Technical

Fingerprinting state of cure of automotive elastomers

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Executive summary

This paper presents the development of pulsed proton Nuclear Magnetic Resonance technique for determining the state of cure of polymeric materials.

Traditionally, crosslink density by swelling technique has been used for the state of cure control on materials and finished products, such as O-rings, gaskets, couplings and other rubber applications.

Swelling as a tool for understanding chemical makeup of the rubber product can be supplemented by the NMR technique providing a more sensitive analysis of automotive elastomeric product variations and quality.

The NMR technique, in conjunction with traditional techniques, helps us understand smaller variation in the rubber chemistry because of its high sensitivity for changes from production and/or aging effects in molecular mobility of the hydrogen atoms along the polymer chain.

NMR testing is non-destructive and can be used to set up benchmarks for quality control. Material process optimization can be evaluated for most elastomers as they contain the hydrogen isotope.

This paper presents the NMR technique for production batches, finished products, plant-to-plant variations and a tool for fingerprinting elastomers to understand the chemical state of the polymeric chains.

The presentation shows the test development effort at Akron Rubber Development Laboratory in the field of NMR "State of Cure Fingerprinting."

The ARDL NMR instrument is a Bruker Minispec mq 20 MHz Pulsed Proton Unit. NMR has been widely used as a chemical structure probe tool.

The solid state NMR pulsed proton instrument is used for measuring the transversal relaxation decay curves to probe the changes in the chemical structure. This in principle can be used to identify the changes in the structures with aging as well as with changes in the formulations of rubber products.

This equipment is a quick tool that can be effectively used with a low capital investment. The sample amount required is 0.1 cubic inches. The time of measurement is small and the test is non-destructive making it a good compound monitoring and quality control tool.

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With the above advantages in mind, the materials under study were investigated with the solid state pulsed proton NMR technique.

Nuclear magnetic resonance

NMR profits from the fact that some nuclei have a resulting magnetic moment. The most commonly investigated nuclei are protons (1H). They are essential parts in many substances and materials like oil, water and polymers.

In a strong external magnetic field (called polarizing field, produced by the permanent magnets in the magnet unit) the magnetic moments can be oriented, and the vector sum of all moments results in a macroscopic magnetization.

The method is to influence the macroscopic magnetization by skillful sequences of RF-pulses, generated by the electronic control unit and transmitted to the sample via the probe head.

The resulting measured NMR signal intensity is a function of the number of atomic moments, contributing to the macroscopic magnetization, caused by the RF pulse sequence.

In this way, for example, the molecular mobility of chains oil, fat or moisture contents of samples can be investigated.

On the other hand, the decay of an NMR signal after RF pulse excitation can be a sensor for the molecular motion of the measured sample.

Because of their different relaxation behavior, solid and liquid parts in one sample can be distinguished clearly so that it is possible to determine the solid liquid ratio in fat samples from an NMR signal (solid fat content/SFC measurements). As a consequence, such different materials can be investigated.

The NMR experiment works on the principle that a change in the chemical structure of a material is picked up by the change in the mobility of the protons—which can be understood by the response to pulses induced to the proton in a static magnetic field by the solid state NMR equipment.

Each hydrogen atom is a spinning charged particle with a magnetic moment. In quantum mechanics, a hydrogen proton could have two discrete orientations.

In the presence of a magnetic field the spin of the protons is rotating along the direction of the magnetic field with a Lamor frequency proportional to the strength of the magnetic field.

Elastomers contain a significant number of protons, located along their polymer chain that can undergo nuclear magnetic resonance.

When a dynamic magnetic field is applied that is perpendicular to the static field and oscillating with the Lamor frequency, the orientation of the spin can be flipped into a plane perpendicular to the static magnetic field while leading to a macroscopic magnetization within this plane.

This macroscopic magnetization can be measured, and its relation after removing the oscillating field can be analyzed.

