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IDENTIFICATION OF HARDENERS IN SOLID EPOXY RESINS BY HIGH-RESOLUTION ^{13}C-NMR

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Abstract—CPMAS ^{13}C-NMR spectra at 75 MHz with spinning side band suppression are presented for a series of epoxy resins cured with a variety of commercially important hardeners. The hardeners can be readily identified from the spectra; the high-field is important for distinguishing between related amine hardeners.

INTRODUCTION

Epoxy resins are used in such diverse applications as adhesives, laminating resins, castings, coatings, encapsulants, flooring etc. The analysis of the cured resins, especially the identification of its components, has great importance when defects or even complete failures occur in the finished products, and for quality assurance especially in structural applications such as in the aerospace industry and in the solving of forensic problems.

Several hardeners (curing agents) are used to cure the base epoxy resins, of which the most widely used is the diglycidyl ether of bisphenol A (DGEBA) and its higher homologues. The final properties of the cured resin depend to a great extent on the type and quantity of curing agent used [1]. Analysis of the uncured resin for production monitoring is performed mainly by chromatographic methods. The literature on the chromatography of uncured epoxy resins is covered in a recent review [2]. The identification of cured epoxy resins was undertaken by thermal degradation followed by a separation method and in some cases by an absolute identification method. Pyrolysis–gas chromatography (Py–GC) [3–5] and pyrolysis combined with both GC and TLC [5] were used. In all these cases, the epoxy base resin–DGEBA could be identified but almost no information could be obtained on the hardeners used. Thermal degradation in vacuum of an epoxy resin cured with 4,4′-diamino diphenyl methane (DDM), cold trapping of the ensuing degradation products followed by GC revealed compounds that could be related to the DDM curing agent [7]. A method combining thermal degradation with TLC termed "thermofractography" was also used to analyse cured epoxy resins [8]. The parent resin–DGEBA, as well as the curing agents DDM and hexahydrophthalic anhydride (HHPA), could be identified. When the resin was cured with triethylene tetramine (TETA), the hardener could not be detected at all [8]. By combining pyrolysis with i.r.-analysis, boron trifluoride and cycloborate ester (boroxine) hardeners could be differentiated in cured epoxy resins [9]. Pyrolysis–mass spectrometry (Py–MS) gave a good mass spectrum of DGEBA when a cured epoxy resin was analysed by this technique but information on the curing agents used was unspecific [10]. Most of the abovementioned methods readily identify the base epoxy resin but give only limited information on the curing agent so that there is a need for a better method for the complete identification of the cured epoxy resins.

In recent years the techniques for recording high-resolution NMR spectra of solids have been developed and have made important contributions to the analysis of plastics [11]. The promise of the technique was shown in 1979 by Garroway *et al.* [12] who presented the 15 MHz ^{13}C CP/MAS NMR spectra of epoxides cured with four common hardeners. We report here on the 75 MHz ^{13}C-NMR of epoxides cured with a wider range of hardeners to investigate how far the spectra can be used to differentiate between the main classes (aromatic/aliphatic acid anhydrides and amines) as well as to identify the specific hardener in each class.

We had available for study samples of Epon 828 (DGEBA) (shell) cured with the hardeners and conditions indicated in Table 1 and the samples represent the epoxide materials most commonly encountered commerically.

The experiment most frequently used to give high-resolution ^{13}C-NMR spectra of organic solids [11] has several components: (a) magic angle spinning (MAS), a high speed rotation of the sample [4–5 KHz) at an angle of 54.7° to the magnetic field (b) high-power proton decoupling (DD) of the ^{1}H–^{13}C dipolar interaction (c) cross-polarization (CP) of the ^{1}H-magnetization of the ^{13}C-nuclei via the dipolar ^{1}H–^{13}C interaction (d) spinning sideband suppression techniques such as a TOSS [13]. The resulting spectra depend on the details of how the experiments are executed and each involves several variable parameters. The MAS and DD components seem essential for the production of high resolution spectra, but, as the setting of magic angle and optimum decoupling can be determined by calibration, it is only the spinning rate that is variable and the effect on the intensity and position of the sidebands is readily understood. The various sideband suppression techniques give rise to some intensity distortions and may be inappropriate for quantitative applications but

Table 1. Hardening agents and cure conditions

Sample		Hardener	Quantity (phr)	Cure
1	HMDA	1,6-Hexamethylene diamine	15	3 hr, 150°C
2	THMD	*N*,*N*,*N*′-Trimethyl-1,6-hexamethylene diamine	25	3 hr, 150°C
3	TETA	Triethylene tetramine	10	2 hr, 150°C
4	MPDA	Meta phenylene diamine	15	1 hr, 120°C; 3 hr, 150°C
5	DDM	4,4′-Diamino diphenyl methane	30	1 hr, 120°C; 2 hr, 150°C
6	DDS	4,4′-Diamino diphenyl sulphone	30	2 hr, 140°C; 4 hr, 180°C
7*	PTA	Phthalic anhydride	75	1 hr, 90°C; 2 hr, 150°C; 16 hr, 180°C
8*	HHA	Hexahydro phthalic anhydride	77	1 hr, 120°C; 3 hr, 180°C
9*	MNA	Methyl nadic anhydride	84	1 hr, 120°C; 7 hr, 180°C
10*	CEA	Chlorendic anhydride	110	1 hr, 100°C; 3 hr, 180°C; 1 hr, 200°C

