SOLID ROCKET MOTOR NDE USING NUCLEAR MAGNETIC RESONANCE

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INTRODUCTION

Solid rocket motors (SRMs) are complex integrated structures. An integral part of an SRM is the adhesive liner, which is used to bond the propellant to the insulator covering the inner surface of the case. In order to ensure SRM performance and reliability, the adhesive liner must be properly cured, of the specified thickness, and free of contamination. The goal of this study is to demonstrate the feasibility of a nuclear magnetic resonance (NMR) method to ensure that these conditions are met.

The design of an instrument to monitor the liner cure and thickness presents difficult and challenging problems. The measurements must be made without contacting the surface, and must be made in the presence of SRM motion during the initial stages of the curing cycle. There are few potential probes capable of operating under these conditions and constraints.

However, nuclear magnetic resonance, an analytical technique commonly used in chemistry, is very sensitive to the details of molecular motion, and NMR has recently been shown to provide detailed information regarding adhesives and adhesive bonds [1], [2], [3]. In addition, studies of SRM adhesives at Hercules Corporation have shown that NMR has the potential to provide detailed information concerning the curing process and the layer thickness of these specific compounds [4].

Furthermore, Quantum Magnetics has recently shown that non-invasive and non-contacting NMR technology can be used in a number of nondestructive evaluation (NDE) and nondestructive inspection (NDI) applications. For example, NMR can be used to detect moisture and surface cracks in the carbon/epoxy composite materials common in aerospace applications [5], and NMR can also be used to discriminate between various elastomeric materials. In addition, Quantum Magnetics has shown that NMR can be used to scan unopened glass bottles to confirm the identity of the contents.

Therefore, at the beginning of this program, it seemed likely that NMR could form the basis of an NDI system for monitoring liner cure and thickness during the SRM fabrication process. This expectation was confirmed by the results reported below.

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TECHNICAL BACKGROUND

The adhesive liner in a solid rocket motor (SRM) is ideally suited to nondestructive inspection (NDI) by nuclear magnetic resonance (NMR). A general description of SRM design, fabrication and materials is presented below. This is followed by an introduction to NMR and a description of the NMR parameters important to SRM adhesive liner NDI.

Solid Rocket Motors

In its simplest form, a solid rocket motor consists of an outer case containing an insulating layer, an adhesive liner, and a propellant. The outer case is fabricated from either filament-wrapped composite or steel. The inner surface of the case is covered with a layer of insulation which, in turn, is typically covered with a thin layer of primer and, sometimes, a barrier coat to prevent chemical migration. The adhesive liner covers the primer/barrier and bonds the insulator to the propellant. The general configuration is shown in Figure 1.

The material set chosen for this study consisted of a graphite composite casing (approximately 126 inches inner diameter) with Kevlar-filled ethylene propylene diene monomer (EPDM) insulator. The primer/barrier layers were approximately two mils thick, and the adhesive liner system was based on polybutadiene polymer which was sprayed on to a thickness of about 15 mils. Details on the material set are presented in Table 1.

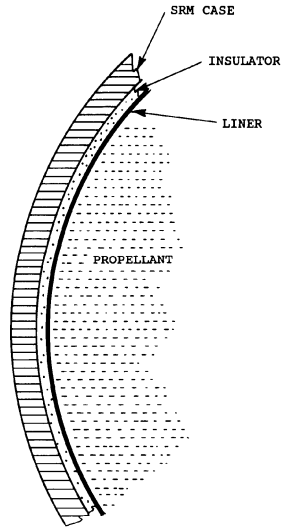

Fig. 1. Generic SRM structure.

Table 1. SRM Material Set.

Component	Material	Thickness (approx., inches)
Case	Graphite-Epoxy Composite	1.0 (126 inch I.D.)
Unsulation	Kevlar-Filled EPDM	0.25
Liner	Carbon Black-Filled HTPB	0.015
Propellant	HTPB	42 - 45

The adhesive liner is an approximate 60/40 mixture of hydroxyl-terminated polybutadiene (HTPB) and carbon black. The carbon black is added to control the viscosity of the uncured liner. However, as the material cures, the carbon black appears to play an important role in the formation of the final product.

Hydroxyl groups on the ends of the polybutadiene chains are strongly attracted to the carbon black and form a structure with locally restricted motion. The free ends of the polybutadiene chains initially exhibit considerable molecular freedom but then, as the cure proceeds, this freedom is restricted by the formation of crosslinks. At the conclusion of the curing process the adhesive liner has essentially two components: locally rigid structures that are highly crosslinked and less rigid structures near the carbon particles which allow restricted molecular motion. This model of the curing process accounts for the two-component relaxation behavior observed in the NMR results presented in the experimental results.

