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NMR detection of thermal damage in carbon fiber reinforced epoxy resins

Steven K. Brady[a,*], Mark S. Conradi[a], Christopher M. Vaccaro[b]

[a] Department of Physics, Washington University, One Brookings Drive, St. Louis, MO 63130, USA
[b] The Boeing Company, Airport Rd. and McDonnell Blvd., St. Louis, MO 63042, USA

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Abstract

Composite materials of epoxy resins reinforced by carbon fibers are increasingly being used in the construction of aircraft. In these applications, the material may be thermally damaged and weakened by jet blast and accidental fires. The feasibility of using proton NMR relaxation times T_1, $T_{1\rho}$, and T_2 to detect and quantify the thermal damage is investigated. In conventional spectrometers with homogeneous static magnetic fields, $T_{1\rho}$ is readily measured and is found to be well correlated with thermal damage. This suggests that NMR measurements of proton $T_{1\rho}$ may be used for non-destructive evaluation of carbon fiber-epoxy composites. Results from $T_{1\rho}$ measurements in the inhomogeneous static and RF magnetic fields of an NMR-MOUSE are also discussed.

Keywords: Relaxation; Polymer; Nde; $T_{1\rho}$; Epoxy; Thermal damage; Aircraft; Composites; NMR-MOUSE

1. Introduction

Aircraft manufacturers are increasingly using carbon fiber reinforced epoxy resins, or "composites," in the construction of aircraft. Examples include both military fighter jets and commercial airliners. In the course of operations, these materials may become weakened by thermal damage from jet blast and accidental fires. Several properties of polymer and reinforced polymer materials have been studied with NMR [1–3], and in this paper we investigate the use of proton NMR to detect and quantify thermal damage in epoxy composite materials used in typical commercial airliners. To this end, we received several carbon fiber-epoxy samples from Boeing, as well as some epoxy resin samples with no carbon fibers imbedded. Some samples were unchanged from their properly cured state, while others were thermally overexposed to varying levels of heat damage.

In studying the samples, we measured the NMR parameters T_1, $T_{1\rho}$, and T_2 looking for any changes in those parameters correlated with thermal damage. The goal of some previous studies has been to understand the chemistry of the epoxy and related systems. We stress that our goal was to test the suitability of NMR relaxation times as non-destructive measures of thermal damage. No attempt was made to resolve the signals into separate components (e.g., chemical shifts) because this would not be practical in a field implementation.

The material may change due to thermal damage, and the spin–lattice relaxation time T_1 can be sensitive to such changes. In particular, the relaxation rate is given [4] approximately by $T_1^{-1} = J(\omega_0)M_2$, where $J(\omega_0)$ is the spectral density of lattice motions at the Larmor frequency (tens of MHz) and M_2 is the motion-modulated part of the dipolar second moment [4] for a typical hydrogen spin. The chemical and physical changes following thermal damage may alter $J(\omega_0)$, and thereby

* Corresponding author. Fax: +1 314 935 6219.
E-mail address: sbrady@hbar.wustl.edu (S.K. Brady).

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T_1. Alternately, thermal damage may break bonds in the structure creating paramagnetic free radicals, the introduction of which is known [5] to reduce T_1.

The rotating frame spin–lattice relaxation time $T_{1\rho}$ is also sensitive to changes in the material. However, while T_1 probes lattice motions at approximately ω_0 (tens of MHz), $T_{1\rho}$ probes lattice motions near the nutation frequency ω_1 ($\omega_1 = \gamma B_1$, tens of kHz). It has been shown [6,7] that $T_{1\rho}^{-1} \approx J(2\omega_1)M_2$. Indeed, $T_{1\rho}$ measurements are widely used to probe motions at tens of kHz [8].

In a comparatively rigid system such as the epoxies studied here, T_2 is determined by the static proton–proton dipolar interactions, as expressed in the static second moment. Qualitatively, T_2 is inversely dependent on the local density of hydrogen nuclei [9]. Thus we would expect to see very little change in T_2 until significant hydrogen content decrease occurs; this level of damage is expected to be obvious upon visual inspection and is not of interest here.

