NUCLEAR MAGNETIC RESONANCE IMAGING OF CURED POLYMERS

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INTRODUCTION

Quantitative nondestructive evaluation (NDE) generally has two goals; the first is to obtain quantitative information about the mechanical and chemical properties of the sample, and the second is to obtain an image of the sample to reveal defects or anomalies. Neither approach independently gives sufficient information about the acceptability of the part, but if combined, the disposition of parts and processes can be determined.

This paper addresses the use of nuclear magnetic resonance (NMR) techniques to investigate the chemical and physical properties and obtain images of cured resins and thermoset polymer systems. Broadline NMR was used to give information about the chemical and physical properties of the material and 2- and 3-dimensional Fourier transform NMR imaging (NMRI) techniques were used to obtain images.

The broadline studies detected the existence of a "mobile" component in an experimental thermoset polymer, the magnitude of which was shown to substantially increase with the addition of rubber and be extremely dependent upon the type of rubber added. The results of the imaging studies demonstrated the ability of this technique to monitor the curing (or cross-linking) of epoxies, revealed a unique rheology pattern in one thermoset polymer plug, detected a "soft" surface layer in a polymer plaque, and monitored the effect of oxidation on the soft layer.

EXPERIMENTAL TECHNIQUE AND PROCEDURE

In the NMR imaging technique, the nucleus observed is nearly always the proton, and the parameters which are usually measured are the relaxation times T1 and T2 [1,2]. The T2 parameter is a measure of how fast the NMR signal decays due to interactions with nearby nuclei. In general, longer T2's correlate with a more mobile polymer or additive.

Because the signal from rigid polymers decays so rapidly (typical T2's are on the order of 20 microseconds), they cannot be imaged by most NMR imag-
ing spectrometers without sophisticated pulse techniques [3]. However, to monitor the cure process or a mobile component of a polymer, standard NMR imaging experiments are viable.

In contrast to NMR imaging, where a separate NMR signal is obtained for each volume element (e.g., 100 μm x 100 μm x 100 μm), only one signal is collected from a sample for breadline NMR. This signal (usually Fourier-transformed into a spectrum) represents an average of the NMR signal from the entire sample contained in the receiver coil. The spectrometer is designed so that the receiver can be rapidly turned on (a few microseconds after the exciting pulse), permitting the detection of rapidly-decaying signals. Thus breadline NMR has the advantage of being able to detect signals from rigid components of a polymer as well as from more mobile components. The term breadline comes from the fact that the Fourier transform of a short T2 (time response) corresponds to a broad frequency spectrum.

Breadline measurements were performed at the Physics Department of the University of Utah, which had a superconducting magnet operating at 81 MHz for protons. The spectrometer was homebuilt with a Matek transmitter, a Matek receiver, and a LeCroy signal averager. The probe had a helical coil 13 mm long and 13 mm in diameter. The number of transients averaged in each breadline experiment was ~100, the number of data points ~2500, the sampling rate 40 nsec/point, the repetition rate was 2.5 sec, and the pulse width was ~2 μsec.

To obtain the NMR images for the resin cure study, the plug was placed in the bore of a horizontal superconducting magnet containing a 6-inch diameter receiver coil. The magnet was part of the General Electric CSI 2T imaging NMR spectrometer at Fremont, California. The spectrometer frequency for protons was 85.5406 MHz. The pulse sequence was a typical spin-wrap imaging pulse sequence [4]. Images of the multiphase resins were obtained using a CSI system which was equipped with shielded gradients. Since the samples provided are ~10 mm in diameter, or less, the probe used was a helix type coil that was ~13 mm in diameter and ~20 mm long. This maximized the "filling factor" (or the volume of the probe occupied by the sample) which, in turn, maximizes the signal relative to the background noise.

The images were generated using 4-8 averages per pixel (NA), a spin echo time (TE) of 1-4 msec, a repetition rate of ~200 msec. The total time of the experiment was typically 1-2 min/slice. In the images the terms field of view (FOV) and matrix or number of points (NP) represent the actual dimensions of the image and the number of pixels, respectively, (e.g., a FOV of 128 mm and a NP of 128 corresponds to a resolution of 1 mm/pixel).

