

Detection and Characterization Of CFC, HCFC AND HFC Gases in Foamed Insulation by High Field NMR Imaging

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1. Introduction

In recent years, there has been considerable concern regarding the environmental impact of chlorofluorocarbons (CFC's). CFC's have been widely used as blowing agents for both cellular polyurethane and polystyrene insulation applications. [1] In many non-critical applications, CFC's are being replaced by non-fluorochemical blowing agents, but in insulation based applications where the final performance of the product is dependent on the superior insulating characteristics of a closed cell network which retains the fluorochemical blowing agent, the use of similar blowing agents will probably need to continue. Hydrochlorofluorocarbons (HCFC's) have been identified as intermediate replacements for the CFC's, but hydrofluorocarbons (HFC's) are likely to become the blowing agents of choice in insulation based products. The eventual environmental fate of the blowing agent combined with the dependency of product performance on the fluorocarbon distribution within the cellular structure requires an accurate knowledge of its spatial distribution over a period of time in order to optimize performance. Currently, there is no reliable and readily accessible technique with which the

distribution of these gases can be detected or monitored.

Microscopic imaging has recently emerged as an excellent technique by which the distribution of mobile fluids in polymeric materials can be monitored. [2] - [8] In principal, it should be possible to perform similar experiments on samples which contain gaseous materials, the limiting factor being the signal to noise. In the present study, we demonstrate that ^{19}F NMR microscopic imaging is ideally suited for measuring the changes that occur in the spatial distribution as a function of time and yields quantitatively reliable information which will be critical to the fabrication of optimized insulating materials.

2. Experimental

Aged foam samples were provided by Dupont Canada and contained either a single fluorinated gas or a mixture of gases. NMR measurements were made on a Bruker MSL 400 spectrometer equipped with a microimaging system. All experiments were performed using the microimaging probe supplied except that the probehead was modified by replacing the vertical saddle proton rf coil by a 16 mm horizontal solenoid coil that was tuned to fluorine (376.13 MHz). The nonselective 90° and 180° rf pulses were 12.5 μs and 25 μs respectively. Quadrature phase cycling was used in all spectroscopic measurements.

One dimensional ^1H NMR spectra were obtained by the standard one pulse method and by the Carr-Purcell spin-echo experiment. The Carr-Purcell NMR sequence was used to determine the T_2 spin-spin relaxation times.[9] The inversion-recovery pulse sequence was used to determine the T_1 spin-lattice times. [10] 1D quantitative spectroscopic data was obtained by using a short 1 μs ring-down delay.

The spin-echo imaging sequence [11] was used for all samples. For samples which contained a single blowing agent, non-selective 90° and 180° rf pulses were used. This reduced the echo time to 2 ms which was advantageous, since spin-spin relaxation time constant, T_2 for the fluorinated gases absorbed into the foam matrix was less than 5 ms. Images were composed of 128 phase encoding steps. The number of transients per experiment was typically 160. The in-plane resolution was typically 270 μm using a frequency encode gradient on the order of 7 G/cm. Due to the short T_1 relaxation time of the fluorinated gases, the recycle delay was 100 ms which allowed the acquisition of an image in under 30 minutes. Concentration profiles were obtained using a frequency selective gradient in a time period on the order of 20 seconds.

Samples which contained a mixture of gases were examined by a spin-echo imaging sequence in which the initial excitation pulse was frequency selective (Gaussian shaped, 300 μs duration). The echo time for this experiment was typically 3 ms.

3. Results and Discussion

To compare the aging characteristics, rectangular samples 1 cm x 1 cm x 2 cm in size were cut from foam boards which had been aged for several months. A variety of fluorinated gases were examined for both polyurethane and polystyrene (high and low density) foams. To devise the most appropriate imaging protocol, it is important to know the relaxation parameters of the ^{19}F nuclei. T_1 was typically 10 on the order of 10 ms while T_2 was on the order of 4 ms. (Table 1). Thus, ^{19}F imaging will be very efficient in that the experiment can be repeated very quickly due to the short T_1 values. The data must also be acquired with a short time between excitation and data acquisition due to the short T_2 value. Using a spin-echo sequence comprised of hard 90° and 180° pulses, the echo time was reduced to 2 ms.