Polymer chains have certain mobility, at least within some sequences or at their free ends, that influences the spin-spin interactions of their protons.

The transverse relaxation of the material therefore gives important information about the mobile behavior of the polymer chains. The change in mobility is affected by a range of changes in the compound's chemical and structural makeup.

A few of the causes and effects are given below:

- chain mobility is strongly affected by crosslink density;
- fillers influence chain mobility;
- additives influence chain mobility;
- crystallinity affects chain mobility;
- incomplete curing can affect chain mobility; and
- temperature affects chain mobility.

NMR testing requires short measurement times and a very simple sample preparation method. This method is unique and fast and allows for determination of the aged state of rubber.

As described, two methods of RF pulsing have been used to evaluate the NMR signals from elastomers under study.

- FID or free induction decay; and
- Hahn Echo Pulse Sequence.

Theory of free induction decay

A variety of techniques of pulsing are employed in the NMR experiment to compare and evaluate chemical structure differences for the materials under study

The free induction decay experiment is the simplest of the NMR pulse proton experiments. The decay curve is analyzed and compared after a 90 RF degree pulse to measure the signal intensity decay changes in the T_2* relation as a function of time.

Experimental

Materials

- O-rings:

Nitrile O-rings are tested in the pulsed proton NMR apparatus from power steering pump.

- Natural rubber engine mounts:

Compounded slabs with varying antioxidant levels and aged at three temperatures, three time durations and three levels of ambient partial pressure levels.

- Aged rubber compounds with carbon black and silica.

Physical properties

- NMR:

Pulsed Proton NMR Testing at 70°C and 20 MHz.

- Tensile testing:

Fig. 1. Free induction decay experiment.

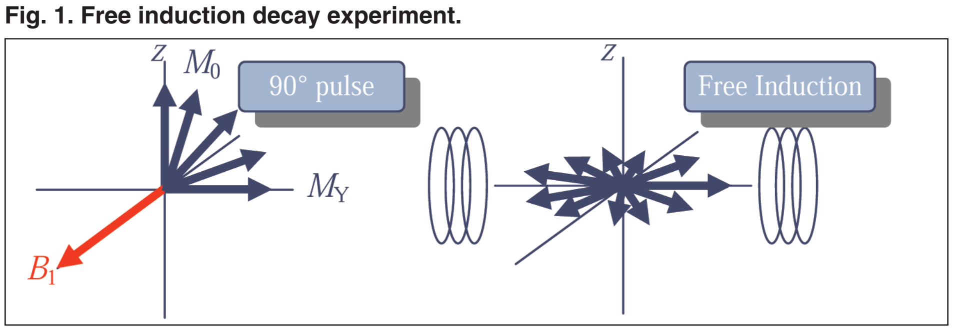


Fig. 2. Relaxation: FID (T_2*)

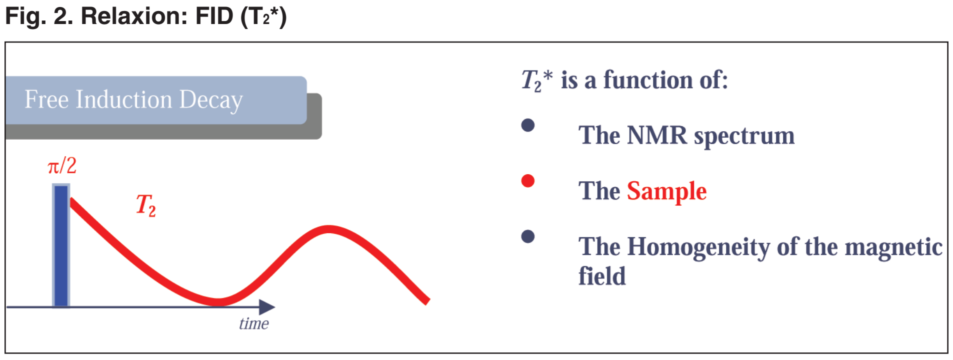


Fig. 3. Free induction decay.

