Published as: Gill, B.D.; Manley-Harris, M.; Thomson, R.A. (2003) Use of natural abundance 15N DEPT NMR to investigate curing of urea–formaldehyde resin in the presence of wood fibers. *Magnetic Resonance in Chemistry* 41, 622–625. DOI: 10.1002/mrc.1219

Use of natural abundance ^{15}N DEPT NMR to investigate curing of urea-formaldehyde resin in the presence of wood fibers

Brendon D. Gill, Merilyn Manley-Harris and Ralph A. Thomson

Chemistry Department, University of Waikato, Private Bag 3105, Hamilton, New Zealand

Abstract

Natural abundance ^{15}N NMR using a DEPT pulse sequence was employed to follow the curing of urea-formaldehyde resin in the presence of wood fiber, fiber extracts and acid or base. The advantages of ^{15}N NMR, large range chemical shifts, simplification of spectra and lack of interference by additives, can be exploited. The disadvantages of low sensitivity and long relaxation delays are offset by using a cross-polarization technique.

Keywords

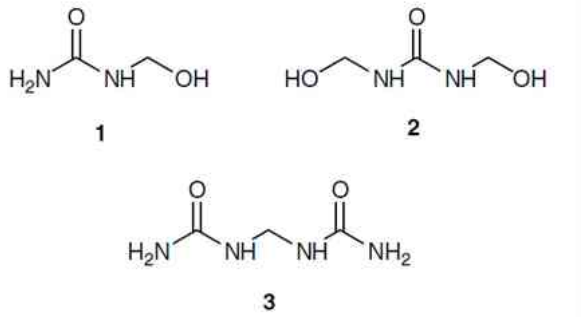
NMR; ^{15}N DEPT; natural abundance; urea–formaldehyde resin; rate of polymerization

Introduction

Medium density fiberboard (MDF) is a dry-formed panel product comprised of lignocellulosic fibers combined with a synthetic resin, usually urea–formaldehyde (UF) resin. During the manufacturing process, fiber, which has been pre-mixed with resin, is formed into a mat and compressed by a heated plate, which serves to cure the resin.

UF resin is a mixture of oligomers of urea and formaldehyde dispersed in a water medium. It is made by reacting 45–54% (w/v) aqueous formaldehyde with urea in varying mole ratios. Initially the reaction is carried out under alkaline conditions to form mono-, di- and trimethylolureas, which are the monomers for polymerization. A subsequent condensation step, under acidic conditions, forms a mixture of oligomers and polymers. Condensation is arrested at the appropriate viscosity by adjustment to alkaline pH. For environmental reasons, excess urea is frequently added after the synthesis reaction to consume any unreacted formaldehyde. This results in the formation of low molecular weight methylol ureas such as N-methylolurea (1) and N,N'-dimethylolurea (2).

Published as: Gill, B.D.; Manley-Harris, M.; Thomson, R.A. (2003) Use of natural abundance 15N DEPT NMR to investigate curing of urea–formaldehyde resin in the presence of wood fibers. *Magnetic Resonance in Chemistry* 41, 622–625. DOI: 10.1002/mrc.1219



Natural abundance ^{15}N NMR has been used to study UF resins[1] and it was found that it was possible to distinguish nitrogens in differing chemical environments within the resin; changes were observed upon curing with reduction of peaks associated with low molecular weight moieties such as **1** and **2** and of the peak for urea. In this study, 20000 scans were used to acquire spectra.

In the solid state, cross-polarisation magic angle spinning (CP/MAS) techniques with ^{15}N NMR spectroscopy have been used to study the structure of cured resin.[2,3] Because of its low natural abundance and small magnetogyric ratio, ^{15}N is not suitable in most cases for CP/MAS studies unless the sample has been enriched. A cured UF resin made with ^{15}N-enriched urea showed[2] peaks in two partially overlapping regions and some assignments were made. It was felt that the ^{15}N experiment revealed less information than the corresponding ^{13}C experiment. High-quality natural abundance ^{15}N NMR spectra were obtained by CP/MAS experiments on UF resins[3] using a large-volume (2.5 cm^3) rotor in a wide-bore spectrometer.

