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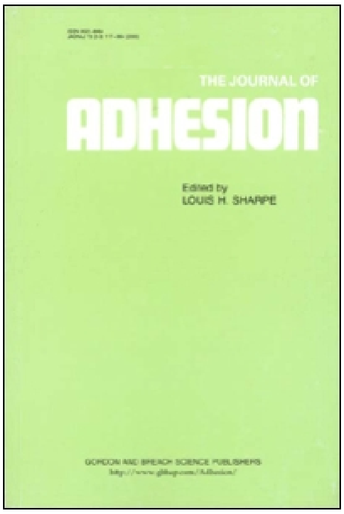

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NMR Imaging of the Interfaces of Epoxy Adhesive Joints

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NMR Imaging of the Interfaces of Epoxy Adhesive Joints

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Nuclear magnetic resonance imaging (NMRI) is used to study epoxy adhesive bonded structures at a proton resonance frequency of 300 MHz. Oligomeric and almost pure monomeric diglycidyl ethers of bisphenol-A, triethylenetetramine and xylene representing typical raw materials of epoxy adhesives are imaged at 25 and 50°C with varying repetition times to optimize measurement conditions for the adhesives. NMR images with good signal-to-noise ratios from the liquid epoxy adhesives are obtained at 50°C using the shortest possible echo times and a repetition time of 1 s. Chemical shift images of the glue-lines are presented and their possible uses in adhesive studies are discussed. The use of NMRI to detect heterogenous resin/resin and resin/curing agent mixtures is demonstrated. A non-invasive glue-line analysis is made of an aluminium/epoxy/aluminium sample with a model debonding by recording cross-sectional NMR images and a proton shadowgram.

KEY WORDS NMR imaging; epoxy adhesives; nondestructive evaluation; heterogenous mixtures; voids; chemical shift images.

INTRODUCTION

The major applications of nuclear magnetic resonance imaging (NMRI) are in medical science, where it is used to produce anatomical images from humans and animals.[1-3] Recent improvements in field strengths, resolution and sensitivity have made this technique useful to chemists, too. Applications of NMRI have been demonstrated in material sciences,[4-8] applied analytical chemistry[9,10] and forestry.[11-14]

Recently, we found that NMRI can provide abundant information about adhesives and adhesive-bonded structures.[15,16] Voids and flaws can be detected during the curing process and joints with thicknesses less than 100 μm can be analysed by this technique.[15] By measuring the relaxation times T_1 and T_2 even more physical and chemical information from the samples can be obtained. It is possible to calculate a proton spin density image and to use this information to optimize pulse sequence parameters, *e.g.* to find inhomogeneieties in glue-lines.[16]

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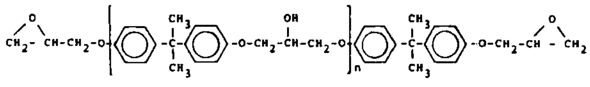
This paper deals with the use of NMRI to study structures bonded with epoxy adhesives. NMR images of typical raw materials of the epoxy adhesives are measured to find optimum conditions for NMRI. The use of NMRI to detect heterogeneous resin/resin and resin/curing agent mixtures is also demonstrated. Finally, a non-invasive glue-line analysis is made to an aluminium/epoxy/aluminium sample with a known debonding by recording cross-sectional NMR images and a proton shadowgram.

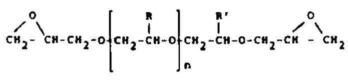
EXPERIMENTAL

Raw materials

Three commercial epoxy resins were studied: Epon 828 (1), a typical general purpose epoxy resin; D.E.R. 332 (2) almost pure monomeric diglycidyl either of bisphenol-A; and D.E.R. 736 (3) a flexible, aliphatic epoxy resin. Typical properties of these resins are listed in Table I. D.E.H. 24 (Dow Chemicals, U.S.A.), triethylenetetramine (4), was used as a curing agent and xylene (5) was chosen as an example of non-reactive diluents. The epoxy adhesive (6) used for gluing the wood blocks and the aluminium plates was formulated as follows: the resin part contained 90% of 2 and 10% of 3; the hardner was 4; and the mixing ratio 100: 13.8. The structures of the materials are given below:



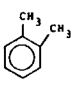
1 n > 0
2 n = 0



3 n = 2 - 7

$H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$

4



5

Samples

The wood samples were made as follows. Typical furniture-grade Finnish pine was lathed to a diameter of 35 mm, sawed to a length of 70 mm and spilt into two