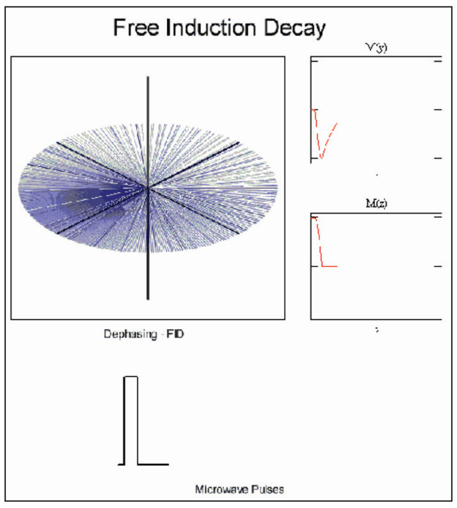
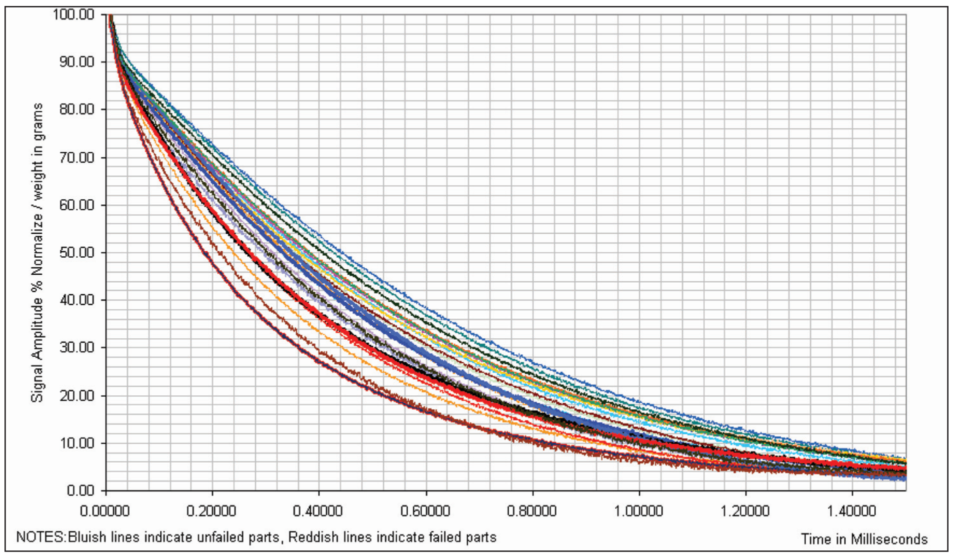


Fig. 4. Free induction decay at 70°C pulsed proton NMR.



Technical

Dumbbell specimens were die cut using an ASTM D 638 Type V dumbbell die and tested per ASTM D 412. Samples were tested at two inches per minute (50.08 cm/minute).

Testing was done in a controlled environmental space maintained at 50-percent relative humidity and at 70°F. Test output includes elongation to break, stress at break, modulus at 25 percent, 50 percent, 100 percent, 200 percent, 300 percent and 400 percent elongation.

- Crosslink density by swelling.

Results and discussions

Nitrile O Rings

See **Elastomers,** *page 20*

Fig. 5. Prediction profiler to maximize output variable.