The adhesive liner is sprayed on the inside surface of the insulator-primer combination to a thickness of about 15 mils. It is cured in air for approximately 48 hours at 60° Celsius, then aged for a similar period of time at room temperature. To minimize thickness variations and prevent sagging, the SRM case is initially rotated at approximately three rpm. After about 12 hours, the liner viscosity is high enough so that the rotation can be stopped.

Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) arises from the magnetic properties of atomic nuclei [6]. When immersed in a steady magnetic field, B_0, the nuclei align with the field and precess at a characteristic frequency called the NMR resonance frequency (or, quite often, the Larmor frequency).

The NMR frequency is proportional to the strength of the applied magnetic field, B_0. The constant of proportionality is different for each nuclear species.

An externally applied pulse of radio-frequency (RF) field at the NMR resonance frequency causes the nuclei to tip away from their equilibrium position and, while still precessing, induce an NMR signal called a free induction decay (FID) into an adjacent detection coil. In NMR, the detection coil is often called the sample coil.

For SRM NDI, there are three important parameters of the NMR response. Two of these parameters are very sensitive to the state of molecular motion in the material under study; the third is sensitive to the total number of nuclei sampled. The characteristics of these three parameters are summarized below and, in addition, illustrated in Figure 2.

The Spin-Spin Relaxation Time, T_2. This is the characteristic time (i.e., the time constant) for the NMR FID signal to decay to zero when the sample is located in a perfectly homogeneous magnetic field. The T_2 times for simple NMR free induction decays are shown in Figure 2.

T_2 is sensitive to low frequency molecular motions and, therefore, T_2 times for liquids and semiliquids (which are generally quite long) are very different from T_2 times for solids (which are generally quite short). As a result, T_2 is a sensitive probe of the details of the molecular motions which occur in adhesive compounds, before, during and after the curing process.

If a compound exhibits two distinct phases, one with more molecular freedom than the other, then often two T_2 times will be evident. A sketch of a two-component NMR free induction decay is shown in Figure 3. The short T_2 component, T_{21}, has initial amplitude M_{01}, while the long T_2 component, T_{22}, has initial amplitude M_{02}.Generally, the short T_2 component is identified with the more rigid phase and the long T_2 component with the more mobile phase.

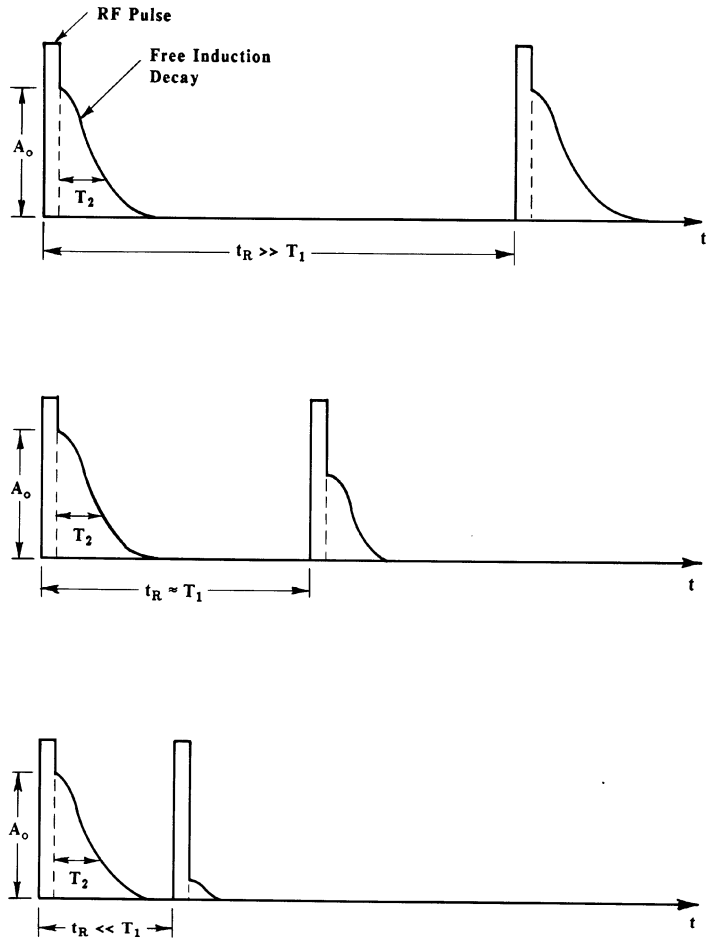

Fig. 2. NMR response characteristics.

