NMR AS A PROBE OF ABSORBED WATER IN GRAPHITE-REINFORCED PLASTIC

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INTRODUCTION

Graphite-reinforced plastic (GRP) is being used increasingly in aircraft applications. This lightweight material, however, is difficult to inspect for impact damage. Generally, the damaged region occurs on the back side of the GRP, where it is least accessible. It has been noted that the damaged regions absorb more water from a humid atmosphere than the undamaged regions. We propose that nuclear magnetic resonance (NMR) detection of the absorbed water may be a feasible method of detecting and locating impact damage in GRP structures.

The electrical conductivity of GRP will clearly cause attenuation of the radio-frequency (rf) magnetic fields in the NMR experiment. Specifically, if one imagines the NMR rf coil to be on the accessible front side of the GRP and the absorbed water to be near the back surface, the skin-effect will attenuate the nuclear spin signal detected by the coil.

Thus, the present measurements were performed to determine the extent of the attenuation by GRP of the NMR signal. Because the NMR sensitivity is expected to be frequency dependent even without the GRP, and the attenuation by the GRP is also frequency dependent, our measurements extend from 2 to 53 MHz. At each frequency we have measured the amplitude of the spin signal and the strength of the rf field H_1 for three configurations. The first configuration uses no GRP and allows us to test our methodology by comparison with well-known theoretical results. The second configuration has the GRP separating the NMR coil and NMR sample -- this is the geometry of the proposed application. The third configuration has the NMR sample and rf coil on the same side of the GRP, so that the only effects of the GRP are to reduce the Q of the rf coil and to distort the rf field lines.

The measurement results are compared to the predictions of a theory combining the usual frequency dependence of NMR sensitivity with attenuation through the skin depth.

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EXPERIMENTAL

The experiments reported here were performed in an iron-core Varian electromagnet (V4012–A) with 12" diameter pole caps and 1.75" pole spacing. The NMR spectrometer was of the super-heterodyne design, with the generation of rf pulses and receiver amplification and quadrature, phase-sensitive detection done at the 30 MHz intermediate frequency. The over-all design is similar to that of spectrometer B described by Waugh et al. [1] To cover the frequency range from 2 to 53 MHz, several receiving pre-amplifiers were employed. Each was tuned to the desired operating frequency.

The NMR sample, rf coil, and the GRP all were housed in an aluminum box located at the center of the magnet gap. The same rf coil was used for all the measurements except 2.0 MHz; the coil was a flat spiral of 13 turns of #26 AWG copper with a ~1 cm outer diameter. The 2.0 MHz coil had the same dimensions except for having 30 turns of a finer wire. Ceramic trimmer capacitors used for tuning and matching the coil to 50Ω resistive were located in the aluminum box at all frequencies at and above 8.5 MHz. The lower frequencies required physically large tuning and matching components, so these were located outside the magnet in a separate box. About two feet of coaxial cable connected the rf coil to the tuning and matching box. Our intention was to minimize the losses that occur in the resonant (not impedance matched) cable [2], whenever possible.

A piece of GRP measuring 3.8 cm × 5.7 cm × 0.24 cm thickness was used. Since this is much bigger than the 1 cm rf coil, it approximates an infinite plane (i.e., we need not worry about the rf fields going around the edge of the GRP). To further reduce the possibility of fields going around the GRP, the GRP was a close fit to the aluminum box, but was electrically insulated from it. The plane of the GRP was horizontal, and the static magnetic field H_0 was horizontal (see Figure 1). The spiral rf coil was horizontal, so it had a predominantly vertical rf field. Thus, the rf field H_1 was nominally perpendicular to H_0, as required for maximum magnetic resonance sensitivity [3].

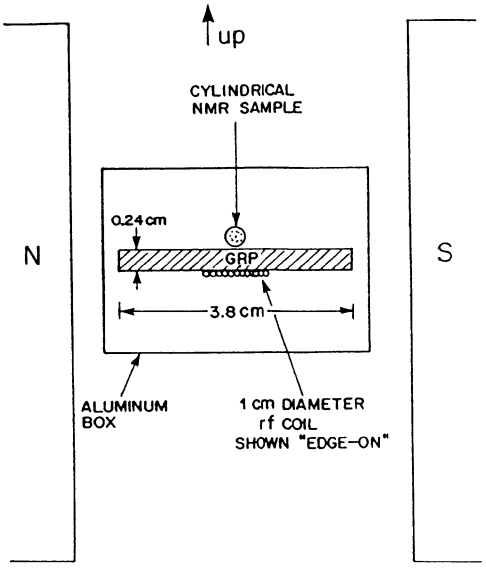

Fig. 1. Sketch of geometry of rf coil, NMR sample, and GRP in the aluminum box in the magnet gap.