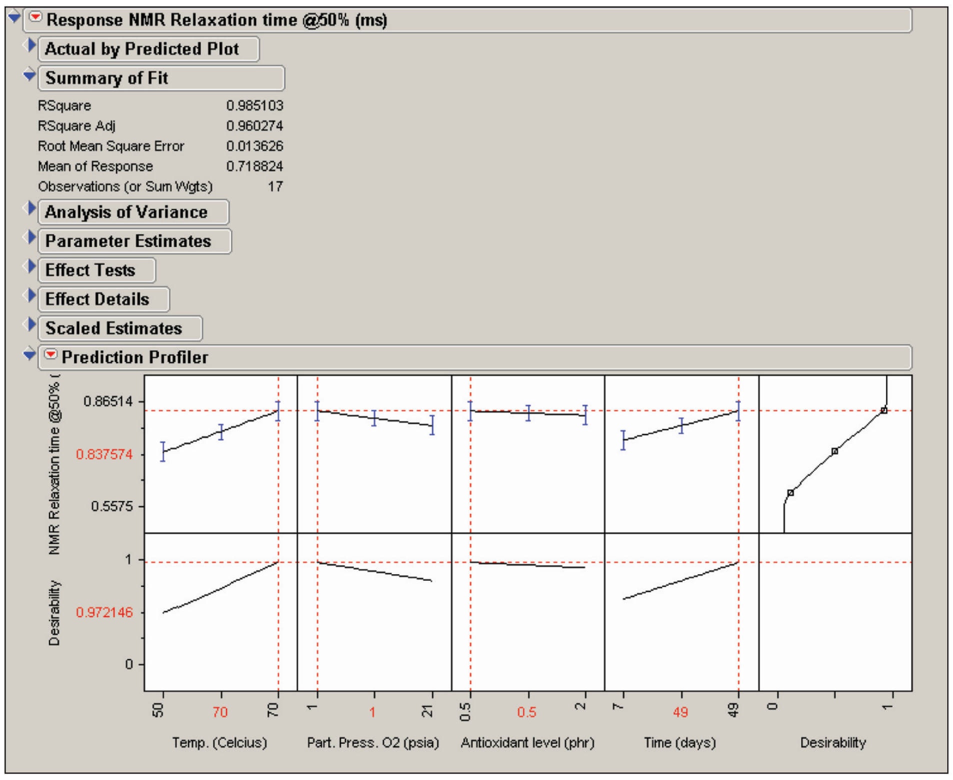
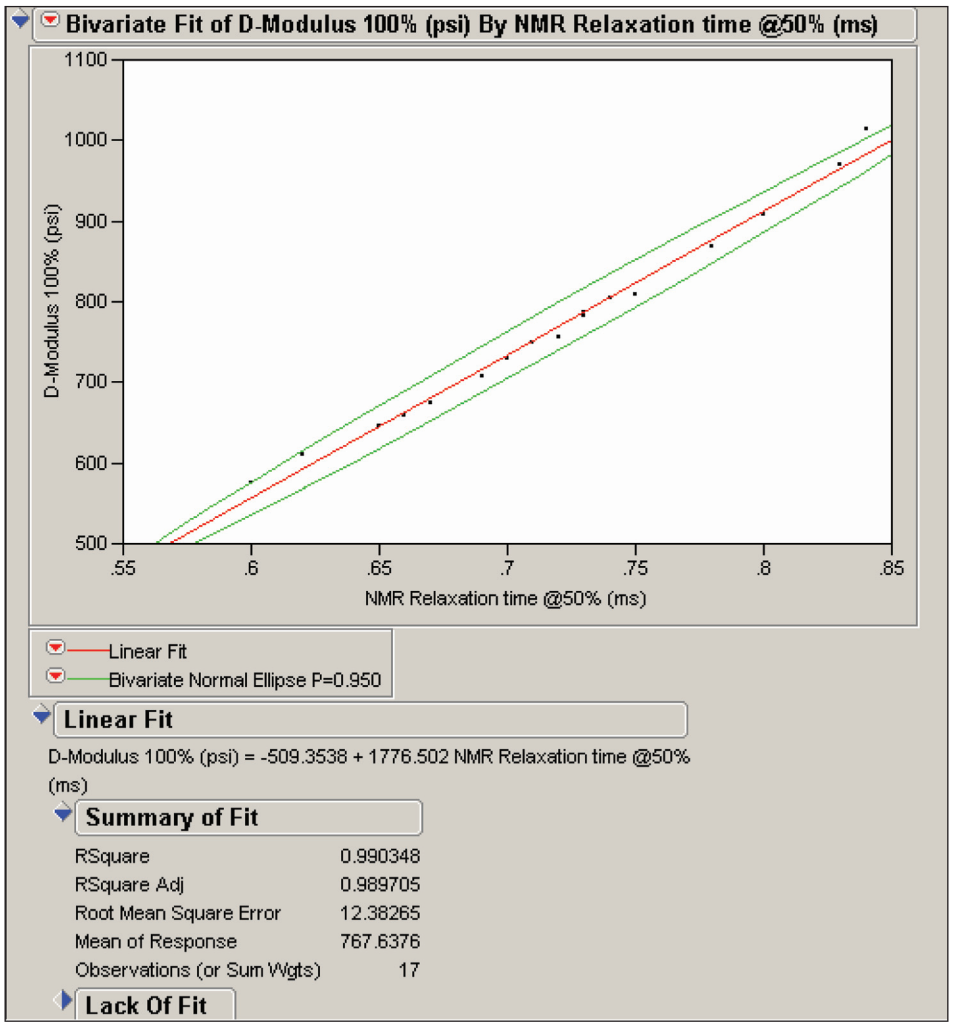