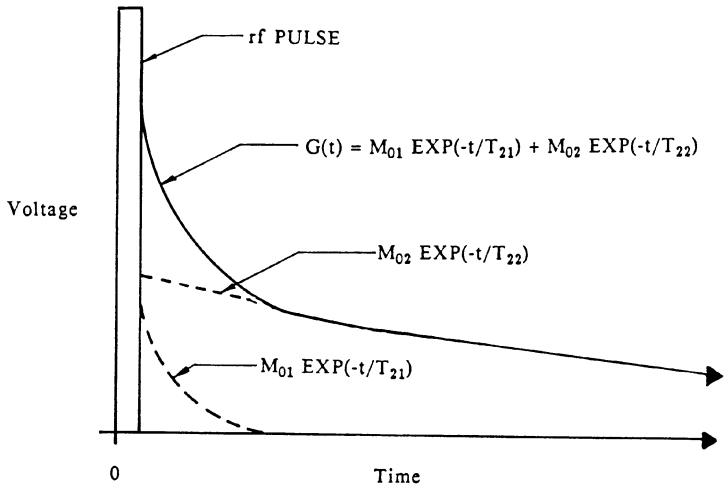

Fig. 3. Shape of two-component NMR free induction decay.

The NMR Signal Amplitude, A_0. The amplitude of the NMR signal immediately following the RF pulse, A_0 in Figure 2, is directly proportional to the number of resonant nuclei in the sensitive region. Only proton, or hydrogen nucleus, NMR was considered for this application because, of all the nuclei in HTPB, only protons provide an NMR signal with an acceptably large A_0.

If there are two distinct compounds in the sensitive region with two distinct T_2 relaxation times, or a single compound with two distinct phases, then the initial amplitudes of the two T_2 components are proportional to the fractions of each in the sensitive region.

That is, in Figure 3, the ratio of M_{01} to M_{02} represents the ratio of short T_2 to long T_2 material in the sample under study. In an adhesive with two distinct phases, such as the HTPB adhesive liner, this ratio changes with time as the material cures and provides a sensitive probe into the state of the curing process.

The Spin-Lattice Relaxation Time, T_1. This is the characteristic time for the nuclear spin system to come to equilibrium with its surroundings following a disturbance. A disturbance may be produced by an applied RF pulse or by a change in the applied magnetic field. Therefore, in an NDI application, the T_1 of the adhesive determines the time required for an individual test and, thus, the maximum data acquisition rate.

T_1 times are generally longer than T_2 times, and like T_2 times, they are influenced by molecular motions. However, T_1 times are sensitive to motions which occur at higher frequencies than those which influence T_2. Therefore, T_1 times often provide independent information which can be used to characterize the curing process.

Proper measurement of these NMR parameters provides critical information about the adhesive liner during the curing process. Adhesive compounds have special NMR properties combining some features of both solids and liquids. An adhesive that cures by crosslinking, such as HTPB, goes from a state of low viscosity to a state of very high viscosity. Therefore, the proton T_2 of the adhesive liner is initially expected to be quite long, and as the cure proceeds, to shorten.

NDI System Requirements

The NMR NDI system must measure both the thickness of the adhesive liner and its state of cure. Since both the liner and the outer case of the SRM are cylindrical in shape, the NMR detection head must conform to this symmetry. In addition, the NMR NDI system must tolerate SRM rotation during the initial stages of the cure and must also accommodate both composite-case and steel-case SRMs.

The SRM adhesive liner NDI application requires a single-sided NMR instrument geometry. In this geometry, a specially designed magnet projects a uniform field into the material under study and a flat NMR detection coil is used to apply the rf pulses and recover the NMR signal.

Several potentially suitable single-sided NMR instrument configurations were identified during the course of this work. The advantages and disadvantages of each of these configurations are currently under study, and our future objectives are to design, fabricate and evaluate such a system.

EXPERIMENTAL DETAIL

Quantum Magnetics has developed a small and compact NMR system specifically for NDE and NDI applications. A prototype of this system was used to take the NMR data reported here.

The Quantum Magnetics NMR NDE system is housed in a PC-sized, rack-mount cabinet and operates at frequencies between 1 and 22 MHz. The system is designed for maximum flexibility, and can accommodate both single-sided and conventional detection head geometries. A sophisticated software package allows automated data collection and incorporates a variety of signal processing options.