^{15}N NMR suffers from other problems besides low sensitivity: the negative magnetogyric ratio means that the nuclear Overhauser enhancement operates in the negative direction and, if conditions are appropriate, may result in complete cancellation of the peak. Additionally ^{15}N has very long relaxation times, which may exceed 10–100 s,[4] which results in very long experimental times because of the long relaxation delays required.

On the other hand, a number of advantages accrue to the use of 15N NMR spectroscopy in the study of curing of synthetic resins. In polymers, a range of chemical shifts spanning 400 ppm are observed,[5] hence there is a smaller likelihood of overlapping resonances compared with ^{13}C spectra. Spectra are also simplified as there are fewer distinct types of nitrogen moieties, making identification and quantitation easier. Furthermore, there is less likelihood of interference by material added to modify curing, e.g. wood fiber.

As part of a larger investigation of the effect of wood fiber and fiber-derived components upon the curing of UF resin, it was decided to investigate the possibility of using natural abundance ^{15}N NMR to study the curing of UF resin in the presence of fiber and of other additives.

Published as: Gill, B.D.; Manley-Harris, M.; Thomson, R.A. (2003) Use of natural abundance 15N DEPT NMR to investigate curing of urea–formaldehyde resin in the presence of wood fibers. *Magnetic Resonance in Chemistry* 41, 622–625. DOI: 10.1002/mrc.1219

Experimental

Materials

UF resin was a gift from Orica, New Zealand (1.00:1 formaldehyde–urea, viscosity 2.2 P at 25 °C; 65% solids; water tolerance 23 mL to 10 g at 25 °C; pH 9.0). Upon receipt, the resin was separated into smaller volume containers and frozen at -20 °C until use. Wood fiber (Pinus radiata) was supplied by Forest Research, Rotorua, New Zealand. Fiber (70 g) was extracted with dichloromethane (3 L) in a Soxhlet extractor over 24 h. After removal of the solvent under reduced pressure, the extract (2.1 g, 3.0%) was kept frozen until use. The extracted fibers were dried at room temperature and kept frozen until use.

Model compounds

N-Methylolurea **1**, N,N′-dimethylolurea **2** and methylenediurea **3** were synthesized according to the methods described by Ludlam.[6] Structures were confirmed by ^{1}H NMR and by electrospray mass spectrometry. ^{15}N DEPT NMR was carried out on saturated solutions of the model compounds in D_2O; primary amines appeared at 74.9 ppm in urea, 74.7 ppm in **1** and 74.5 ppm in **3**; secondary amines, the signals for which were inverted with respect to the primary amines, appeared at 93.6 ppm in **3** and 100.0 ppm in **1** and **2**.

^{15}N NMR spectroscopy

Spectra were recorded using a Bruker AC-300 FT NMR spectrometer fitted with a 10 mm multinuclear probe (30.398 MHz for ^{15}N) operating at 55 °C. Spectra were recorded using the DEPT pulse sequence[7] with composite pulse decoupling, over a spectral width of 3125 Hz (102 ppm), using 32K data points giving a digital resolution of 0.38 Hz per point, with a ^{15}N (90°) pulse of 15 μs and a ^{1}H decoupler pulse of 18 μs. Spectra were referenced externally to liquid NH_3 at 25 °C;[8] this has the advantage of giving positive chemical shifts. Deuterium lock was obtained by using D_2O in a coaxial tube. For an acceptable signal-to-noise ratio, 300 scans were accumulated with a repetition time of 6 s for each scan. This corresponded to 30 min per spectrum. To follow curing, 32 spectra were acquired over the course of 16 h. The primary amine peaks in each spectrum (73.5–76.5 ppm), which are attributable in part to chain ends but which mainly originate from urea and from **1** and **3**, were integrated as one unit and relative to the first spectrum, which was assigned the value of 1.00.

