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# MAGNETIC RESONANCE BASED DIAGNOSTICS FOR POLYMER PRODUCTION AND SURVEILLANCE

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## Abstract

In an effort to develop a magnetic resonance based diagnostic tool to be used for polymer production and surveillance, we have investigated the use of magnetic resonance imaging (MRI) and unilateral relaxometry. MRI provides a spatial map of the polymer, which can be correlated to the structure heterogeneity. Though highly detailed information can be obtained with MRI, the high equipment cost and expertise required to operate the system makes it a poor choice for a production setting. Unilateral relaxometry via the NMR MOUSE provides rapid, inexpensive polymer screening, useful in the development in new polymer parts or to identify potentially defective components. The NMR ProFiler (originally called the NMR MOUSE) was procured by Kansas City originally for production support of the W80 LEP with future applications as a surveillance diagnostic. A robotic autosampler has been designed allowing the detection of several components without the need for any human interaction. A summary of the qualification experiments and results to date from the ProFiler and the robotic unit will be presented.

### Introduction

Elasotomeric engineering parts, such as those employed in aerospace applications, can be subject to complex and harsh aging conditions including complex strain fields. When combined with structural heterogeneities due to processing inefficiencies, the result can be complex, heterogeneous aging of parts. This dramatically complicates lifetime estimates or system models for component performance. Nuclear magnetic resonance (NMR) spectroscopy is routinely used to investigate structural and dynamic properties of polymers[1] and has found extensive use in the investigation the effects of long-term exposure to chemically, thermally, or radioactively harsh environments on polymeric materials. NMR parameters such as transverse ($T_2$) relaxation rates and residual dipolar coupling constants have been correlated with other chemical and mechanical tests such as DSC, GPC, and DMA to determine preliminary service lifetimes in a variety of polymers.[3] NMR offers the advantage of being able to probe simultaneously structure and dynamics *in situ*, in controlled environments, on samples of various shapes. Standard high field NMR methods, however, are ill suited to provide non-destructive two or three dimensional maps of part structure due to production or aging heterogeneities.

MRI offers the ability to obtain a spatial map of the crosslink densities, which can be correlated to the overall structural inhomogeneity within the polymer materials.[4] MRI techniques have been employed to examine material properties, including, but not limited to, molecular motion, cross-link densities, the kinetics of crosslinking curing, rubber vulcanization, curing times for thermosetting polymers, and copolymer desiccation of elastomers.[5-7]

Another method currently in use is unilateral relaxometry with a low-field device such as the NMR MOUSE (MObile Universal Surface Explorer). Originally commercialized for the tire

industry as an analytical tool for determining defect sites, the NMR MOUSE is a transportable, inexpensive and easy to use system based on the principles of NMR.[8] [Note that the MOUSE is now being sold commercially by Bruker Optics as the minispec ProFiler and will be referred to as the ProFiler hereafter.] Low field NMR uses the same principles of traditional NMR spectroscopy, but since only relaxation information is obtained, the normal high resolution that is typically required for complete structural analysis is not needed and inhomogeneous static ($B_0$) or excitation ($B_1$) magnetic fields can be employed to significantly reduce the required foot print of the spectrometer. Numerous examples of the use of low field NMR for polymer analysis exist in the literature.[7,9-11]


**Figure 1.** Photo of ProFiler magnet unit scanning a W80 OPP.

## Experiment

### *Materials*

The DC745 polymers used in this study were obtained from Dow Corning as Silastic® 745U and crosslinked with 0.55 wt% peroxide curing agent. The polymer was formed into a slab or molded into an outer pressure pad (OPP, part number 422431) for the W80.

### *Magnetic Resonance Imaging*

All MRI experiments were performed on a Bruker Avance 400MHz equipped with a high-resolution microimaging system with either a 25mm rf coil or a 5mm rf coil depending on the size of the sample. Detailed experimental parameters have previously been published.[7]

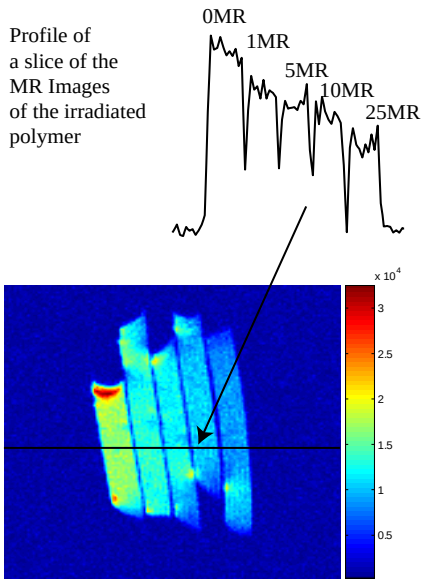


**Figure 2**. 2D $T_2$ weighted water/fat suppression MRI experiment on polymers exposed to different levels of radiation dose. The contrast parameter is $T_2$ relaxation time, with higher signal intensity indicating lower crosslink density.