2. Experimental

We studied three groups of samples: small, carbon fiber-epoxy composite pieces, larger composite pieces, and epoxy resin pieces without carbon fibers. The thermally overexposed, small composite pieces were held at temperature in air for 2 h, while the other pieces were overexposed in air for only 15 min. In every case where a sample was cut to fit into an NMR tube, cutting was done after any heat damage was applied. T_1 and $T_{1\rho}$ measurements were performed in a 1.3 T electromagnet and a 0.47 T permanent magnet, each having a homogeneous static magnetic field. T_2 measurements were made only in the 1.3 T electromagnet. $T_{1\rho}$ measurements were also made in the inhomogeneous static magnetic field of an NMR-MOUSE [10] at a static field strength of 0.37 T. We note that the samples with imbedded carbon fibers have a skin depth at our frequencies of order 0.5–1.0 mm [11], so that the RF field B_1 is inhomogeneous in all cases.

The NMR-MOUSE was part of a Bruker Minispec system, and it came with two stock NMR probes. The conductive carbon fibers in the composite samples coupled inductively with the probes. Eddy currents in the carbon fibers detuned and de-coupled the stock probes well beyond their tuning and coupling adjustment ranges. So, a new probe was constructed for use with the NMR-MOUSE. A "figure-8" coil was held in a groove machined into the Teflon face-plate. The coil was wound from Teflon-insulated, stranded copper wire of 0.4 mm diameter; the coil was free of acoustic coil disease. The figure-8 coil follows the design of Anferova et al. [12], and is illustrated in their Fig. 5, with their probe having two stacked figure-8 coils compared to our single figure-8. The spatial dependence of the transverse RF field components of a figure-8 coil have been described [12]. The new probe tuned and coupled properly, even with carbon fiber-epoxy samples. Electrical losses in the carbon fibers gave the overall resonator a low Q of about 4, compared with a stock probe's Q (with no sample) of about 50. The low Q decreased the signal-to-noise and contributed to large measurement uncertainties of $T_{1\rho}$ with the NMR-MOUSE.

3. Results and discussion

For comparison among samples with different levels of heat damage, $T_{1\rho}$ of the small composite samples and the resin samples was measured in the 1.3 T magnet via a pulsatile spin-lock experiment. In every case, the equilibrium magnetization was tipped into the plane with a 90° pulse, the phase of which was alternated from $+x$ to $-x$, along with the receiver phase. Immediately after the initial 90° pulse was a train of 500, 3.3 μs spin-locking pulses in the y phase. From the end of one spin-locking pulse to the beginning of the next, 6.7 μs of inspection time was allowed to record the magnetization. This time was long enough to allow receiver recovery, but still short enough for an effective pulsatile spin lock. The magnetization was inspected in each window and was always found to decay exponentially with time during the spin lock. A representative data set is shown in Fig. 1.

The $T_{1\rho}$ values of composite and resin samples, all measured at 21 °C, are shown in Fig. 2 as functions of the heat treatment temperature. Calculated from the measured 90° pulse lengths and the spin-lock pulse duty

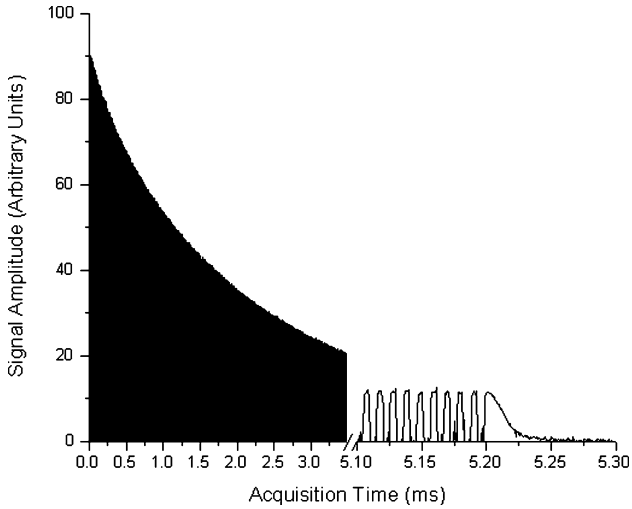

Fig. 1. An example of data from pulsatile spin-lock measurements of $T_{1\rho}$. The magnetization exhibits a single-exponential decay with time. A free induction decay is clearly visible from the magnetization remaining after the final spin locking pulse. Note the break and scale change in the time axis.