Preparation of samples for NMR

Resin (3 mL) was taken from the freezer and poured into a 10 mm NMR tube. A thermometer was immersed in the resin. The tube was warmed in a water-bath. Once the appropriate temperature (55 °C) had been achieved, the thermometer was exchanged for the coaxial lock tube

and the sample placed into the spectrometer. In samples to which wood fiber, extracts, acid or base were added, the respective additive was stirred with the cold resin (10 mL) for 1 min and then the mixture (3 mL) was transferred into the NMR tube and warmed as above. Five replicates of each experiment were performed.

Results and Discussion

Model compounds 1–3 gave clear spectra using a ^{15}Nproton detected single quantum coherence (DEPT) pulse sequence, with a total time for acquisition of 30 min (Figure. 1). Both single and multiple quantum coherence pulse sequences are commonly used in conjunction with ^{15}N enrichment[9] and a ^{15}N DEPT sequence has been used in dynamic experiments to monitor the fate of $^{15}NH_3$ from enriched cisplatin upon reaction with reduced glutathione.[10,11] However, the results obtained with the model compounds indicated that it would be possible to monitor the course of curing of the UF resin using natural abundance ^{15}N DEPT NMR.

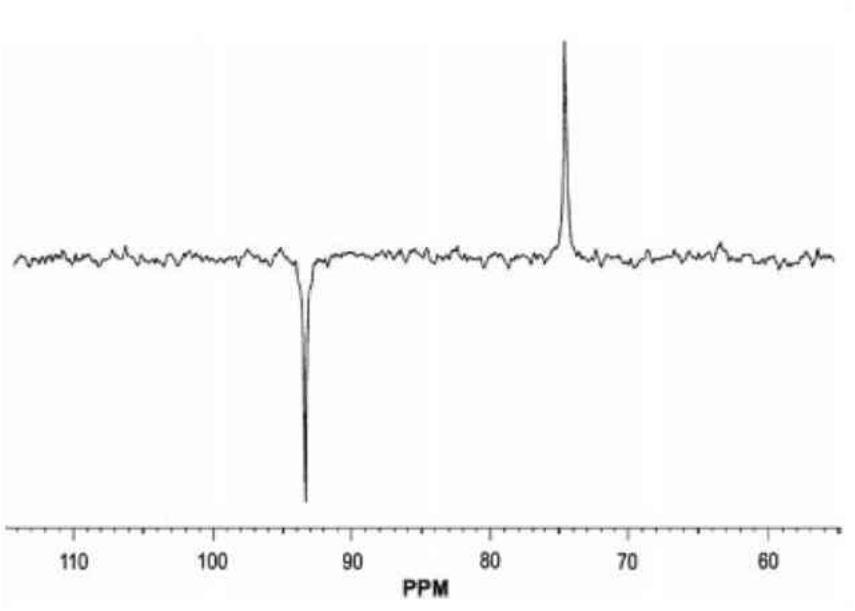


Figure. 1 ^{15}N DEPT natural abundance spectrum of methylenediurea **3** (179 scans, line broadening 2.0)

For quantitative work, an internal standard is desirable. For this ^{15}N DEPT experiment, the internal standard should have at least one proton attached to nitrogen, preferably with a single ^{15}N environment to give a single sharp line. The signal of the internal standard should occur in a region somewhat displaced from the resonances of interest but not too far, and the ^{1}J (^{15}N,^{1}H) coupling constant should be sufficiently similar to that of the compounds present in the resin (85–95 Hz).[12]

The compound in question must also be readily soluble in an aprotic deuterated solvent in the coaxial lock tube.

Aniline, which had a shift of 54 ppm (neat) and which has a coupling constant of 78.5 Hz,[13] was chosen as a suitable internal standard. However, when a ^{15}N DEPT experiment was run using freshly distilled aniline in DMSO-d6, no signal was obtained despite optimization of the experimental conditions for aniline. To minimize aniline–aniline intermolecular H-bonding effects, which might interfere with the DEPT experiment, the aniline was successively diluted with DMSO-d6 until a signal was obtained at 60 ppm (1:17 dilution). Unfortunately, this yielded a peak only 10% of the height of the NH_2 urea peak when used in conjunction with the resin. Using a Schlenk line, a sealed coaxial tube was prepared containing ^{15}N-enriched aniline in DMSO-d6 at the appropriate dilution. This gave a clear single aniline peak of the appropriate height. However, over the course of 16 h, the aniline signal disappeared. Changing the solvent to chloroform-d1 resulted in the same effect.