Figure 1 shows the ^{19}F image of a sample of polystyrene foam of rectangular cross-section which has been cut from the outside edge of a sheet of foamed insulation. The sheet has been aged at room temperature for 14 months. The concentration of gas

($\text{CH}_3\text{CF}_2\text{Cl}$) decreases from the outside edge inwards. The quantitative distribution of cell gas is also obtained from an examination of the image projection (Figure 1B). This shows the actual distribution as a function of distance. Although there is only minute quantity of fluorinated gas present in the sample, an image is easily obtained at high magnetic fields due to the high sensitivity of the ^{19}F nucleus and its short spin-lattice relaxation time (10 ms).

Figure 1. Concentration of $\text{CH}_3\text{CF}_2\text{Cl}$ in a sample of insulating foam which has been aged 14 months.

(a) Projection. (b) Spin echo image.

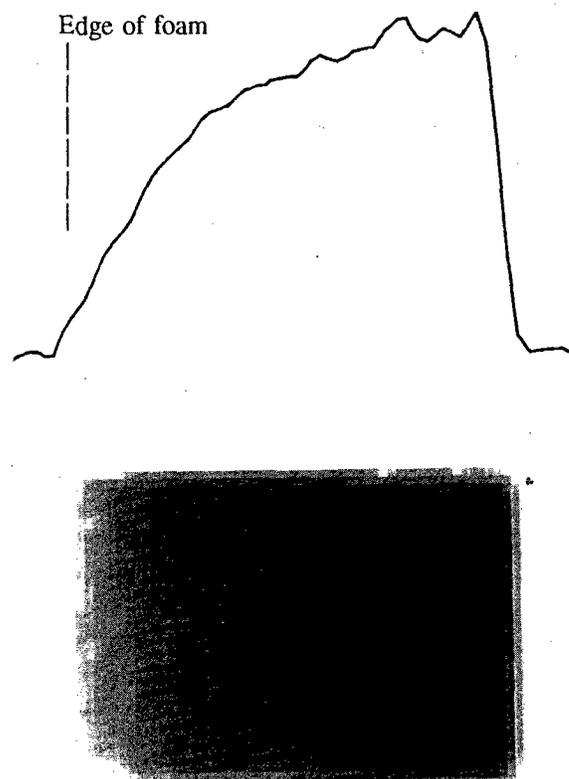


Table 1: ^{19}F NMR Relaxation Behaviour of CFC, HFC and HCFC gases in Insulating Foams

| Foam | Cell Gas | T_1 | T_2 | δ |
|--------------|-----------------------------------|-------|-------|----------|
| Polyurethane | CFCl_3 | 3.6 | 5.4 | -5.0 |
| Polyurethane | CF_3CHCl_2 | 13.3 | 3.7 | -85.9 |
| Polystyrene | CF_2Cl_2 | 4.4 | 4.5 | -13.5 |
| Polystyrene | $\text{CH}_3\text{CF}_2\text{Cl}$ | 4.9 | 4.2 | -53.1 |
| Polystyrene | $\text{CF}_3\text{CH}_2\text{F}$ | 7.4 | 3.0 | -85.0 |
| | | | | -246.4 |

T_1 and T_2 are in ms.

Polystyrene samples which had been formed using a mixture of blowing agents (CF_2Cl_2 and $\text{CH}_3\text{CF}_2\text{Cl}$) was also examined. The distribution of the two gases was compared in samples which had been aged two months and 14 months (Figure 2). The concentration and distribution of CF_2Cl_2 gas in the two samples is similar. However, the concentration of $\text{CH}_3\text{CF}_2\text{Cl}$ as a function of distance from the foam edge has substantially decreased. This implies that the loss of CF_2Cl_2 is somehow slowed by the presence of the $\text{CH}_3\text{CF}_2\text{Cl}$. These observations have been verified by one-dimensional spectroscopic measurements in which a calibrated standard has been used.

Figure 2. (a) Concentration of CF_2Cl_2 gas (i) after 2 months and (ii) after 14 months

