix temperatures of 170 °C.

Observation of swelling of crumb rubber in asphalt has been extremely difficult, but these results clearly show that swelling of tire rubber in asphalt is a significant mechanism in crumb rubber modification of asphalt, at least for larger pieces of rubber.

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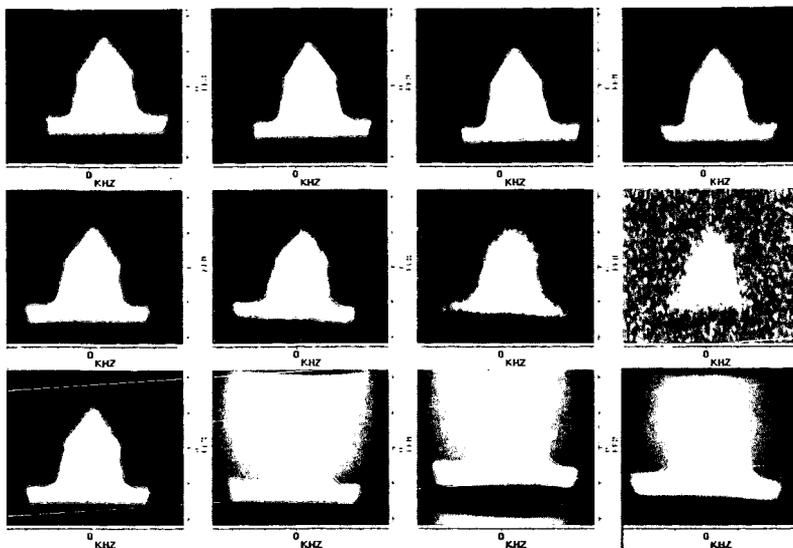


Figure 1. NMR images showing the cross section of a conical piece of natural tire rubber taken after heating at 170 °C for (a): 0, (b) 2, (c) 8, and (d) 24 hrs. (top) natural tire rubber heated in the absence of asphalt; (middle) natural tire rubber heated in the presence of asphalt. Both sets of 4 images were acquired when the sample was at room temperature. (bottom) natural tire rubber heated in the presence of asphalt and imaged while the sample cooled to room temperature.

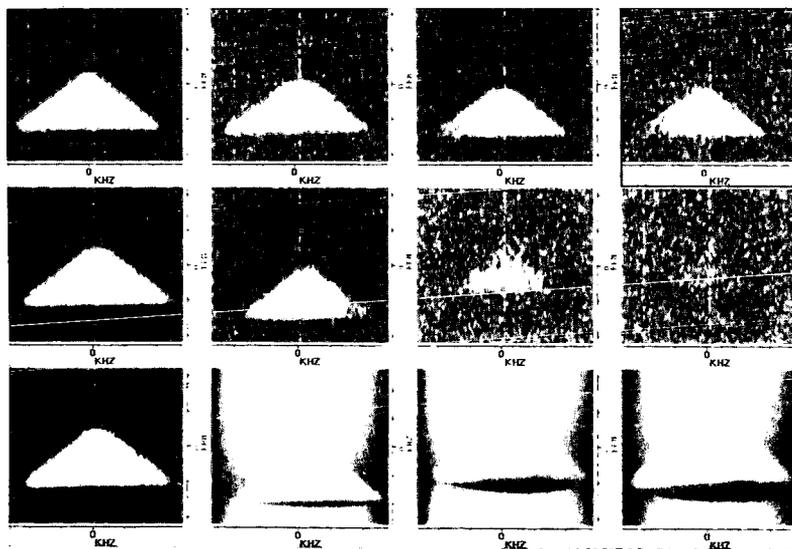


Figure 2. NMR images showing the cross section of a triangular prism-shaped piece of styrene-butadiene tire rubber taken after heating at 170 °C for (a): 0, (b) 2, (c) 8, and (d) 24 hrs. (top) styrene-butadiene tire rubber heated in the absence of asphalt; (middle) styrene-butadiene tire rubber heated in the presence of asphalt. Both sets of 4 images were acquired when the sample was at room temperature. (bottom) styrene-butadiene tire rubber heated in the presence of asphalt and imaged while the sample cooled to room temperature.