TABLE I
Typical properties of the studied epoxy resins

	1	2	3
Epoxy resin	Epon 828	D.E.R. 332	D.E.R. 736
Supplier	Shell Chemical Co.	Dow Chemicals U.S.A.	
Viscosity, 25°C, Pas	11–15	4–6	0.03–0.06
Epoxy equivalent weight	185–192	172–176	175–205

equal parts by Huonekalutehdas E. Rintamaki Oy (Finland). A trough (50 mm long, 11 mm wide and 3 mm deep) was cut into one of the wood pieces. The images were collected within 60 minutes after the application of the epoxy adhesive 6. Glue line thicknesses of less than 100 μm (Figure 2a) and 150–500 μm (Figure 2b) were measured with a micrometer and the joint thickness was varied by putting tape between the wood samples.

The aluminium sample consisted of two aluminium plates (20 × 20 × 2.0 mm) and the epoxy adhesive 6. A piece of plastic (0.8 mm thick) was used to control the joint thickness.

NMRI measurements

The NMR images were obtained on a Bruker MSL 300 FT-NMR spectrometer, operating at a proton frequency of 300 MHz. The spectrometer was equipped with a MINI-imaging accessory and with a probe for a sample size of 60 mm diameter. NMR images were collected on an ASPECT 3000 computer and transferred to a MICROVAX II *via* ETHERNET for further data processing.

The experiments were typical Carr-Purcell[17,18] spin-echo pulse sequences with selective 90-degree and non-selective 180-degree pulses with CYCLOPS phasing. Typical duration times for the 90-degree pulse were 2 ms and for the non-selective 180-degree pulse 400 ms. The gradient strengths were 2–3 G/cm. Four scans were accumulated to produce images with 256 × 256 pixels from a slice approximately one millimeter thick. Repetition times were 0.5, 1 or 4 s and echo time 12 ms. A repetition time of 1 s corresponds to a total acculation time of approximately 17 minutes. Images were acquired either at 25°C or at 50°C by using an air heater connected to the probe. The wood samples and the aluminium sample were acquired with a spin echo time of 12 ms and a repetition time of 0.5 s at 25°C. The aluminium sample was situated in the xz-plane of the magnetic field, where z is defined as the direction of the magnetic field. Non-selective pulses were used to obtain a shadow through the adhesive plane. The images of the homogenous and heterogenous mixtures were obtained with a repetition time of 1 s.

RESULTS AND DISCUSSION

Practical proton NMRI of adhesives requires that the resins, hardener and or solvents of the adhesive under investigation (i) contain hydrogen atoms; (ii) have proton T_1 relaxation times of not more than a few seconds; and (iii) have proton T_2 relaxation times longer than a few milliseconds.

Epoxy resins contain sufficient hydrogen atoms to produce NMR images. The T_1 relaxation times for the typical uncured bisphenol-A type epoxy resins are less than 1 s over the temperature range 20–100°C.[19] The T_2 relaxation times for the low viscosity epoxy resins are typically much greater than 10 ms, but for the high-viscosity, high-molecular-weight epoxy resins the T_2-values are too short for practical imagining at room temperature. Fortunately, the T_2-relaxation times increase with temperature and in most cases they can be expected to be longer than 10 ms at temperatures of 50–100°C.[19]

Signal-to-noise (S/N) ratios for the raw materials

To optimize measurement conditions a composite sample consisting of five glass vials was built and filled with the epoxy resins 1, 2 and 3, polyamine curing agent 4 and xylene 5. Cross-sectional NMR images from this sample were collected, keeping the spin echo time at 12 ms and varying the temperature and the repetition time of the measurements.

At 25°C the epoxy resin 1 showed no signal with the repetition times of 0.5 s and 1.0 s. The S/N ratios for the resin 2 and xylene were also low (Table II), while the aliphatic resin 3 and the curing agent 4 showed sharp images. The very poor improvement in S/N ratios of the resins 1 and 2 obtained by increasing the repetition time from 0.5 s to 1.0 s indicates that the limiting relaxation process is the spin-spin relaxation rather than the spin-lattice relaxation. For samples 3, 4 and 5, however, the increase in repetition times allows more complete spin-lattice relaxation and, thus, higher signal intensities are observed.