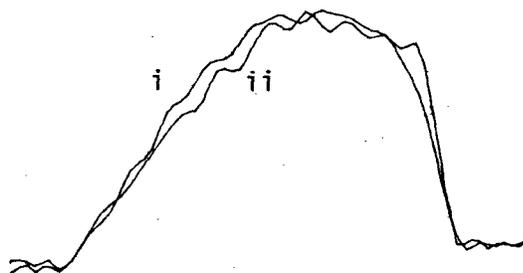
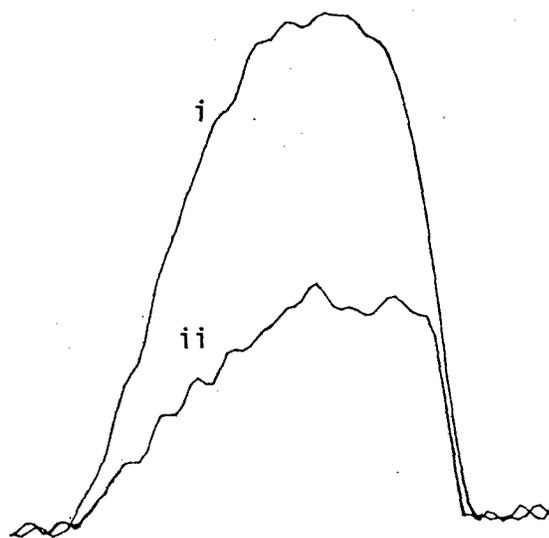


Figure 2. (b) Concentration of $\text{CH}_3\text{CF}_2\text{Cl}$ gas (i) after 2 months and (ii) after 14 months



In a separate study, a cylindrical piece of insulating foam which had been formed using $\text{CH}_3\text{CF}_2\text{Cl}$ was then treated to $\text{CF}_3\text{CH}_2\text{F}$ in an oven at 80°C . Chemical shift selective imaging was performed on the sample and revealed that the post-treatment gas has penetrated the outside edge of the foam and has formed a ring, approximately 2-3 mm in thickness. (Figure 3a) The initial blowing gas, $\text{CH}_3\text{CF}_2\text{Cl}$ has an almost uniform distribution in the centre of the foam, which decreases smoothly to the outside edge and includes the volume occupied by the $\text{CF}_3\text{CH}_2\text{F}$ gas (Figure 3b). The loss of $\text{CH}_3\text{CF}_2\text{Cl}$ is substantially less in these samples as compared with samples that had been placed in the oven (in air). Thus, in the presence of a fluorinated gas, the blowing agent is lost at a much slower rate.

Figure 3. (a) Concentration of $\text{CH}_3\text{CF}_2\text{Cl}$ gas.

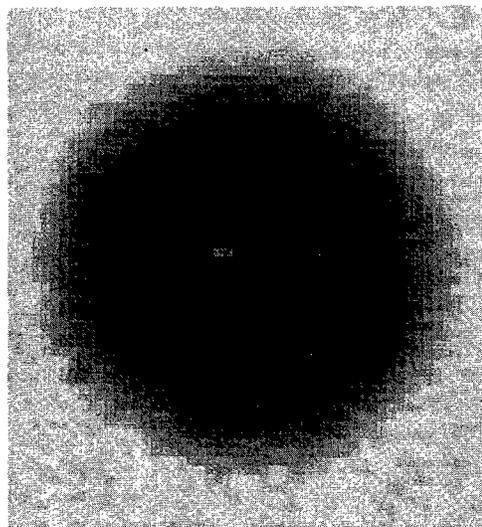
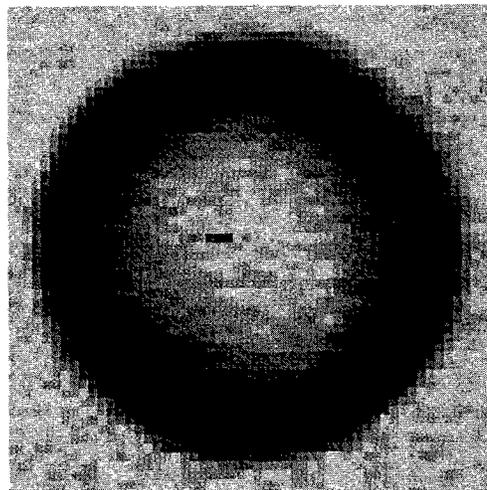


Figure 3. (b) Concentration of $\text{CF}_3\text{CH}_2\text{F}$ gas.



4. Conclusions

These data are typical of those we have obtained on a variety of fluorocarbon gas/foam matrices and clearly indicate that ^{19}F NMR microscopic imaging is ideally suited for measuring the distribution of fluorinated hydrocarbons in polystyrene and polyurethane foams. Presently, a protocol is under development which will ensure that quantitatively reliable information is being obtained. This will allow us to monitor the changes that occur in the spatial distribution as a function of time (accelerated aging tests) or as a function of blowing agent. This information can then be used to optimize the fabrication of these insulating materials.

5. References

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