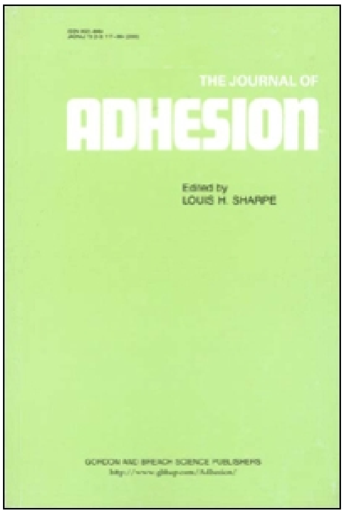

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On the Analysis of Composite Processing Using Magnetic Resonance Imaging (MRI)

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NOTE

On the Analysis of Composite Processing Using Magnetic Resonance Imaging (MRI)

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KEY WORDS Magnetic Resonance Imaging, solvent ingress, relaxation times, variable temperature.

The utility of magnetic resonance imaging (MRI) as a means of non-destructively investigating the distribution of internal defects has recently been demonstrated by imaging the distribution of water-filled voids within pultruded rods.[1] Manufactured from glass-filled nylon and polyester, the samples were soaked in a water bath at 80°C for 25 weeks allowing water to ingress. The same work, however, also highlights one of the major problems found in materials MRI, namely the quantification of results. As pointed out by the authors, the particular experimental conditions used to obtain the images discriminate in favour of mobile water molecules having long spin-spin relaxation times (T_2), *i.e.* those in voids and defects. This is because the experimental echo times (T_e) used were limited by hardware considerations to longer than 40 ms. In the imaging experiment, the total signal observed is proportional to the echo amplitude, $S(t)$, and

$$S(t) \propto \exp(-T_e/T_2).$$

Water ingressed into the bulk polymer is strongly hydrogen bonded, leading to a dramatic shortening of T_2.[2] Table I shows the T_2 values observed from water ingressed into a block of unfilled nylon 6.6 at various temperatures. These were obtained with a Bruker MSL-200 spectrometer equipped with mini-imaging accessories, using a standard CPMG sequence.[3] It can be seen that use of an echo time of 47 ms will leave hydrogen-bonded molecules invisible to the imaging experiment.

Accurate quantitative measurement of both the free and hydrogen-bonded water is vital in order to correlate imaging data with weight uptake measurements and to deduce mechanisms of ingress into such composite materials. For example,

TABLE I
Spin–spin relaxation times of water ingressed into a solid block of nylon 6.6 at various temperatures

Temperature/°C	27	37	47	57	67	77	87	97
T_2/ms	0.9	1.7	3.0	4.9	6.4	7.8	9.3	10.1

ingress may occur *via* diffusion of water through the bulk polymer, rather than along defect lines or the polymer/fibre interface. If a bulk diffusion mechanism is responsible for filling internal defects and voids, then differences observed between samples manufactured from various polymer types may be due only to the different diffusion rates through the bulk polymer: defects may still be there, but have not yet been reached by the solvent front.

Recent developments in materials MRI have enabled echo times as short as 1 ms to be employed, allowing the imaging of short T_2 species in 2- or 3-dimensions.[4] Furthermore, variable-temperature operation allows the lengthening of T_2 values (as in Table I) by increasing the degree of molecular mobility present, increasing the sensitivity of the imaging experiment. It is, therefore, possible to obtain images of the hydrogen-bonded water distribution within nylon, and other polymer samples. Figure 1 shows typical images obtained from blocks of nylon 6.6 generated as a function of time exposed to water at 100°C. These 128 × 128 pixel images were obtained with an echo time of 2.9 ms, a recycle delay of 1 s and maximum gradients of 10 gauss/cm. The experiments were run at 67°C to increase the signal-to-noise ratio, with each image requiring

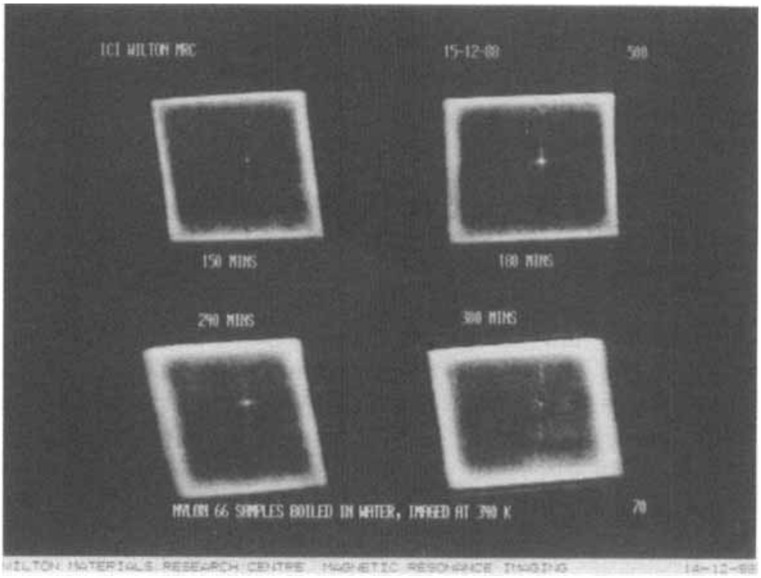

FIGURE 1 Typical images obtained at 67°C from blocks of nylon 6.6 exposed to boiling water for 150, 180, 240 and 300 minutes.

