Evaluation of Automated Low-Field NMR Relaxometry For Analysis of Polymers

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Abstract

Screening studies and a Design of Experiment were performed to evaluate measurement variation of a new, non-destructive NMR test system designed to assess age induced degradation of Outer Pressure Pads. The test method and results from 76,746 measurements are described indicating that a metal support strut adjacent to the front position of the test chamber interferes with the measurements and that there is a measurement property gradient from the front to the back of the chamber. Also, obvious compression set areas on a surveillance OPP were not detected, but hidden, internal voids within a newly molded OPP were detected.

Summary

New surveillance tests are being evaluated to improve diagnostics on aged polymer cushions and pads of Lawrence Livermore National Laboratory (LLNL) systems. A novel instrument has been designed using Nuclear Magnetic Resonance (NMR) coupled with automated data collection. A prototype has been installed at the Kansas City Plant (KCP) to evaluate its use for surveillance testing. The miniSpec ProFiler determines the ^1H NMR spin echo time constant, T_2 , which provides an indirect measure of average crosslink density as an indicator for extent of degradation with age. Initial tests of the new system identified anomalous random noise in measurements, variance in curve fits, and possible error caused by a nearby metal component adjacent to measurement locations within the chamber. Consequently, several screening studies and a Design of Experiment (DOE) were performed to better understand this variation.

A total of 76,746 measurements were taken during various screening tests and the Design of Experiment to determine the effect of Outer Pressure Pad (OPP) position on T_2 values within the automated NMR's measurement chamber. The results indicate that a metal support strut adjacent to the front position in the chamber interferes with the measurement and that there is a measurement property gradient from the front to the back of the chamber. Also, the NMR failed to identify obvious compression set areas on a surveillance OPP that had been previously detected by manually rotating the OPP beneath the ProFiler. In addition, the ProFiler was able to detect hidden, internal voids within a newly molded OPP. Non-magnetic parts have been ordered to replace the metal parts causing interference, and testing will be repeated to determine the effect of the new plastic parts.

Discussion

Scope and Purpose

The purpose of this project was to evaluate new surveillance methods based on Nuclear Magnetic Resonance testing in order to improve diagnostics on polymer cushions and pads of LLNL systems. Because OPP production plans were stopped, the scope was modified to develop this test for surveillance OPP diagnostics and other applicable materials, accomplished through the installation and validation of the miniSpec ProFiler at KCP.

Activity

Background

In order to improve diagnostics on polymer cushions and pads of LLNL systems, new surveillance tests are being evaluated to detect crosslink density changes with age. A new test method has been developed and validated based on a unique system design using an NMR coupled with automated data collection¹. A prototype system has been installed at the Kansas City Plant to evaluate its use for surveillance testing. This equipment comprises an automated robotic system that was developed jointly with Bruker Optics, Inc., miniSpec Division (Woodlands, TX) to allow multiple measurements without operator intervention. Large-scale manual sample measurements with the ProFiler are impractical, and are also prone to measurement error because of variation in placement of the probe during repeated measurements. The precise control offered by the robotic system greatly minimizes this variation. The miniSpec ProFiler determines the ^1H NMR spin echo time constant (T_2), which provides an indirect measure of average crosslink density. The magnet of the NMR ProFiler, is mounted to a modified commercial Autosampler (produced by Duratech Inc., Waynesboro, VA) and controlled via an attached PC for automated NMR measurements (Figure 1).

Figure 1. MiniSpec NMR and automated robotics system (Note: EMI enclosure is not shown).

Previous work focused on rotating OPPs beneath a stationary ProFiler, and also on determining the proper orientation alignment of the magnet over the OPP during motion control by the Autosampler¹. Subsequent screening tests identified anomalous random noise in measurements, variance in curve fits to determine T_2 , and possible measurement error caused by nearby metal components adjacent to arbitrarily assigned measurement locations within the chamber (Figure 2). Consequently, several screening studies and a DOE were performed to understand this variation.

Figure 2. OPP measurement locations.