At 50°C all the materials show good S/N ratios with a repetition time of 1.0 s. The epoxy resins 1 and 2, which undoubtedly have the shortest T_2-relaxation times, lose a portion of their signal intensities with an echo time of 12 ms. On the other hand xylene, which is known to have long proton T_1 relaxation time (purified para-xylene: methyl protons 11.9 s and aromatic protons 22.2 s at

TABLE II
The S/N-ratios of the studied raw materials of the epoxy adhesives with varying temperature and repetition times

T (°C)	TR (s)[b]	TE (ms)[c]	S/N-ratios[a]				
			1	2	3	4	5
25	0.5	12	1	3	36	49	4
	1.0	12	1	4	50	66	8
50	0.5	12	17	23	38	38	4
	1.0	12	27	32	50	54	7
	4.0	12	27	32	56	68	16

[a] S/N-ratio: The average intensity of 400 pixels from the signal part (S) divided by the average intensity of 400 pixels from the noise part (N) in the image.

[b] Repetition time.

[c] Spin echo time.

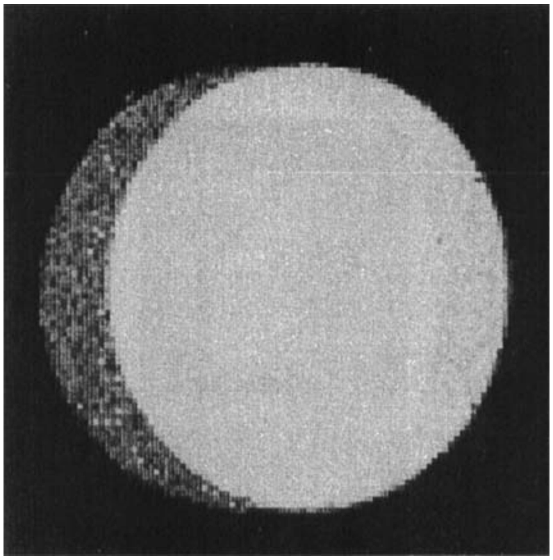


FIGURE 1 A cross-sectional chemical shift image of xylene in a vial. Separate images are due to the aromatic and the methyl protons of xylene and they are separated 4.8 ppm from each other.

33°C),[20] could be imaged with the full signal intensity only by using long repetition time. However, as depicted in Figure 1, the NMR image of xylene with a S/N ratio of 7 can be computer enhanced to yield a quality image using noise filtering techniques.

Most adhesive formulations contain high viscosity resins that are mixed with low viscosity resins, diluents or hardeners and can be imaged without problems. As an example, epoxy resin 1, which did not show signals at 25°C, was formulated with the flexible epoxy resin 3. Epoxy resin 1 and 3 mixtures of 9:1 and 4:1 measured at 25°C with a repetition time of 0.5 s and the echo time of 12 ms resulted in images with S/N ratios of 9 and 16, respectively.

Chemical shift images

The NMR image of xylene in a vial (Figure 1) shows a unique feature of NMRI. Instead of displaying just a single image, the sample is represented by two overlapping images. These separate images arise from the aromatic and the methyl protons of xylene, which resonate 4.8 ppm from each other. The intensity ratio of the methyl protons to the aromatic protons is 2.1 in the image, differing from the natural ratio of 1.5 in the molecule. The main reason for this difference can be found in the different T_1 relaxation times of the methyl and the aromatic protons (see S/N ratios for the raw materials), which leads to the more effective relaxation of the methyl protons during the repetition of the pulses.

The chemical shift images appear along the read gradient direction (x-axis). Therefore, the positioning of the sample relative to the gradients is reflected in