When it became apparent that the use of an internal standard was not without difficulties, a different approach was sought. The primary amine peaks are attributable principally to urea and to low molecular weight oligomers, **1** and **3**, which are in solution in the resin. This assumption is borne out by the sharpness of the peaks obtained in this liquid sample type of experiment. More rapidly relaxing, partially solid, polymeric material would give broad peaks that would merge with the background. Additionally, the contribution from a polymer to the primary amine peaks will decrease relative to nitrogen signals in other environments as molecular weight increases. Figure 2, which shows a stacked series of plots taken every 4 h up to 16 h, shows that there is a gradual diminution in height of the primary amine peaks but no broadening occurs. Hence it is possible to observe the

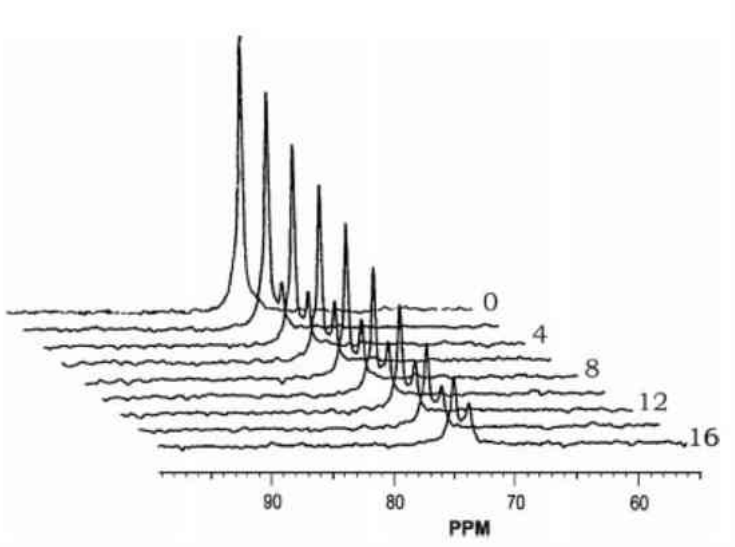


Figure. 2 Intensity decay of primary amine peak with time (0–16 h) during the course of curing of UF resin.

disappearance of urea and low molecular weight oligomers without interference by solid, polymeric material. It was assumed that the signal obtained at time zero represented all of the urea and low molecular weight oligomers, **1** and **3**, present at that time and therefore it was possible to measure a fractional decrease by integrating the peaks obtained at different times relative to that obtained at time zero.

To monitor the course of a reaction, 32 spectra were acquired successively over 16 h and integration of the primary amine peaks gave the fraction remaining at any given time. In unmodified UF resin 60% of these amine groups had been reacted after 16 h (Figure. 3). The shape of the curve obtained indicates that polymerization was not complete at this point. When 3% (w/v) of wood fiber was added to the UF resin, there was an acceleration of the reaction and at 16 h just over 70% of the amine groups had been consumed (Figure 3), although, once again, it appeared that the reaction was not complete.