### *The NMR ProFiler:*

The NMR ProFiler (Bruker Optics, minispec Division) consists of a computer, tabletop spectrometer console and preamplifier, and a magnet unit. The magnet unit consists of two permanent magnets with anti-parallel magnetization producing a $B_0$ field parallel to the surface of the unit, as shown in Figure 1. The ProFiler can be held by hand or by a robotic controller (purchased through Bruker Optics from DuraTech) and scanned systematically over the entire surface of the OPP. The spatial resolution is approximately 1.5 $cm^2$, about the width of two ribs, which is of comparable size to the deformed areas of the pads. Experimental details can be found in Herberg, et al.[7]

## Results and Discussion

NMR spectroscopy has been used to determine relative motional properties in polymers for some time. The relaxation properties obtained through high resolution NMR experiments has been shown to correlate with various mechanical

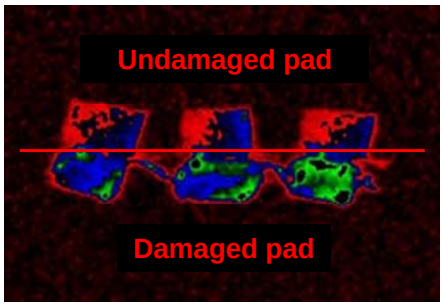


**Figure 3.** 2D $T_2$ weighted water/fat suppression MRI experiments of damaged section and pristine section of DC745. The contrast parameter is $T_2$ relaxation time, with higher signal intensity indicating lower crosslink density.

properties of polymers. For example, the $T_2$, or spin-spin, relaxation time is generally considered to be inversely proportional to the polymer crosslink density.

Both the $T_2$ weighted Single Point Imaging NMR and the $T_2$ weighted water/fat suppression MRI experiments can be used to map out the location of different cross-linking densities, ultimately determine the quality or homogeneity of intact polymers.[7] Since the effects of γ-radiation and thermal degradation on siloxane polymers have been shown to lead to changes in crosslink density and motional dynamics, these changes have been measured in NMR observables such as $T_2$ relaxation times and residual dipolar couplings. The $T_2$ weighted water/fat suppression MRI images of polymers that were exposed to different doses of radiation are shown in Figure 4. This MRI data clearly displays the same trends as high resolution NMR, where $T_2$ decreases and cross link density increases with increasing radiation dose.

To show how MRI techniques can be used to obtain crosslink densities of a non-ideal damaged section and a pristine section of a DC745 polymer pad, we performed 2D $T_2$ weighted MRI experiments on these pads. The 2D $T_2$ weighted MR Images are shown in Figure 3. The undamaged pad section is characterized by a fairly uniform $T_2$ throughout the material part with exception of the lower signal intensity at the surface. Consistent with the high field data shown above, the damaged pad was characterized by areas of brighter signal due to increased $T_2$ relaxation time, or higher mobility of the polymer network. It is important to note that brighter signals are present in patches in the interior of the polymer pads, which may be due combined effects of cross-link density and compression set. The MRI data shown here confirms that the damaged DC745 pads, after service, can be described by heterogeneities in the mobility of the polymer network through the pad. Areas of the pads without the heterogeneity do not seem subject to this deformation.

While MRI offers highly detailed information, systems capable of detecting intact polymer components can cost up to $2M and require experienced users, so they are best suited for research labs instead of production facilities. However, low field NMR systems are relatively inexpensive (~$60K) and are designed with a user-friendly interface, ideal for a production setting. Low field NMR systems have been used to detect chemical changes in the deformed sections of damaged DC745 pads via changes in the $T_2$ relaxation time. In fact, it was shown that low-field NMR could be a valuable tool in the production of new polymer parts by screening new pads and identifying potentially defective pads. However, in most quality control and production settings, thorough evaluation and qualification of the test methods is often required.