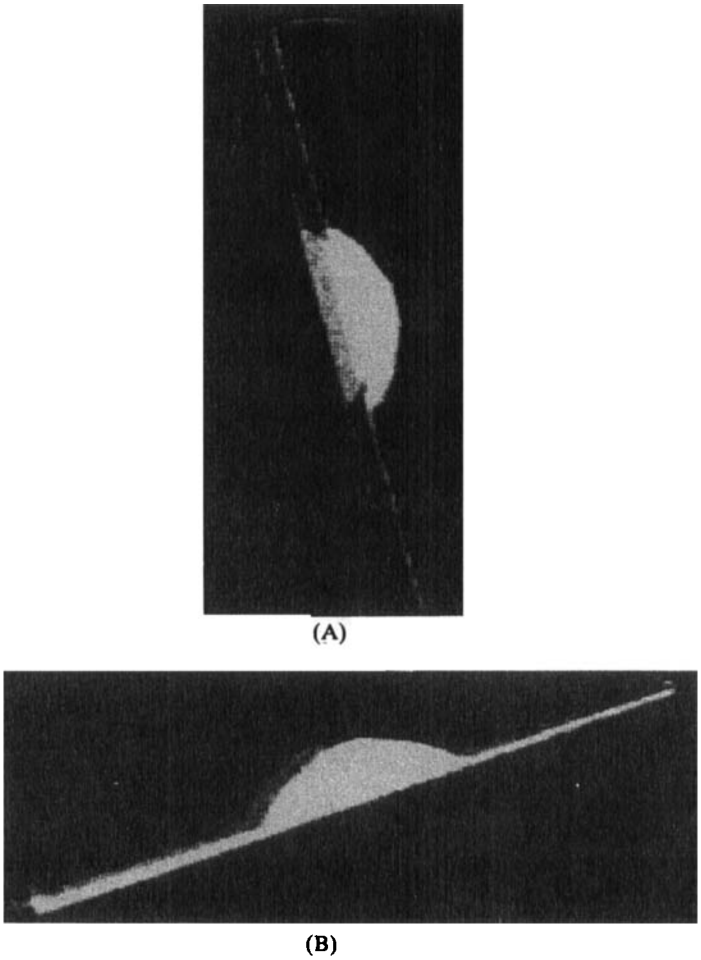


FIGURE 2 A cross-sectional image of the sample consisting of two wood blocks bonded together with the epoxy adhesive 6. A half-circle trough in the middle of the joint is 3 mm deep and 11 mm wide. Glue-line thickness is less than 100 μm in (A) and 150–500 μm in (B). Chemical shift ghost images appear along the read gradient (x-axis) and, thus, the positioning of the sample affects the image.

the image. The images shown in Figure 2 are obtained from the wood samples bonded together with the epoxy adhesive 6. The bonded samples have 3 mm deep and 11 mm wide, half-circle troughs in the middle of the glue-lines. In Figure 2a the glue-line of less than 100 μm is perpendicular to the read gradient. Two separate images of the glue-line and the trough are visible: one is due to the aromatic protons of the main component 2 and the other is due to the methyl protons of the resin 2 with minor contributions of the protons of the curing agent 4 and the resin 3. The resonances of the other protons are less intense and, therefore, they do not affect significantly the image with a S/N ratio and a resolution encountered here.

The image in Figure 2b depicts the same type of sample, but now with an angle of approximately 30 degrees relative to the x-axis. The glue-line thickness is 500 μm in the left part and 150 μm in the right part of the sample.

There are methods to suppress the chemical shift effects in the NMR images.[21] These methods are developed mainly for medical imaging purposes and they can be used to obtain better contrast and resolution of the tissues. Presently we are working with different techniques to eliminate chemical shift artifacts, in typical adhesive samples. However, since the chemical shift images are also a source of additional chemical information, they can probably be used to determine, *e.g.*, the resin/resin and the resin/curing agent ratios in two-component adhesives.