Three configurations of sample, coil, and GRP were used as detailed in Figure 2. The first configuration, labeled W/O, had the GRP sheet replaced by a plexiglass (insulating) piece of the same dimensions. The W/O configuration was tested to see if the measurement procedures could reproduce well-known theoretical results for NMR sensitivity. The second configuration, "GRP-back", had the sample on the opposite side (the back side) of the GRP from the NMR coil. This configuration is that of the intended application. The third configuration, "GRP-front", had the sample on the same side of the GRP as the NMR coil; the GRP's only effects are Q reduction of the coil and distortion of the rf field pattern of the coil. The attenuation of the rf fields through the GRP is not directly measured in configuration GRP-front. In GRP-front, the distance from the sample to the coil was the same as in GRP-back.

To allow for rapid and reproducible interchanges between the three configurations, the construction was "modularized". The NMR sample was glycerol, a convenient proton-bearing liquid. It was sealed into a 0.5 cm diameter hole drilled into a plexiglass piece. The rf coils were epoxied to plexiglass pieces. Thus, the sample, rf coil, and GRP or plexiglass could be rapidly re-arranged, and secured with two clamp screws.

We verified several times by removing the sample that the observed NMR signals came from the glycerol, and not from protons in the construction materials or GRP or plexiglass. The protons in the solids have short T_2 values less than 50 μsec, so that they are not observed on the long time base used for observation of the glycerol signal (long T_2; T_2^* is magnet limited to typically 4 msec).

The amplitude of the NMR free induction decay (FID) was determined as follows. Typically, 100 FIDs were signal averaged. The amplitude of the signal was then extrapolated to zero time, to get the initial value of the signal. The extrapolation was not major: the observed signal at times just after the receiver had recovered was always greater than 95% of the extrapolated value. An rf signal generator (H–P 606, 50Ω output with calibrated attenuator) was connected to the spectrometer, in place of the rf probe. By comparing the receiver output with the NMR FID and signal generator as inputs, we assigned an amplitude to the FID in units of microvolts, at 50Ω impedance. This direct substitution method does not require the spectrometer rf input impedance to be 50Ω. Rather, it requires that the rf generator and NMR probe both be 50Ω resistive

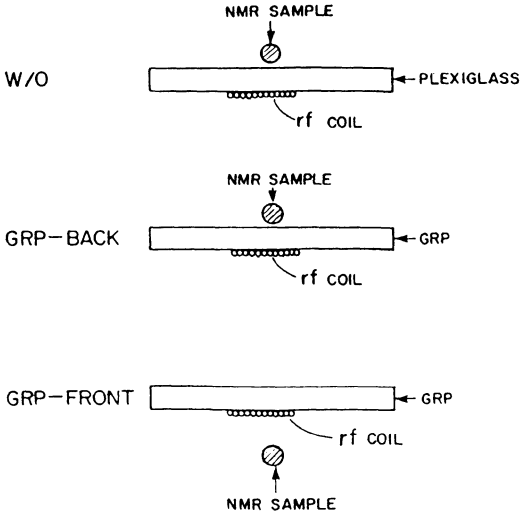

Fig. 2. Sketch of the three sample-rf coil-GRP configurations used in the measurements. The aluminum box is not shown.

at the operating frequency. In fact, the probe was always matched to be 50Ω resistive. Thus, the values reported reflect the amplitude of the FID from the rf probe; in no way is the noise figure, bandwidth, or any characteristic of our particular receiving apparatus involved.

The rf field amplitude H_1 was measured by determining the rf pulse length t_w that yielded a FID of maximum amplitude. We took this as a $\pi/2$ pulse (an average nutation angle of $\pi/2$ across the sample), so that $\gamma H_1 t_w = \pi/2$. Obviously, this is some average H_1 across the sample.

The H_1 amplitude will vary as the square root of the rf power delivered to the probe. Clearly, the nuclear spins care only about the power in the fundamental. We measured this power by using the spectrometer's receiver as a convenient, narrow-banded device already at hand. The rf pulses (that ordinarily were delivered to the probe) were attenuated 100 dB and fed into the receiver. Because the pulses are at the exact spectrometer frequency, the phase detector outputs are dc. These were added by Pythagoras' theorem to get the total amplitude. This amplitude was compared to that obtained when feeding the H–P 606 into the receiver. Thus, this measurement is also a "direct substitution" technique. By comparing the receiver outputs for the cases of the attenuated rf pulse and the signal generator as inputs, the pulse power in the fundamental was determined.

RESULTS AND DISCUSSION

The signal strengths for the three configurations are represented graphically in Figure 3. The values of $\gamma H_1/2\pi$ (the nutation frequency) appear in Figure 4. The $\gamma H_1/2\pi$ values have been corrected for transmitter power variations, using $H_1 \propto P^{1/2}$. The figure refers to a 100 watt input to the rf probe.