Simulated Data and Measurement Methodology

OPPs are marked at a single location by an ink pen with a + mark on the outer rib. T_2 is measured in 5° increments counterclockwise around the OPP at radii centered over the gaps at 62, 69, 77, and 84 mm. An idealized data set shows the difference in T_2 values after simulated measurements of an OPP for three conditions (Figure 3):

1. The black symbol (\) shows the baseline position with the + mark at 12:00 position on the OPP (i.e., away from the front of the chamber).
2. The blue symbol (/) shows measurements after turning the OPP by 180° (i.e., the + mark is at 6:00 position on the OPP placing it closest to the front of the chamber).
3. The red circle (o) shows measurements with the + mark in the 12:00 position on the OPP away from the front of the chamber and then flipping the OPP upside down, i.e., with the ribs contacting the glass.

First, a test OPP (#1) was measured in the baseline position. Then, these individual data measurements were assigned to be the same after rotating or flipping the part; thus, assuming that there is no external interference on the measurements. With no interference (or experimental error), the three curves are identical in the top plot and represent the unrealistic goal of the measurement system to be exactly repeatable and thereby independent of OPP orientation.

Figure 3. Simulated data of rotating or flipping OPP. (Units for T_2 are ms)

Pad Position denotes the sequential measurement locations starting with position 0 at 12:00 on the OPP at a radius of 62 mm. The miniSpec moves radially out from the inner gap to 69, 77, and 84 mm, and then moves counterclockwise 5° repeating this sequence while incrementing the number locations from 0 to 287. The middle plot shows the T_2 values versus theta angle position around the OPP. Theta is the ProFiler rotational angle relative to the chamber with theta = 0° at 12:00, i.e. back of chamber, theta = -90° at 9:00, theta = 180° at 6:00, i.e., front of chamber and theta = 90° at 3:00. At angle theta = 0, the Pad Position is location 0 and the + mark is farthest away from the front of the chamber. Chamber position is the location relative to the chamber at the theta measurement angle; as if the OPP were sitting in the chamber with locations marked on the glass.

If the data is independent of relative chamber position, then data measurements should have relatively low variability and have an appearance similar to the top plot after rotations. Plotting data by chamber position or theta helps to identify areas in the chamber that are more or less sensitive to variance.

Repeatability Study

A repeatability screening test was performed at position A by measuring OPP #1 five times (Figure 4). Each of the five test runs consisted of performing three replicates per OPP for a total of 4,320 measurements. The OPP was lifted off the glass and replaced between each run. The difference between the average T_2 of the entire OPP for the middle three runs was not statistically significant. The first and last run showed a statistically significant difference from the other two runs but the magnitude of difference was small (~ 3 ms). The most unusual feature of the results is a bump in noise level and a dip in the average T_2 values that corresponds to a location at the front of the chamber where an adjacent metal support strut is located.

Figure 4. Repeatability measurement test for OPP #1 in position A. (Units for T_2 are ms).

T_2 error is calculated by the miniSpec software and is a measure of the quality of the data fitting algorithm for the bi- or mono-exponential decay curve. Figure 5 shows that occasionally (153 measurements (3.5%)) the algorithm is randomly less successful and produces T_2 values that may or may not be outliers. This behavior supports taking multiple replicates for data measurement to either deliberately omit any outliers from the analysis or average them together to mitigate their influence.

Figure 5. T_2 Error, T_2 , and signal to noise ratio (S/N) values. T_2 Error outliers (>1.2) are bold symbols in top graph and the associated T_2 and S/N values are in the middle and bottom graphs. (Units for T_2 are ms.)

Data on OPP #1, obtained prior to the test, revealed that $T_2 = 70\text{ms}$ for damaged areas and $T_2 = 90\text{ ms}$ for undamaged areas¹. The average T_2 by pad position for the five replicates shows a patterned distribution with a maximum of 67.8 ms and a minimum of 34.3 ms (Figure 6). The compression set areas on the ribs of OPP #1 are shown by highlighted symbols and depict results differing from the previous study in which the OPP was rotated by hand beneath a stationary ProFiler. The present study obtained T_2 values that are lower, and there is no clear correlation between low T_2 and the areas of compression set.