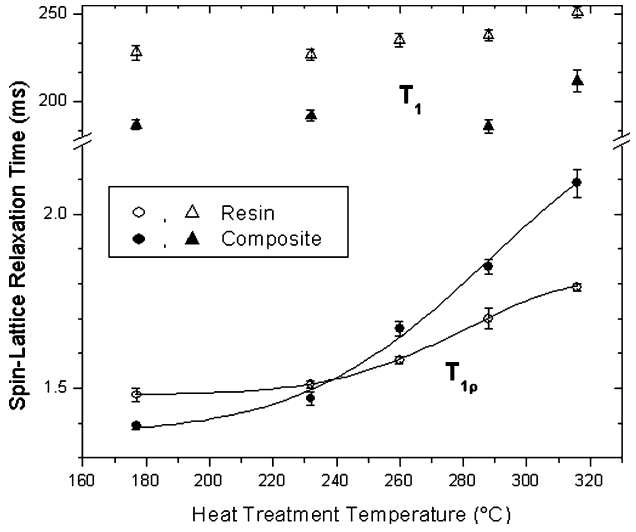

Fig. 2. Spin–lattice relaxation times in the rotating and laboratory frames of composite samples and epoxy resin samples as functions of the temperature of heat treatment. All data were taken at 21 °C. T_1 values appear at the top, $T_{1\rho}$ values are at the bottom; the curves are simply guides to the eye. Note the different scales for $T_{1\rho}$ and T_1. While substantial changes in $T_{1\rho}$ are apparent, T_1 is comparatively insensitive to heat treatment.

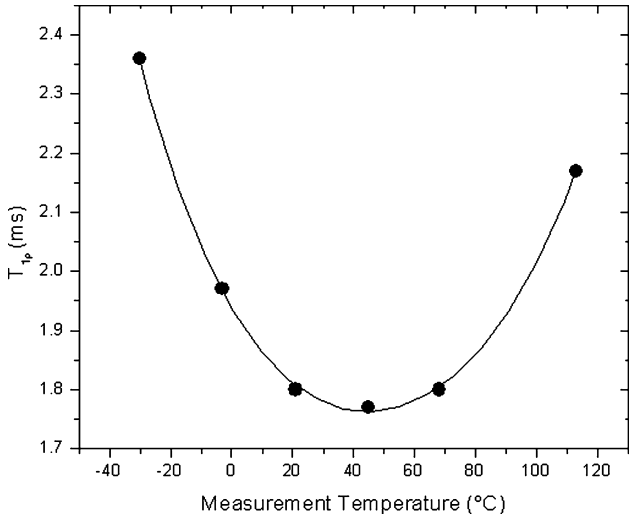

Fig. 3. $T_{1\rho}$ values measured at different temperatures for a small, composite sample that had been previously thermally damaged at 260 °C, showing a minimum near 45 °C. The curve is simply a guide to the eye. The effective spin-locking field strength for these measurements differed slightly from that of the composite $T_{1\rho}$ measurements of Fig. 1.

fraction, both the composite and resin samples had very similar effective spin-locking field strengths of 30 and 32 kHz, respectively. Individual measurements comprised 100 signal averages requiring about 2 min. Each point in Fig. 2 is the average value from at least five measurements, and the associated uncertainty represents plus-or-minus one standard deviation of the individual measurements.

In both the pure resin and composite samples, $T_{1\rho}$ increases essentially monotonically with increasing heat damage. It is also apparent from Fig. 2 that the fractional change of $T_{1\rho}$ is greater in the material with carbon fibers than without; this may be due to the longer time of heat treatment of the composite samples. The $T_{1\rho}$ of the most damaged composite sample is 1.5 times that of the least damaged composite sample, compared with a factor of 1.2 increase over the same range in the pure resin samples. These features indicate that $T_{1\rho}$ could be used for the detection of heat damage in aircraft.

The $T_{1\rho}$ relaxation time as a function of the *measurement* temperature is presented in Fig. 3 for a small composite sample (with previous exposure to 260 °C for 2 h). The comparatively mild heating in the data of Fig. 3 did not cause further thermal damage, as verified by $T_{1\rho}$ measurements at 21 °C following each elevated temperature measurement. A classical minimum of $T_{1\rho}$ is exhibited near 45 °C, consistent with the rate of some lattice motion passing through $2\omega_1$ at that temperature. The minimum is broad, suggesting a wide dispersion of motional rates in this amorphous material. The other possible relaxation mechanism, unpaired electron spins, seems unlikely. First, such materials have small ESR signals, prior to thermal damage [13]. Second, if electron spins were the dominant source of relaxation, one would expect $T_{1\rho}$ to decrease with increasing thermal damage, opposite the observed trend. Third, the observed single-exponential spin-locked magnetization decays with time constants of order 1 ms would require that every ^{1}H nuclear spin be within a spin diffusion distance (estimated at about 1.4 nm) of an electron spin. This case corresponds to an improbably high density of free radicals. In short, it appears that lattice motions modulating dipolar interactions are responsible for the $T_{1\rho}$ minimum of Fig. 3; it is very likely that changes in these motions produce the variations of $T_{1\rho}$ with thermal damage.