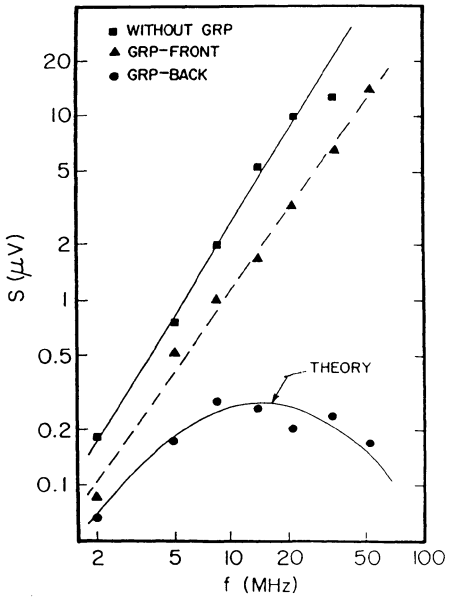

Fig. 3. Signal strength S as a function of frequency for the three configurations. S was always determined by the direct substitution of an rf signal generator. The solid, straight line is fit to the data without GRP. The dashed line is an eyeguide. The solid curve is from the theory.

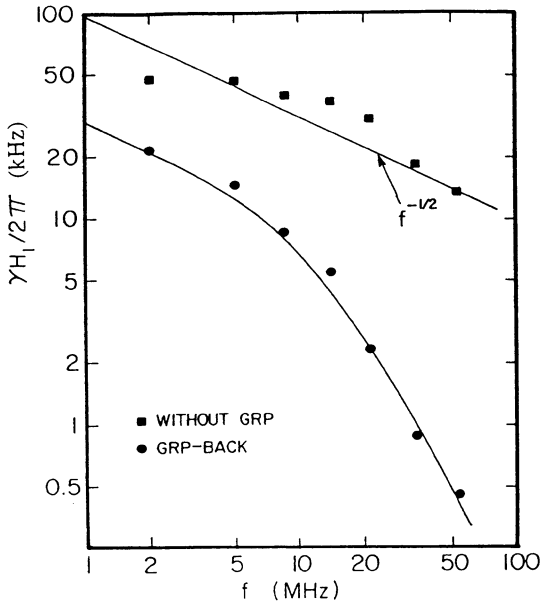

Fig. 4. Rf field strength H_1 expressed in frequency units as a function of NMR frequency. The straight line represents $f^{-1/2}$ dependence and roughly fits the data without GRP. The curve through the GRP-back data is an eyeguide.

The solid squares in Figure 3 were taken without any GRP present. The signal S varies with Larmor frequency f according to $S \propto f^{1.68}$, as indicated by the line through the data. This experimental variation may be compared to the theoretical prediction [3] with Q independent of frequency: $S \propto f^{1.5}$. If the Q of the NMR coil is limited by ohmic skin losses in the coil, the Q will vary [4] as $f^{1/2}$ and the NMR signal will have an additional $Q^{1/2}$ variation. Thus, this model predicts $S \propto f^{1.75}$. The experimental variation reported here is between these two predictions. This agreement with theory indicates the reliability and essential correctness of our measurement strategy.

The solid triangles in Fig. 3 are the NMR signal amplitudes for configuration GRP-front. The signals are smaller than for the graphite-free configuration, indicating that the loading of the coil Q by the GRP reduces the NMR signals. The reduction in signal strength becomes more pronounced at higher frequencies, but the frequency dependence is weak.

The solid circles in Fig. 3 represent the NMR signal amplitudes in configuration GRP-back. This is the configuration in which the NMR coil and NMR sample are located on opposite sides of the GRP. Compared to the graphite-free configuration, the signals from GRP-back are strongly attenuated; the attenuation increases rapidly with frequency.

The frequency variation of the signal strength in the GRP-back configuration is due to two effects: the strength of the spin signal S in the absence of GRP is $S \propto f^{1.5}$ (changing this to $f^{1.68}$ or $f^{1.75}$ makes negligible changes in the predictions) and the GRP attenuates the spin signal according to its skin depth. Thus, the prediction is

$$S = Af^{3/2} e^{-t/\delta} \tag{1}$$

where A is an arbitrary constant, t is the thickness of the GRP and δ is the frequency-dependent skin depth. The skin depth is given by

$$\delta = \left[\frac{2}{\mu_o \sigma 2\pi f}\right]^{1/2} \tag{2}$$

where $\mu_o = 4\pi \times 10^{-7}$ in MKS units and σ is the electrical conductivity of the GE GRP samples, experimentally determined as $\sigma = 2.5 \times 10^4\ \Omega^{-1}m^{-1}$, as determined by William A. Edelstein of GE.