Fig. 6. Correlation between the modulus at 100-percent elongation and the NMR free induction decay signal.



Elastomers

Continued from page 19

Fig. 4 shows the free induction decay curves for O-ring made of nitrile rubber from the field. The blue colored lines show lower differences in chain mobility compared to the red colored curves. The free induction decay curves indicate chain mobility. The curves ranked the failed O-rings compared to the intact O-rings.

Natural rubber engine mounts

Fig. 5 shows the use of a prediction profiler used to maximize the output variable, in this case elongation to break and NMR free induction decay time to relation in milliseconds at 50-percent normalized amplitude.

The design of experiments studied the effect of time, temperature, antioxidant and partial pressure of oxygen for natural rubber tire belt coat compound on material property using NMR technique.

Fig. 6 shows an excellent correlation between the modulus at 100-percent elongation and the NMR free induction decay signal.

Filler effects: silica– carbon black

Fig. 7 shows the decay curves indicating that the curve shifts to the right with aerobic aging as well as anaerobic aging. This indicates a reduction in the chain mobility.

The fast decay curve portion of the data indicates that there is a trend switch between the silica and carbon black filled rubbers for the aerobic and anaerobic regions.

In addition the carbon black-filled rubbers reduction in relation time is more significant for the aerobic oven aging as compared to the silica-filled rubber compound.

Conclusions

The NMR experiment is a quick and useful tool in testing finished engineering products. This presentation illustrated the utility of this technique to fingerprint and benchmark chemistry changes in three types of compounds with applications such as O-rings, natural rubber engine mounts, tire belt coat compounds and silica and carbon black filler effect.

NMR is an effective tool to study potential field failures in nitrile O-ring samples.

This paper illustrated the ability of the NMR experiment to correlate aging mechanisms using statistical design of experiments for natural rubber formulations used in engine mount applications.

It was discovered that the rubber chain mobility at various layers allowing us to understand and fingerprint the tire to tire variations in cure as well as tire aging effects. NMR can be an effective tool to study rubber filler interactions.

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Karmarkar worked as a staff engineer before his current assignment at ARDL. Karmarkar has been active in test development and tire aging research. He has published more than 10 scientific articles and presentations on tires, automotive, aerospace, medical products and predictive materials research. He published a thesis on aircraft composite design optimization at the University of Akron before joining ARDL.

Abraham Pannikottu is manager of ARDL Engineering Group. He has experience as an engineer with a custom mixer and leading manufacturer of reclaimed rubber and latex gloves. Pannikottu's capabilities include compression stress-relaxation of polymers, thermal and dynamic mechanical analysis, conductive polymer applications and medical applications for rubber and plastics.

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Fig. 7. Pulsed proton NMR free induction decay curve.