Figure 6. Average T_2 and noise associated with compression set on OPP #1 in chamber position A. Red X symbols show the compression set area on OPP #1. (Units for T_2 are ms, units for X and Y are mm.)

Although the compression set area on OPP #1 was not clearly detected at chamber position A, two internal voids within newly molded OPP #2 were discovered by the ProFiler (Figure 7). These voids are not visible but their locations can be easily confirmed by feeling or stretching the OPP.

Figure 7. Average T_2 and noise associated with internal voids on OPP #2. Red X symbols show internal void locations. For the bottom two graphs, the red symbols are chamber positions A & B, green symbols are chamber positions C & D, and blue symbols are chamber positions E & F. (Units for T_2 are ms, units for X and Y are mm).

Other Testing

Tests were performed at position A by measuring three replicates of OPP #1 under the following conditions: before and after rotating by 180° , before and after flipping upside down, and after six months between measurements. OPP #1 was measured in position A at two different gains and once after six months (Figure 8). The lower gain produced lower noise, as expected, but it also shows that the average T_2 noise measured six months later is slightly lower. This observation is noted here but the cause, e.g., ambient temperature conditions, instrument drift, etc., is not known. Again, the most relevant feature is the bump in noise levels that corresponds to a location at the front of the chamber where an adjacent metal support strut is located.

Figure 8. OPP measured in position A – blue & black symbols are 115 dB gain, red symbols are 109 db gain. Data for blue symbols was measured six months earlier than the data for the black symbols. (Units for T_2 are ms).

OPP #1 was measured in position A for three conditions at gain=115 dB (Figure 9):

- The black symbol (\) shows the baseline position with the + mark at the 12:00 position on the OPP (i.e., away from the front of the chamber).
- The blue symbol (/) shows measurements after turning the OPP by 180° (i.e., the + mark is at the 6:00 position on the OPP placing it closest to the front of the chamber).
- The red circle (o) shows measurements with the + mark in the 12:00 position on the OPP away from the front of the chamber and then flipping the OPP upside down, i.e., with the ribs contacting the glass.

The average T_2 for three replicate measurements by pad position is clearly affected by OPP orientation as the data is not similar to Figure 3. Also, the proximity of the adjacent metal strut induces a bump in the noise data as discussed previously. Flipping the OPP upside down reduces the noise level. This is due to bringing the extra mass of rubber at the back of the part into closer

proximity to the Profiler. By flipping the OPP over, additional mass replaces some of the void volume closer to the probe, leading to reduced noise and a better signal.

Figure 9. Average T_2 and noise vs. scan location on OPP showing interference from adjacent metal parts. (Units for T_2 are ms).

Design of Experiment

A Design of Experiment (DOE) evaluation of the robotics chamber was performed to determine the effects of the local environment on the NMR measurement repeatability. The DOE was designed to map all of the OPP locations in the chamber by measuring six individual OPPs in each of the six measurement locations. This was done in order to determine if there is a neutral measurement area unaffected by relative OPP position. The Autosampler was programmed to take 288 measurements in 5° increments around the OPP centered over the gaps between the ribs at radial distances of 62, 69, 77, and 84 mm. Three replicates were measured per condition (864 measurements per OPP) comprising 76,746 total measurements. The DOE had the following factors:

- Six OPPs
 - 3 surveillance – #5, #6, & #1
 - 3 newly molded - #2, #3, & #4
- Two gain settings - 109 or 115 dB
- Six chamber measurement locations – A, B, C, D, E, & F

There were 269 (0.86%) outliers that were omitted from the analysis, 264 T_2 Error (>1.3) plus four $T_2 = -1$ and one $T_2 = 0$ out of 31,104 measurements.

Data for the 109 dB gain setting is not included because previous work determined that a standardized gain setting of 115 dB is recommended for the OPPs.