RESULTS AND DISCUSSION

The first application presented is the curing of a typical two-part epoxy resin system. During the cure process, the polymer chains will cross-link, which decreases molecular motion. A decrease in motion will be detected as a shortening of T2 (i.e., the more cross-linked the material, the darker the image). At final cure (~48 hours) the T2 is ~20 μsec, which is typical for such rigid materials.

A cylinder, 1 inch in diameter by 2 inches in length, was filled with four layers of resin. Cure times for the layers from top to bottom was 0, 3, 8, and 27 hours (Figure 1). In addition to the curing, a 1.5 mm glass rod was inserted along the cylinder axis as a spatial resolution gage.
Notes: Cure differences and a glass rod used as a resolution gage (arrows) are clearly seen on the images. TE = 4 msec, Matrix = 64 x 64 x 128, NA = 2, FOV 64 mm x 64 mm, slice thickness = 2 mm.

Figure 1. Imaging of a two-part resin system. TE = 4 msec, NP = 64 x 64 x 128, NA = 2, FOV 64 x 64 mm

Data was collected using a very short echo time, 3-D volume method (TE = 4 msec) and displayed as a set of 16 cross-sectional slices from front to back of the cylinder. Cure differences and the glass rod (Slices 8 and 9) are clearly resolved in the images.

The spectrometer used could not image signals with decay times less than ~ 2 msec which occurred after eight hours of cure. The image of this region then appears with an intensity of zero.

The experimental thermoset polymers used for the experiments discussed below were manufactured by dissolving rubber (EPDM, SBR, or EPR) into liquid formulations containing an olefin monomer, which was then polymerized.

Figure 2 shows a comparison of the broadline NMR frequency spectrum of the polymer with and without rubber. The figure on the left corresponds to no rubber. Apparent in the figure is a broad Gaussian shaped spectrum associated with the rigid cross-linked polymers and a small (~3%), narrow Lorentzian shaped spike associated with mobile constituents such as residual monomer and additives (antioxidants, etc.). In contrast, the figure on the right is associated with the same polymer with ~3% rubber added. In the figure, the effect of the rubber additive is observed where the narrow component now consists of ~15% of the sample. The amount of the mobile component relative to the rigid phase can be determined from the relative peak areas provided that the spectra have been obtained under conditions where the proton spins in each phase are fully relaxed between pulses.

The next experiment was to vary the amount of rubber to determine its effect on the fraction of mobile component (Figure 2). Two different rubbers were added; styrene butadiene rubber (SBR) and EPDM. As expected, the fraction increases as the rubber level increases. However, as observed previously, the fraction of mobile component greatly exceeds the rubber
content. This excess cannot be accounted for by residual monomer, which is typically less than 1%. Except for residual monomer, the difference between the amount of rubber and the amount of mobile component is the amount of mobile (or uncross-linked) polymer. Thus, when rubber is added, there are two mobile materials, rubber and mobile polyolefin.

Evidence supporting the idea that the dispersed rubber phase contains polyolefin comes from transmission electron microscopy (TEM) of a plaque containing EPR, a saturated hydrocarbon rubber. When the plaque was stained with osmium tetroxide and examined using TEM, filament-like areas less than 1 μm across were observed. These stained areas must contain an olefin, because saturated hydrocarbons are not stained by osmium tetroxide. The matrix does not stain because the matrix is glassy and not very permeable to the stain. The areas containing EPR and polyolefin as a separated cophase are more permeable because the EPR is below its Tg. (An alternative explanation is that the monomer is concentrated in EPR; further experiments would be necessary to determine whether monomer is more soluble in EPR than in the polymer matrix.)

The measurement unit for the amount of rubber or residual monomer in molded parts is different from the measurement unit for the amount of mobile component as determined by NMR. Normally, the amount of rubber or residual monomer is expressed as wt%. However, NMR counts the relative numbers of protons present, and the number of protons per unit weight of SBR, for example, is not the same as the number of protons per unit weight of polymer. Therefore, for the results presented, the amount of rubber is expressed as the wt% of hydrogen in the rubber. The amount of mobile component reflects the amount of hydrogen which is in the mobile phase.