*1 phr *N*,*N*-benzyl dimethyl amine added.

greatly simplify higher-frequency spectra such as the 75 MHz ^{13}C-NMR spectra of this study. It is the use of CP and the parameters employed that are the likely source of variations in spectra since the cross-polarization can discriminate against the more mobile portions of the polymer molecule but may be important for detection of signals from the more rigid portions. Some preliminary experiments were performed to investigate some of the components of the experiment but it was concluded that, for the materials, the MAS/DD/CP–TOSS combination was optimum. Without TOSS the spectra were excessively complex and in spectra accumulated without CP the signals arising from the hardener moieties were less distinct, perhaps, because the crosslink regions are the more rigid parts of the structure. However, satisfactory MAS/DD spectra were obtained without excessively increased accumulations suggesting that there is substantial mobility in much of the lattice.

EXPERIMENTAL

The spectra were recorded at 75.5 MHz using a Bruker AM 300 spectrometer. The samples, as coarse granules, were contained in alumina rotors and spun at 5 kHz in a Bruker dual-bearing broad-band MAS probe at ambient temperature (300 K). The magic angle was adjusted for optimum signal with a KBr sample and ^{13}C 90° and 180° pulse angles were determined (4.8 and 9.6 μsec) using a sample of adamantane. High-power pulsed ^{1}H-decoupling (80 W) was provided by a Bruker 300 MHz/120 W amplifier. In order to refocus the sideband intensities into the central peak, the 90° ^{13}C pulse was followed by the TOSS sequence [13]. CP spectra were recorded with 1 msec contact time; 4 K data points were acquired with 5 Hz/pt resolution using a recycle time of 1 sec. Typically, 512 transients were accumulated and treated with 16 Hz line broadening. Chemical shifts were referenced to the DGEBA signal for the ^{13}CMe$_2$ nucleus (42 pm) [14].

RESULTS AND DISCUSSION

The ^{13}C-resonances (Fig. 1) invariant throughout the series are due to the nuclei of the crosslinked DGEBA. They have been assigned previously [12, 14] and are indicated in the spectrum of No. 1. Signals characteristic of the hardeners are marked throughout the spectra and the chemical shifts collected in Table 2.

Materials derived from the four acidic hardeners (7–10) are easily identified by the signal of the C=O group which ranges from 166 to 173 ppm. These four materials are also readily differentiated by other characteristic signals, 9 by the CH_3 signal and the strong CH signal, 8 by the characteristic CH_2 signal, 7 by the enhanced aromatic signal B and 10 by several unique signals. A general feature of the materials from acidic hardeners is the broad OCH_n signal E which presumably reflects contributions from several (CO)OCH species. Spectra from the epoxides produced with amine hardeners (1–6) display a broad signal at *ca* 55 ppm which can be ascribed to species containing a variety of CH_2N or CHN moieties but there is little difference in this signal for the various hardeners except that for 2 the region is filled in as a probable result of unresolved N–CH_3 resonances. Predictably, the materials 1 and 3 cannot be readily distinguished but there is a shoulder at *ca* 24 ppm in 1 which can be assigned to CH_2 groups three bonds removed from N. The spectra of products of aromatic hardeners should be recognisable by differences in the aromatic region but, as the DGEBA has four signals (ABCD) in the region, the differentiation may depend on intensity differences. The product 4 shows characteristic extra signals in the aromatic region which are assignable to CH *ortho* to two NH_2 groups [or *ortho*

Table 2. ^{13}C chemical shifts of hardener specific signals of Fig. 1

1	55 ppm (N–CH_n, $n = 1,2$); 24 ppm (C–3/4 HMDA)
2	40–55 ppm (N–CH_n, $n = 1,2,3$); 24 ppm (C–3/4 THMD)
3	55 ppm (N–CH_n, $n = 1,2$)
4	149 ppm (C–1/3 MPDA); 102 ppm (C–1/4/6 MPDA) 55 ppm (N–CH_n, $n = 1,2$)
5	55 ppm (N–CH_n, $n = 1,2$)
6	152 ppm (C–1 DDS); 55 ppm (N–CH_n, $n = 1,2$)
7	167 ppm (C=O); 128 ppm (aromatic PTA)
8	173 (C=O); 42 ppm (CH HHPA); 25 ppm (CH_2HHPA)
9	172 ppm (C=O); 48 ppm (aliphatic MNA); 16 ppm (CH_3)
10	166 ppm (C=O); 102 ppm (CO_2); 80 ppm (CHCl); 54 ppm (other CH CEA)