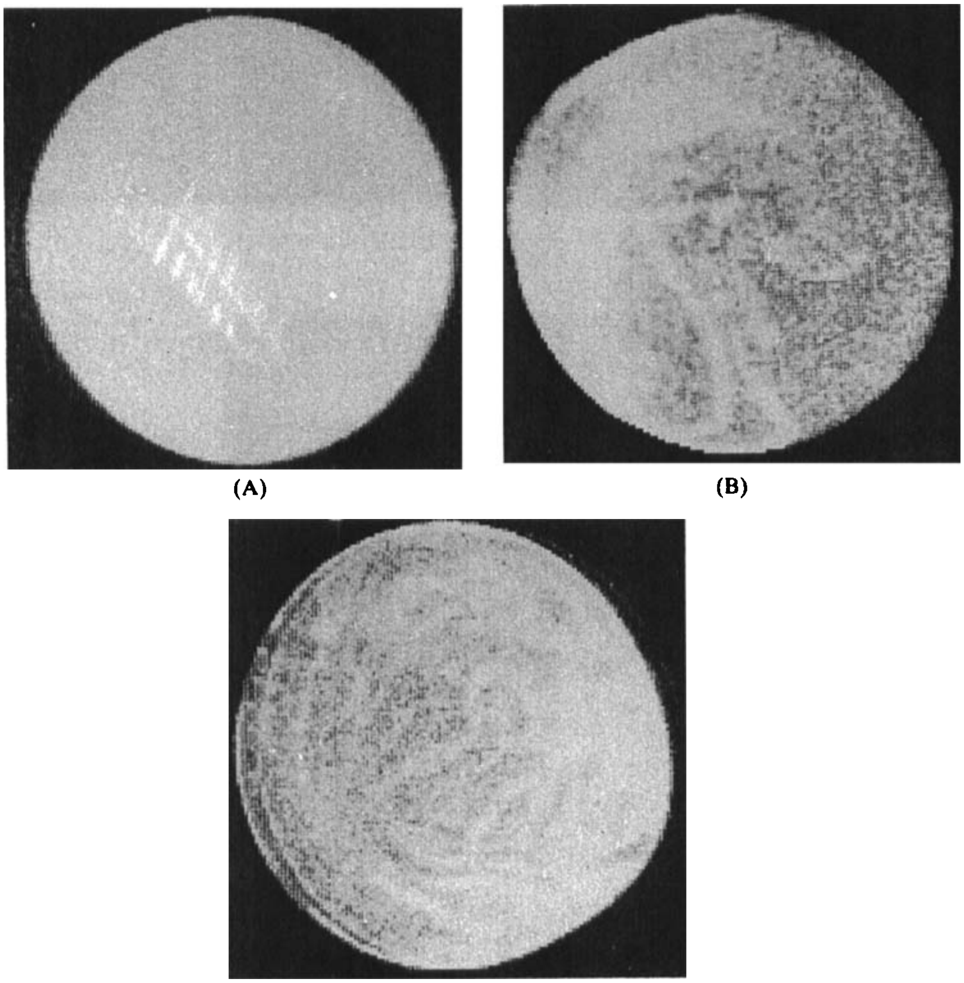


FIGURE 3 (A) A homogeneous mixture of the epoxy resins 2 and 3 (5:1). (B) A heterogeneous mixture of the epoxy resins 2 and 3 (5:1). The flexible epoxy resin 3 shows higher signal intensities. (C) A heterogeneous mixture of the epoxy resin 2 and the polyamine curing agent 4 (100:13). The curing agent 4 is delineated with higher signal intensities.