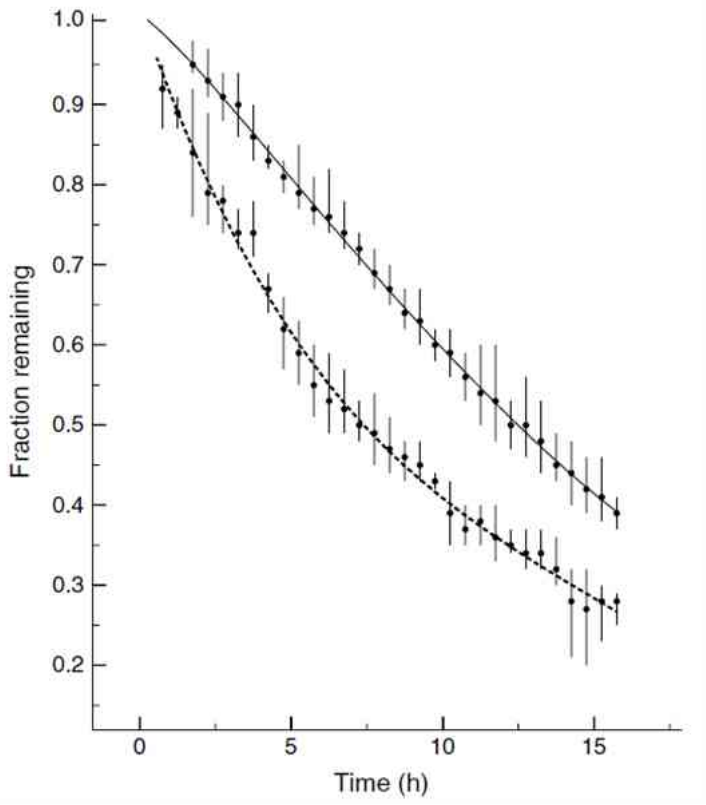


Figure. 3 Fraction of primary amine groups remaining during the course of curing of UF resin alone (solid line) and UF resin with 3% wood fiber added (dashed line). Error bars show the range of values obtained for five replicates.

The rate acceleration is probably due to acid catalysis by the wood fiber. Addition of wood fiber causes a drop in pH and it was possible to emulate the curve that was obtained with resin plus fiber

by using resin alone and adjusting the pH with acetic acid. Similarly, readjustment of the pH with sodium hydroxide, after addition of the wood fiber, served to cancel the acceleration. Fiber which had been previously extracted with dichloromethane did not cause a rate acceleration but addition of 1.0% (w/v) of the dichloromethane extracts did. However, addition of the extracts caused a lowering of pH and once again the curve obtained could be emulated by adjustment of the pH of the resin with acetic acid. The increase in viscosity and the effective dilution of the signals due to the resin place a limit on how much solid material can be added to the resin and 3% (w/v) represents the maximum amount used in these experiments.

Conclusion

The results obtained show that it is possible to use the ^{15}N DEPT sequence in a dynamic experiment to follow the curing of a polymer that contains nitrogen functionalities without recourse to enrichment.

Acknowledgement

B.D.G. was supported by a grant from Forest Research, Rotorua, New Zealand.

References

1. Ebdon JR, Heaton PE, Huckerby TN, O'Rourke WTS, Parkin *J. Polymer* 1984; 25: 821.
2. Myers GE. *Macromolecules* 1985; 18: 1482.
3. Chuang IS, Maciel GE. *Polymer* 1994; 35: 1621.
4. Brevard MR, Granger P. *Handbook of High Resolution Multinuclear NMR*. Wiley: New York, 1981.
5. Levy GC, Lichter RL. *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy*. Wiley: New York, 1979.
6. Ludlam PR. *Analyst* (London) 1973; 98: 107.
7. Doddrell DM, Pegg DT, Bendall MR. *J. Magn. Reson.* 1982; 48: 323.
8. Srinivasan PR, Lichter RL. *J. Magn. Reson.* 1977; 28: 227.
9. Tate S, Masui Y, Inagaki F. *J. Magn. Reson.* 1991; 94: 625.
10. Berners-Price SJ, Kuchel PW. *J. Inorg. Biochem.* 1990; 38: 305.
11. Berners-Price SJ, Kuchel PW. *J. Inorg. Biochem*. 1990; 38: 327.
12. Mason J. In *Multinuclear NMR*, Mason J (ed). Plenum Press: New York, 1987; 335.
13. Randall WW, Ellner JJ, Zuckerman JJ. *J. Am. Chem. Soc.* 1966; 88: 622.