NMR data is generally dependent on frequency and, early on, it was determined that 5 MHz was the highest frequency likely to be employed in this application. Therefore, these NMR data were taken at 5 MHz, corresponding to an applied field of 1,175 Gauss.

An uncured sample of HTPB/carbon black adhesive was prepared at Hercules Corporation and stored at about -15° Celsius until the NMR measurements began. Insulator and primer samples were also obtained from Hercules.

EXPERIMENTAL RESULTS

The results of a 90-hour run of proton T_1 and T_2 measurements, taken at 5 MHz and the proper cure temperature of 60° Celsius, are shown in Figures 4 through 7. Initially, the NMR signal was characterized by a single T_2 time of about 30 milliseconds, but at about two hours into the cure, two distinct T_2 times were clearly evident.

The short-T_2 component of the NMR signal is described by time constant T_{21} and amplitude M_{01}, and the long-T_2 component by T_{22} and M_{02}. The dependences of T_{21} and T_{22} on cure time are shown in Figure 4. Zero time represents the point when the sample temperature was raised to 60° Celsius.

As shown in Figure 4, between two hours and seven hours, T_{22} drops dramatically from almost three seconds to less than 50 milliseconds. Therefore, this parameter provides a sensitive probe of adhesive liner state-of-cure in the two to seven hour time period of the curing cycle. For short times, between zero and two hours, the long-T_2 component, T_{22}, was too small in amplitude, and too long in duration, to determine accurately with the experimental parameters used.

The short-T_2 component, T_{21}, plotted in Figure 4, and on an expended scale in Figure 5, drops less abruptly than T_{22}. T_{21} drops smoothly from about 30 milliseconds to about 6 milliseconds over the period from zero to about 40 hours. Therefore, T_{21} provides independent information on the liner state-of-cure much further into the curing cycle.

During data acquisition, the gain of the NMR receiver was not controlled. Therefore, the amplitudes of the two T_2 components, M_{01} and M_{02}, taken individually, are not meaningful. However, since both M_{01} and M_{02} are measured at the same time, their ratio is independent of gain fluctuations.

The ratio of M_{01} and M_{02} is plotted in Figure 6. This quantity falls almost linearly, by more than a factor of 50, during the first six hours of the cure. Therefore, the ratio of M_{01} and M_{02} provides a third independent probe into the adhesive curing process.

The results of T_1 measurements taken at 5 MHz and 60° Celsius are shown in Figure 7. The data are sparse because T_1 and T_2 could not be taken simultaneously and the NMR system was set up to acquire T_2 data automatically. The liner T_1 drops by more than 26% over the 90-hour cure time, and thus provides a fourth independent probe into the curing process.

The 5 MHz, 60° Celsius T_1 and T_2 data are summarized in Table 2. NMR results for all three important materials, the insulator, the primer and the adhesive liner (both cured and uncured) are included.

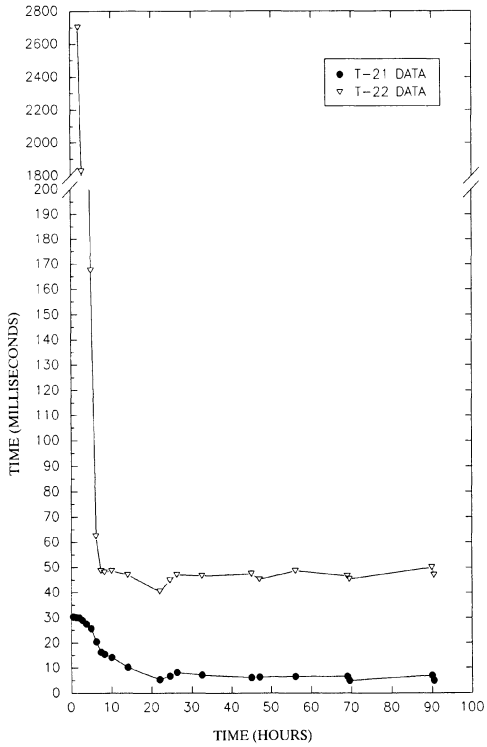

Fig. 4. T_{21} and T_{22} versus cure time.