Since it is impractical to place entire aircraft or large parts of aircraft into homogeneous magnetic fields of high strength, we attempted to measure $T_{1\rho}$ of the larger composite samples with an NMR-MOUSE. The inhomogeneous static magnetic field and resulting large bandwidth of the NMR-MOUSE yield signal-to-noise ratios much lower than those typically found with laboratory magnets. Additionally, $T_{1\rho}$ measurements are known [14] to suffer from even lower signal-to-noise than simple echo measurements with an NMR-MOUSE. Compared to insulating materials, the electrical conductivity of the composite samples reduces the coil Q, leading to smaller signal-to-noise. As a result, $T_{1\rho}$ values measured with the NMR-MOUSE had too much uncertainty (typically ±30% after 1.6 h of signal averaging at each of five durations τ of conventional spin-locking pulses) to reliably differentiate damaged from undamaged samples.

We note here an interesting eddy current effect observed while configuring the NMR-MOUSE to operate with samples of varying levels of thermal damage. With the NMR-MOUSE probe tuned to resonate at 15.85 ± 0.05 MHz while in contact with the undamaged sample, it was found to resonate at 15.36 ± 0.17 MHz while in contact with any of the thermally damaged samples. This frequency shift of the probe tuning was confirmed on multiple samples with and without thermal damage, multiple times. The result is consistent with heat damage in the composite material breaking links within and/or between carbon fibers, causing the material to be less conductive at the RF. The reduced eddy currents in the sample increase the overall inductance of the sample/probe system, driving the probe's resonant frequency lower.

Fig. 2 shows laboratory-frame T_1 values for the larger composite samples as well as those of the epoxy resin samples, all measured in the 0.47 T magnet (20 MHz). Measurements of T_1 were performed by the inversion-recovery method. The small measurement uncertainties shown (<2%) indicate good reproducibility of the measured values. The data exhibit excellent fits to single-exponential recovery curves. Pieces were cut from three corners of the undamaged composite sample, and all three were found to have the same T_1 to within measurement uncertainty, indicating that T_1 is constant throughout the sample. The T_1 values measured in the 1.3 T magnet (53 MHz, not shown) for the small composite samples are all ≈40 ms longer than those in Fig. 2, and follow a similar trend. The small size of the fractional changes in T_1 and their non-monotonic trend with increasing heat damage indicate that T_1 is not useful as a signature of heat damage.

At each temperature, the samples without carbon fibers have longer T_1 values than similarly treated samples with carbon fibers. The carbon fibers may have significant hydrogen content, so that we record relaxation rates averaged over the two populations. However, the single-exponential behavior of both T_1 and $T_{1\rho}$ recoveries in the composite materials argues against this. Also, the epoxy resin for the two kinds of samples may come from different batches. Finally, we cannot rule out that the lattice motions in the resin are perturbed by the presence of the fibers.

As discussed in Section 1, the spin–spin relaxation time T_2 was not found to be a good measure of heat damage. T_2 of the small composite samples measured by integration of their free induction decays was about 10 μs, regardless of heat damage. We also used a solid echo sequence ($90°_x$–τ–$90°_y$-echo) with five values of τ ranged from 10 to 50 μs. The peak echo amplitude decayed exponentially with 2τ with a time constant of 30 μs. Small variations in this value were uncorrelated with the extent of heat damage and are believed to be measurement noise.

4. Conclusions

The rotating frame spin–lattice relaxation time, $T_{1\rho}$, was found to be readily measurable in a homogeneous magnetic field, and monotonically correlated with heat damage in carbon fiber-epoxy and epoxy resin samples. This suggests that NMR measurements of proton $T_{1\rho}$ may be used for non-destructive evaluation of such materials. Measurements of $T_{1\rho}$ in composite materials were also performed with an NMR-MOUSE, where large measurement uncertainties due to small signal-to-noise ratios made distinction among samples of varying heat damage impossible. Changes in RF eddy currents were apparent between undamaged and damaged composites, presumably due to fibers breaking or losing electrical contact upon thermal exposure. Measurements of T_1 and T_2 of composite samples showed that these relaxation times are not correlated with thermal damage.

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