The measurement of noise in Position A was found to be significantly affected by an adjacent metal part for all the OPPs. Furthermore, noise is also affected by position within the chamber, i.e., the noise tends to decrease towards the back of the chamber (Figure 10).

Figure 10. Noise correlation for all OPPs by location in chamber. Position A is top graph, Positions B-E are in the middle graph. Bottom plot shows average noise of all OPP measurements by position.

Measurements on the newly molded OPPs have a slightly higher average T_2 than the parts returned from surveillance (Figure 11). Measurement variation is also displayed in Figure 11 by plotting the coefficient of variation of the mean at each pad position versus the average T_2 at each pad position.

Figure 11. T_2 values by OPP. (Units for T_2 are ms and units for average Coefficient of Variation (CV) are %).

The following figures (Figures 12-22) plot T_2 by either individual pad positions or by overall OPP averages that show the statistically significant differences both within OPPs and between chamber locations. A clear pattern of interference is seen at the front of the chamber that shows a decreasing gradient for positions located toward the back of the chamber.

Figure 12. Property dependence by chamber position showing a statistically significant gradient from the front to back. Each data point represents the average of all six OPPs. (Units for average T_2 are ms, units for average Coefficient of Variation are %, average signal to noise ratio (S/N) and average noise are dimensionless.)

Figure 13. Average T_2 measurements at pad positions showing property gradient by chamber position. Each data point represents the average of all six OPPs at a single pad position at a single OPP position. (Units for average T_2 are ms, units for average Coefficient of Variation are %, average signal to noise ratio (S/N) and average noise are dimensionless.)

Figure 14. Average T_2 for OPP #2 increases towards back of chamber and within OPP variation is reduced. See Figure 13 color code to determine position in chamber. (Units for T_2 are ms).

Figure 15. Average T_2 for OPP #3 increases towards back of chamber and within OPP variation is reduced. See Figure 13 color code to determine position in chamber. (Units for T_2 are ms).

Figure 16. Average T_2 for OPP #4 increases towards back of chamber and within OPP variation is reduced. See Figure 13 color code to determine position in chamber. (Units for T_2 are ms).

Figure 17. Average T_2 for OPP #5 increases towards back of chamber and within OPP variation is reduced. See Figure 13 color code to determine position in chamber. (Units for T_2 are ms).

Figure 18. Average T_2 for OPP #1 increases towards back of chamber and within OPP variation is reduced. See Figure 13 color code to determine position in chamber. (Units for T_2 are ms).

Figure 19. Average T_2 for OPP #6 increases towards back of chamber and within OPP variation is reduced. See Figure 13 color code to determine position in chamber. (Units for T_2 are ms).

Figure 20. Average T_2 by OPP and chamber position. Position A is red, position B is orange, position C is green, position D is black, position E is purple, and position F is blue. (Units for T_2 are ms).

Accomplishments

A total of 76,746 measurements were performed during various screening tests and a DOE to determine the effect of OPP position on T_2 value within the measurement chamber of a new automated miniSpec ProFiler NMR.

Future Work

Non-magnetic parts have been ordered to replace certain metal parts and will be installed in an attempt to eliminate measurement interference. Additional testing will be performed to determine if the plastic parts reduce the level of interference. An update to this report will be released summarizing all of the results and making a recommendation on the suitability of the ProFiler Autosampler method to measure OPP degradation for surveillance.

Additional areas for future work are as follows:

- If interference is reduced to an acceptable level, the untested OPPs can be measured and analyzed to look for trends in data.
- Request Bruker to modify Autosampler program to measure individual OPP locations instead of all six locations per run.
- Evaluate ProFiler's ability to measure flat cellular silicone pads or other materials.
- Consult with LLNL on how best to use the T_2 data to set pass/fail/monitor acceptance criteria on surveillance OPPs.

References

1. Sarah C. Chinn, Angela Cook-Tendulkara, Robert Maxwell, Hilary Wheeler, Mark Wilson, Z. Harry Xie, *Qualification Of Automated Low-Field NMR Relaxometry For Quality Control Of Polymers In A Production Setting*, Polymer Testing 26 (2007) 1015–1024.