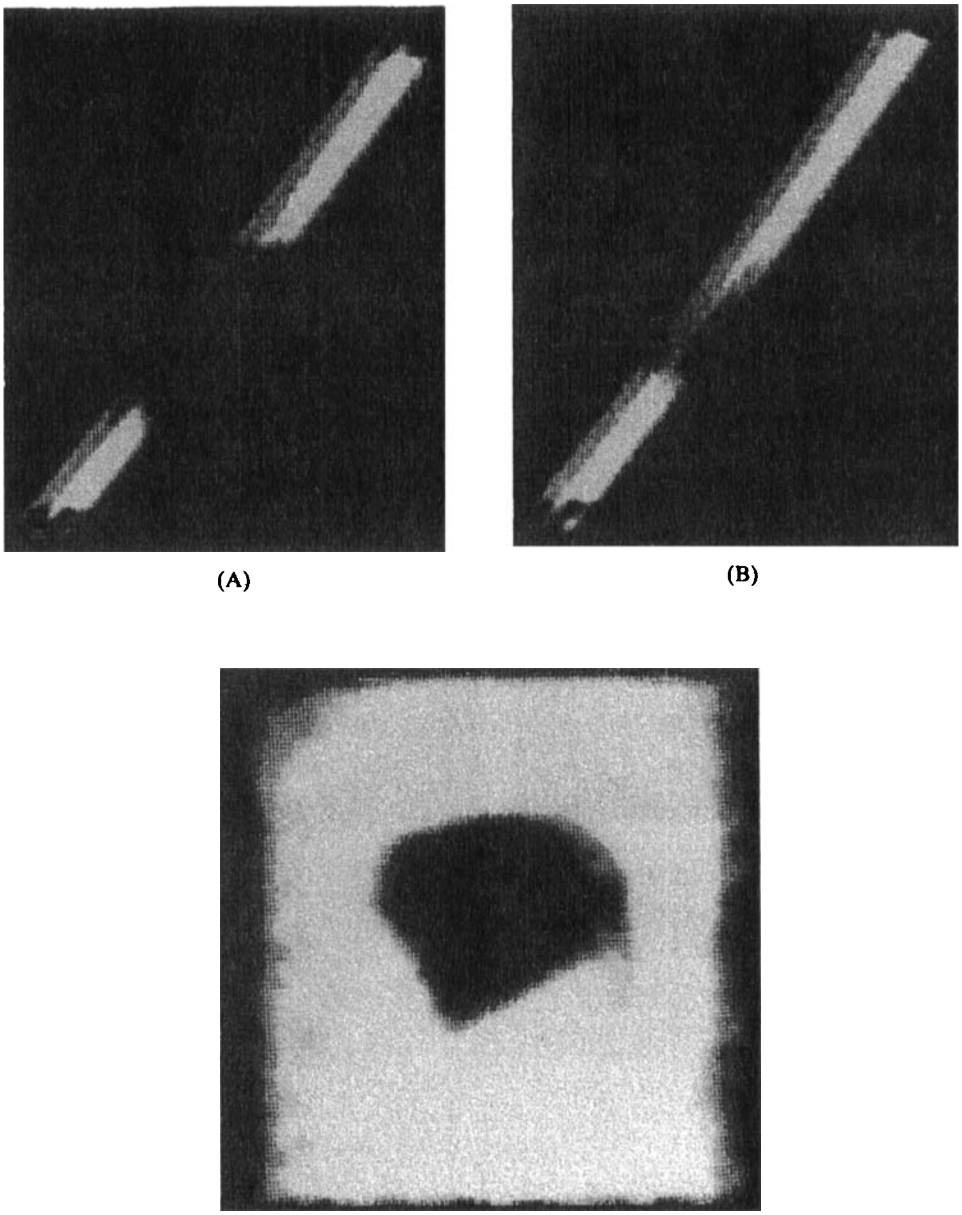


FIGURE 4 A complete glue-line analysis of the aluminium/epoxy/aluminium sample. (A) and (B) depict cross-sectional NMR images from the sample showing a 800 μm thick glue-line with an area 10 mm wide (maximum) without any adhesive. (C) Proton shadowgram that is acquired through the adhesive layer gives the actual shape and size of the void. (A), (B) and (C) confirm the homogeneity of the adhesive.

Homogeneous and heterogeneous mixtures

The epoxy resins 2 and 3 were mixed (5:1) very carefully in a plastic vial to produce a mixture, the image of which is shown in Figure 3a. The uniform intensity of the signals throughout the sample confirms the homogeneity of the mixture. The image acquired with less stirring of the same resins is depicted in Figure 3b. The flexible epoxy resin 3, with more favorable relaxation properties is delineated with much higher signal intensity than resin 2. Similarly, a heterogeneous mixture of the epoxy resin 2 and the curing agent 4 can be visualized (Figure 3c).

The possibility of detecting inhomogeneities in adhesives is a unique benefit of the NMRI method. The high resolution makes it possible to see even minor heterogeneities in the actual thin glue-lines.[16] These characteristics of NMRI could be used to analyze the quality of the adhesive and of the glue-line, at the same time, by acquiring images from the bonded sample prior to curing. Since very often epoxy adhesives, for example, are cured at temperatures well above 100°C, the detection of inhomogeneities or voids before curing could save the materials and allow reapplication of the adhesive.

Glue-line analysis

Figure 4 depicts a complete glue-line analysis of a sample made of two aluminium plates and the epoxy adhesive 6. The cross-sectional NMR images (Figures 4a and 4b) show an adhesive layer 800 μm thick, with an area 10 mm wide (maximum) in the middle of the joint without any adhesive. Although these images give a lot of information about the size of the void, it is possible to get the actual geometry of the void by acquiring a cross-sectional NMR image in the plane of the adhesive layer or by producing a shadowgram through the adhesive. Figure 4c depicts the proton shadowgram of the bonded sample, from which the shape and the area of the void can be obtained. The images in Figure 4a, b and c confirm the homogeneity of the adhesive.

CONCLUSIONS

The results show that NMRI can be used to study uncured or partially cured epoxy adhesive joints noninvasively. Information regarding the adhesive composition and the glue-line quality can be obtained in the early curing stages of the epoxy adhesives. Most likely, the majority of the liquid epoxy adhesives are suitable for NMRI studies, although the high viscosity adhesives produce images with good S/N ratios only at elevated temperatures.

The very broad linewidths observed in the resonances of rigid polymers and resins make it impossible to image totally-cured adhesives with the present state of this instrumentation. However, very recently, interest has developed in new techniques for solid state NMR imaging, as well.[22–24]

Acknowledgements

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