Linear regression of the data in Figure 3 gives a slope of 1.2 for SBR, and 1.6 for EPDM. Thus, the mobile component generated when rubber is added consists of 1 part rubber and 0.2 parts polyolefin for SBR, and 1 part rubber and 0.6 parts polyolefin for EPDM. This is an important difference between the two types of rubber, showing that EPDM is more effective in generating a given level of mobile component.
To confirm that the narrow peak in the broadline NMR spectrum is associated with the rubber, broadline NMR measurements were performed at low temperatures. At the rubber Tg, the line should broaden as the rubber becomes less mobile. In Figure 4, line widths are plotted vs temperature for SBR and EPDM. A break in the line occurs for SBR at about 225K, corresponding to the Tg for this rubber as determined by dynamic mechanical analysis (DMA). For EPDM, the transition is broader, occurring in the range of 275 to 285K, which is near the Tg of 275K measured by DMA. This agreement of Tg values between NMR and DMA confirms that the narrow peak is associated with the rubber.

![Figure 3. Linear regression of fraction of mobile component, as determined by broadline NMR vs wt% rubber adjusted for relative hydrogen content. The fraction increases faster when EPDM rubber is used.](image)

The broadline NMR experiments show that the rigid portion of the thermoset phase polymer has a line width of about 35,000 Hz, corresponding to a T2 of 15 μsec (T2 = 1/(2 \times \text{line width}) for a Gaussian line shape). Having such a short T2, the signal from the rigid part of the polymer decays too rapidly for the imaging spectrometer used in this work.

However, the line width for the mobile component is 500 to 7000 Hz, corresponding to T2's of 600 to 45 μsec (T2 = 1/(\pi \times \text{line width}) for a Lorentzian line shape). Previous NMR imaging experiments showed that T2's in the 600 μsec range are sufficiently long that the mobile component can be imaged. The mobile component corresponding to a T2 of 600 μsec is associated with rubber, which is present as a dispersed phase. Thus the NMR imaging experiment in this work is selective for the dispersed phase.
Figure 4. Breadline NMR line width of the narrow component vs temperature for plaques containing SBR and EPDM. The break in each curve is the Tg of the mobile component in the polymer as measured by NMR.

Figure 5 shows the NMRI of the aged and unaged thermoset polymer plaques where the resolution for the image is 125 μm. The samples were 3 mm thick plaques. Both plaques contained SBR and the antioxidant formulation. In Figure 5 the unaged sample has a soft layer on the top surface and the aged sample has a dark band at the surface that is in contact with the unaged sample. One possible explanation for the loss of the soft region in the aged sample is that cross-linking occurred at the "soft" surface. If this is true, then the soft region is associated with either an increased rubber concentration (or at least an increased amount of the matrix was affected by the rubber in the soft surface regions), or the soft region is associated with a greater amount of mobility (longer T2) for the mobile component.

Figure 6 shows an NMRI of a thermoset polymer plug with a scan resolution of 250 μm. The plug was molded by pouring neat resin mixed with rubber into
Figure 6. NMR image of a plug containing EPDM rubber. The adhesive in the label taped to the plug shows up as a bright arc on the right-hand side of the image.

a 13 mm ID test tube, then breaking the test tube after the matrix had cured. As can be seen in the image, the process of molding the polymer produces an interesting rheology pattern (somewhat resembling the splitting of a cell). Also observed is a piece of surgical tape, used as a sample label, that was wrapped halfway around the plug (in the image the tape appears as a bright ~1 mm thick semiring around the surface).

CONCLUSIONS

Based on the results of this work it is clear that NMRI is becoming one of the most versatile nondestructive techniques available. With the resolution of current spectrometers reaching levels of 20 μm or less for liquids and with the capability of imaging harder and harder materials, it is inevitable that this technique will become a dominant nondestructive method for materials research, as it has for medical research. In addition, broadline NMR process and quality control applications such as resin curing and measurement of component constituents are viable and affordable.

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