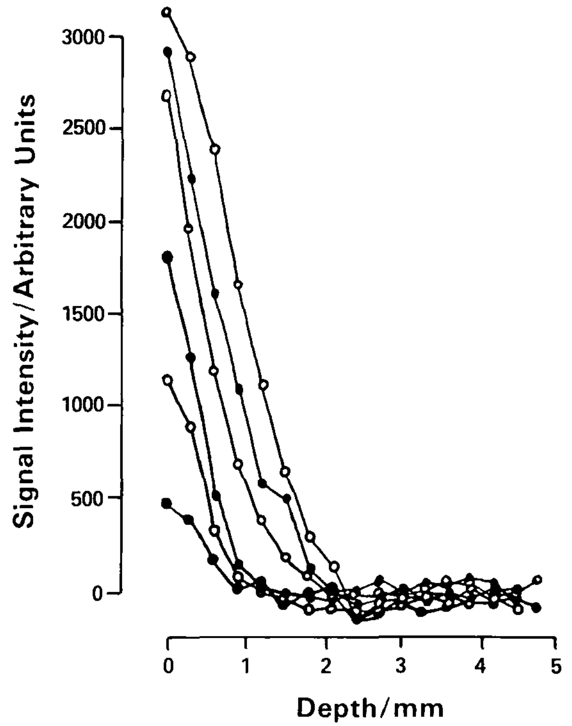

FIGURE 2 Profiles obtained from a series of images of water ingressed into a series of blocks of nylon 6.6. These samples were exposed to water at 100°C for 30, 60, 120, 240, 360 and 480 minutes.

just over 2 minutes to record. Figure 1 also illustrates the signal-to-noise level obtainable with short echo time imaging. Figure 2 shows the water ingress profiles obtained by subsequent image analysis. It can be seen that the water has ingressed to a depth of 2 mm after boiling for 8 hours.

In a situation where both free and hydrogen-bonded water is present, as in defective nylon composites, and both species are imaged, image intensities cannot be directly compared to give quantitative measurement of relative proportions; the effect of the differing T_2 values must be considered. This may be done by recording images as a function of echo time, extrapolating the observed intensities back to zero echo time to give quantitative values. This also gives the ability to distinguish between different physical types of water environment present, either bound or free. Figure 3 illustrates that excellent correlation can be found between weight uptake and true image intensity for the unfilled nylon 6.6 sample. For the case illustrated here, the sample weight, W, and the observed total signal intensity, I, have the following linear relationship:

$$S(\mathrm{mg}) = 0.0170(\pm 0.0015)I + 517(\pm 2).$$

It is apparent that care should be taken when attempting to draw quantitative conclusions from magnetic resonance images, especially when long experimental

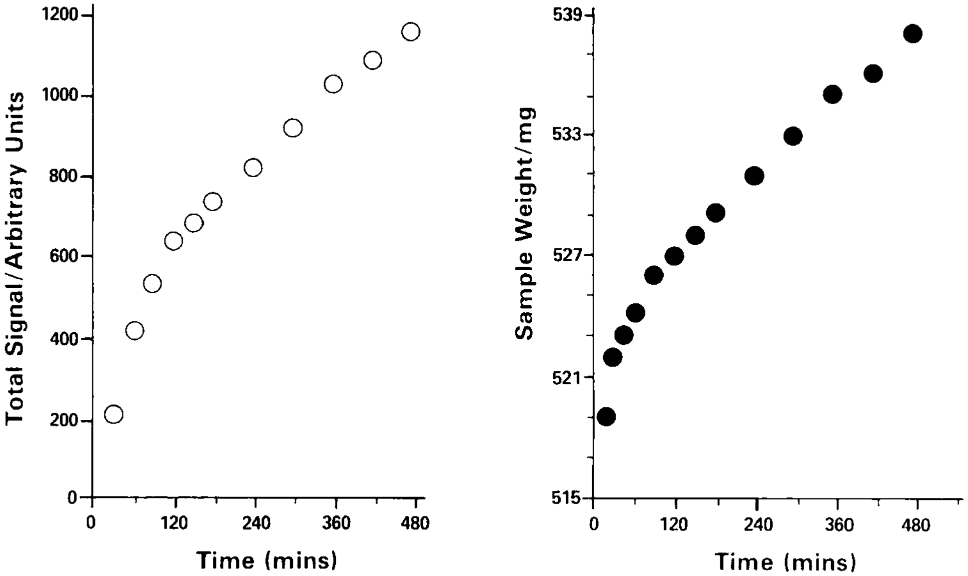

FIGURE 3 (a) Plot of the total image intensity (arbitrary units) *versus* boiling time and (b) plot of the sample weight *versus* boiling time. An excellent correlation is found between the total image intensity and weight uptake.

echo times are used. Techniques are available to overcome the problem of obtaining images from short-T_2 water in nylon, giving the complete picture of water ingress, preferably as a function of time to allow ingress mechanisms to be inferred. MRI can thus be used to map the position, environment and concentration of water in nylon samples specifically, and solvents in polymers and composites generally.

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