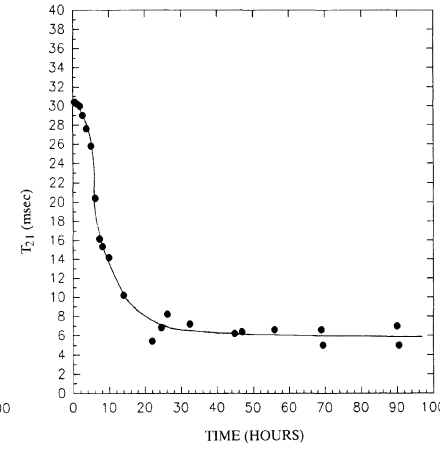

Fig 5. T_{21} versus cure time.

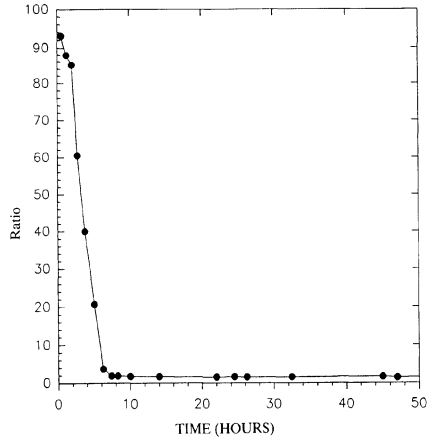

Fig. 6. Ratio of M_{01} to M_{02} versus cure time.

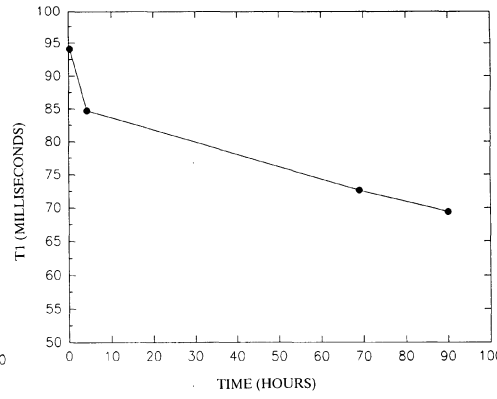

Fig 7. T_1 versus cure time for adhesive liner.

Table 2. Relaxation Results At 60° Celsius.

Sample	T_1 (msec)	T_2 (msec)
Insulator	21.	1.4
Primer	24.3	1.4
Adhesive Liner (Uncured)	94.1	30.4
Adhesive Liner (Cured)	71. (a)	5.9 (b) 47.3 (b)

(a) From FID measurements at 69 and 90 hours.
(b) Two-component T_2 relaxation.

For all states of cure, the T_1 and T_2 times for the adhesive liner are significantly longer than the T_1 and T_2 times for the primer and the insulator. These data show conclusively that an NMR NDI instrument is capable of distinguishing the NMR signal of the SRM liner from the signals of the insulator and the primer.

In addition, it should be noted that there is an indication that the long-T_2 component of the liner NMR signal has a long-T_1 component associated with it (see Table 2). If so, this provides a fifth independent NMR variable to monitor during the cure. However, we did not have the resources to explore this issue further.

CONCLUSION

The results of this study show that NMR is a suitable non-contacting NDI technology for monitoring the adhesive liner during SRM fabrication. The NMR response from the liner is readily distinguished from those of the insulator and the primer, and thus the SRM liner thickness can be determined directly from the NMR signal.

In addition, NMR provides four independent probes into the liner state-of-cure. Two of these probes, T_{21} and M_{01}/M_{02}, provide highly specific and identifiable markers during the first 10 hours of the cure. The other two probes, T_{22} and T_1, allow the curing process to be tracked virtually the entire cure cycle.

REFERENCES

1. A.O.K. Nieminen and J.L. Koenig, "NMR Imaging of the Interfaces of Epoxy Adhesive Joints", Journal of Adhesion **30**, 47 (1989).
2. A.O.K. Nieminen and J.L. Koenig, "Chemical Shift Effects in NMR Imaging of Adhesives and Adhesive Joints", Applied Spectroscopy **43**, 1358 (1989).
3. A.O.K. Nieminen, J.W. Liu and J.L. Koenig, "NMR Imaging of Adhesive-Bonded Structures", Journal of Adhesion Science and Technology **3**, 455 (1989).
4. E. VanderHeiden and M. Sullivan, "NMR for Evaluation of Casebond Cure, Thickness and Coverage", Hercules Corporation report of work carried out under NASA Contract NAS8-37802.
5. L.J. Burnett, D.A. Bertone (D.Thorson) and R.E. Sager, "Single-Sided NMR for Moisture Content Evaluation of Composites", Final Report on US Navy Contract N68335-88-C-0329, September 1988.
6. C.P. Slichter, Principles of Magnetic Resonance, 2nd Edition, Springer-Verlag, Berlin, 1978.