The solid curve passing through the GRP-back data in Fig. 3 was obtained from the above theory. In Eqs. (1) and (2), the only adjustable parameter is A. The fit to the data is remarkable, particularly in light of its simplicity. Effects not included in the theory are the reduction of coil Q by the GRP and the distortion of the field lines by the GRP. Evidently, these effects are not large or, at least, are not strongly dependent on frequency. In any event the above simple theory explains the data and undoubtedly includes the most important effects from the GRP. Finally, it must be remarked that the $f^{3/2}$ and $e^{-t/\delta}$ conspire to make the signal amplitude nearly constant over a decade in frequency (se Fig. 3).

The variation of $\gamma H_1/2\pi$ in the graphite-free configuration is displayed in Fig. 4. The straight line passing through the data represents the $H_1 \propto f^{-1/2}$ variation predicted by simple theory [3] with a constant coil Q. The general trend in the data follows the $f^{-1/2}$ line, but there are substantial (±25%) deviations from the line. We believe the deviations are due to our method of determining H_1, namely measuring the pulse width that yields the maximum signal amplitude ($\pi/2$ pulse). A null method would be much more precise; for example, one could measure the pulse width of a π or 2π nutation (these yield zero signal). However, these null methods were not useable in the presence of the GRP because of the extremely inhomogeneous H_1.

The field strength H_1 was substantially decreased in configuration GRP-back. This can be understood as the attenuation $e^{-t/\delta}$ through the classical skin depth. The extent of attenuation is measured by the ratio of H_1 without GRP to the H_1 in configuration GRP-back. This ratio is about 20 at 34.52 MHz, substantially smaller than the ratio of signal amplitudes (about 50) in the two configurations. At other frequencies the situation is similar: the NMR signal is decreased to a greater extent than the H_1 field. For homogeneous H_1 field, the attenuations in the two directions should be equal, according to a reciprocity theorem. It is our belief that these two measures of attenuation by the GRP differ because of the extremely inhomogeneous H_1 on the back side of the GRP. Such H_1 inhomogeneity will make it impossible to nutate all the spins by $\pi/2$ simultaneously, causing the NMR signal to be weaker. In the limit of extremely inhomogeneous H_1, spin signals will be observed only from the fraction of the sample residing in the region of strong H_1. The result will be that the sample is effectively smaller in volume and the spin signals will be reduced accordingly.

A test of NMR to detect absorbed water at a damaged region appears in Fig. 5. The small signal in the upper trace is due to moisture and the small amount of water in undamaged GRP. The spin signal from the absorbed water at the damage is evident in the middle trace. The 1000 signal averages provide an acceptable signal, but require ~5 minutes. Thus for this GRP (0.3 cm thick) NMR is not adequately sensitive for useful, rapid scanning (1 cm^2 in 1 second). Going to higher field strengths will not improve the sensitivity, as shown by Fig. 3. The lowest trace in Fig. 5 emphasizes that the GRP attenuation is the problem: by simply moving the coil to the damaged side of the GRP, the sensitivity is greatly improved.

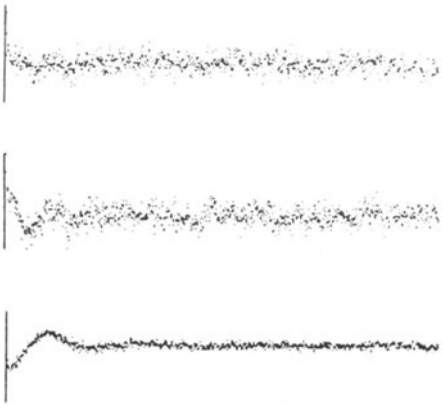

Fig. 5. Test of NMR to detect absorbed water at a damaged site.
Upper trace: an undamaged region for comparison.
Middle trace: damaged region on back side with NMR coil on front side.
Lower trace: Improved sensitivity obtained by moving coil to back (damaged) side.
All are 1000 averages (~5 minutes); gain reduced on lower trace.

CONCLUSIONS

NMR can be used to detect absorbed water at impact damaged sites in GRP. However, with the practical case of a receiving coil on the front side and damage on the inaccessible back side, the spin signal is attenuated through the GRP. Our measurements show a broad maximum in sensitivity as a function of frequency. A simple theory explains this as the competition of two terms: the usual increase in NMR sensitivity with frequency and the increasing GRP attenuation with frequency. The theory fits the data to a remarkable extent, with only one adjustable parameter.

For a GRP sample (0.30 cm thick) tested here, we have detected absorbed water at a damaged site. However, the sensitivity is inadequate for rapid scanning of large surfaces (1 sec for 1 cm^2).

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