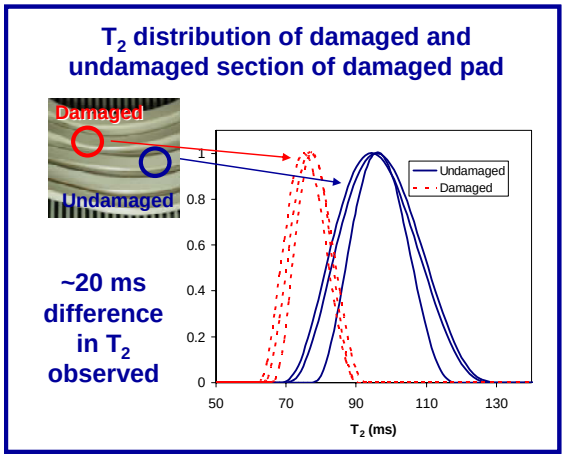


**Figure 4.** NMR ProFiler results on damaged W80 outer pressure pad.

The first step in the implementation of the ProFiler to the OPP issue was to verify that the sensitivity of the ProFiler to the expected $T_2$ differences is great enough and that the data obtained here match the trends observed with high-resolution NMR. Figure 4 shows the ProFiler results on an actual damaged OPP. Here, differences in $T_2$ relaxation time between a damaged and undamaged section of a real pad can clearly be seen. Numerous qualification tests were performed to determine the exact experimental parameters to be used, the effects of the rib geometry in the OPPs, and the effect of curing of the DC745 components. An example of one of these tests is shown in Figure 5. Here, a "Design of Experiment" was performed with different cure and experimental parameters. The interaction plot indicates that the ideal parameters are 1024 scans, 600 echoes, with an echo time of 0.5 ms. However, decreasing the number of scans from 1024 to a more reasonable 128 scans only increases the $T_2$ error by 0.44% while decreasing the total experiment time six-fold.

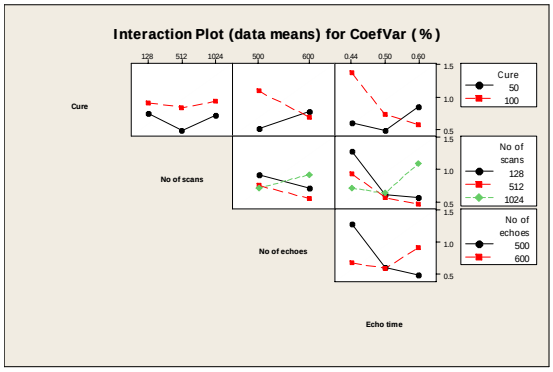


**Figure 5.** Interaction Plot for coefficient of variance response variable.

In order to reduce the opportunities for human error and reduce the amount of time needed to physically operate the NMR MOUSE in the production setting at KCP, a robotic autosampler was developed. This automatic inspection system was developed in collaboration with Bruker Optics, Inc. and DuraTech and is shown in Figure 6. The autosampler was designed to measure six OPPs automatically without the need for human interaction. The original design included a triple axis robotic arm that holds the MOUSE magnet unit and lowers it down onto the pad and moves it in a pre-programmed pattern around the entire pad, sampling each section of the pad. After an entire pad is scanned, the MOUSE moves onto the surface of the next pad and continues until all six pads have been scanned.

Initial tests were performed using the robotic autosampler to determine if a damaged section of a pad could be distinguished. Using the intended sampling pattern which took advantage of the three-axis robotic arm, a large amount of scatter was observed across the pad. The difference in $T_2$ value between the damaged and undamaged section of the pad was not discernable in the large amount of scatter. It was determined that the rib geometry led to inconsistent coverage by the MOUSE magnet unit. As the MOUSE unit moved to different sections of the pad, each detection spot contains a different overall volume of the sample. However, by adding a fourth axis in a radial dimension, the same sample volume could be detected all around the pad. With the fourth axis included, the amount of point-to-point scatter decreased substantially and it is easy to detect deformed areas. In preliminary studies to determine potentially defective *new* components, several new OPPs were scanned and a number showed potential areas of deformation, as demonstrated in Figure 7. Here, the region where the $T_2$ drops by ~20 ms indicates a region of the new pad that is susceptible to damage. In fact, hardness testing on this pad shows a softening of this region. Future testing will reveal whether this pad is in fact defective.

**Figure 6.** Robotic Autosampler designed by Bruker and DuraTech. A similar autosampler will be installed at KCP.

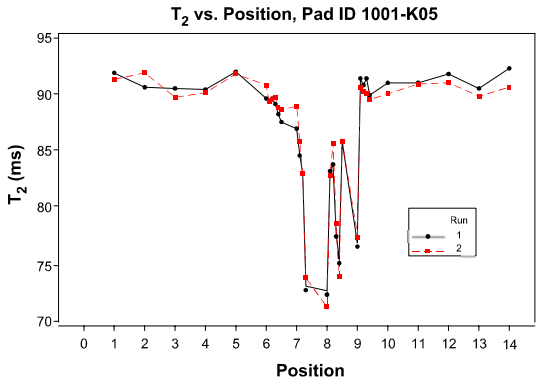


**Figure 7**. ProFiler scan around a new OPP, showing areas of potential damage indicated by a drop in $T_2$.

## Conclusions

Magnetic resonance imaging and low field NMR using the NMR ProFiler were investigated as possible diagnostic tools for polymer production and surveillance. MRI provides information rich data suitable for a laboratory setting. The NMR ProFiler is an inexpensive tool capable of revealing potentially defective components in a plant setting. Numerous qualification activities have been performed on the ProFiler at KCP and a four-axis robotic autosampler was developed for human-free scanning of multiple components with radial geometry, such as a W80 outer pressure pad.

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