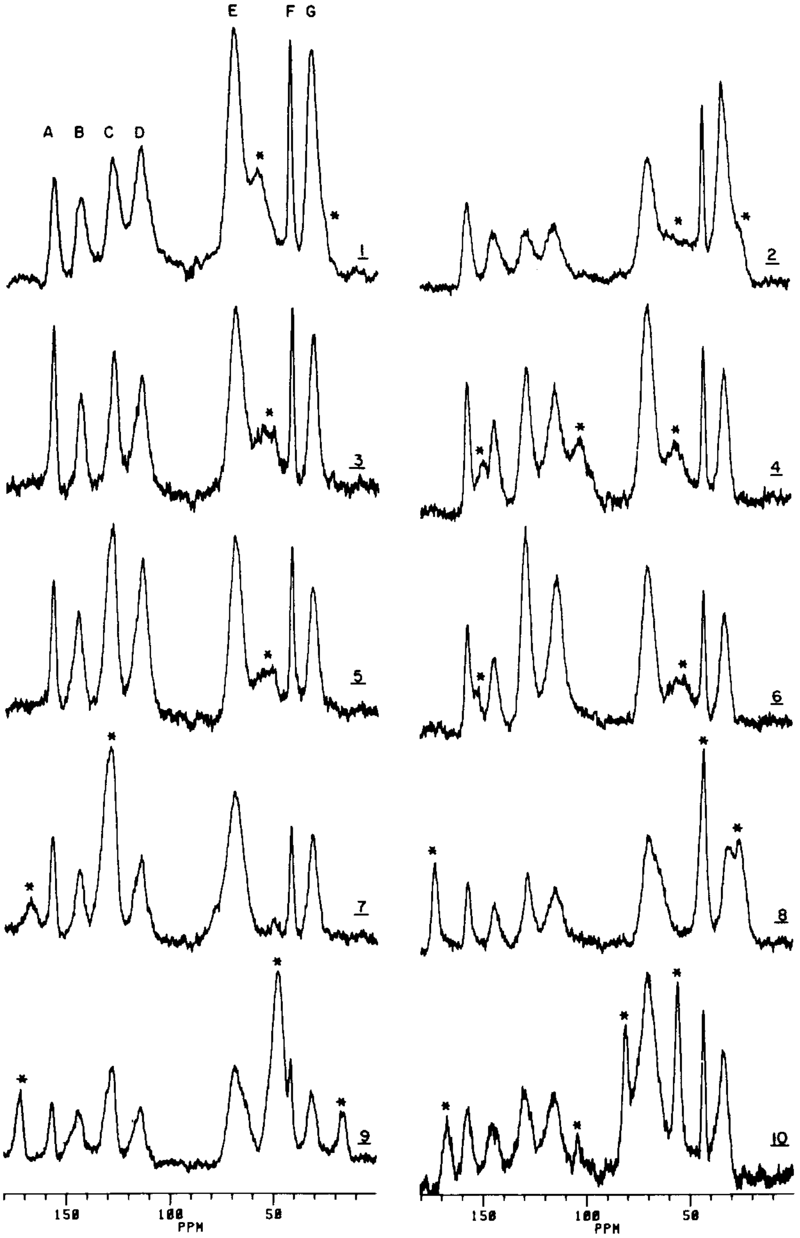

Fig. 1. ^{13}C CPMAS spectra of the materials 1–10. The signals of the base epoxy DGEBA are indicated A–G in 1 and asterisks throughout mark the hardener specific signals.

and *para* to NH_2 groups] (102 ppm) and to the CN signal (149 ppm) and so this material is easily identified. The other aromatic amine hardeners might be expected to give an analogous signal at *ca* 149 ppm and such a signal is apparent for 6. The spectrum for 5, however, gives no clear signal for the aromatic CN nor does the spectrum show any separate signal for the benzylic CH_2 group and so cannot be readily differentiated from the spectrum of 3. However, the spectra given by the *para* disubstituted hardener materials show increased intensity of specific resonances; if the signal for the quaternary aliphatic carbon of DGEBA (signal E, Fig. 1) is taken as an intensity standard, the spectra for 5 and 6 show noticeably more intense aromatic CH resonances C and D.

In conclusion, each material gives a detectably different spectrum and the acid hardeners, in particular, present little problem in identification. With such a complex instrumental technique, it is important to question the reproducibility of the spectra and it is therefore encouraging that the spectrum reported by Garroway *et al.* [12] for an epoxide hardened with MNA is so closely similar to our spectrum of 9. The value of high-field spectroscopy becomes apparent with the amine hardeners where the extra dispersion allows distinction between some aliphatic hardeners, for example, 1 and 3.

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