

Probing the cure of ^{13}C labelled bisphenol A dicyanate ester in carbon fibre reinforced composites using solid state ^{13}C NMR, SEM and FTIR

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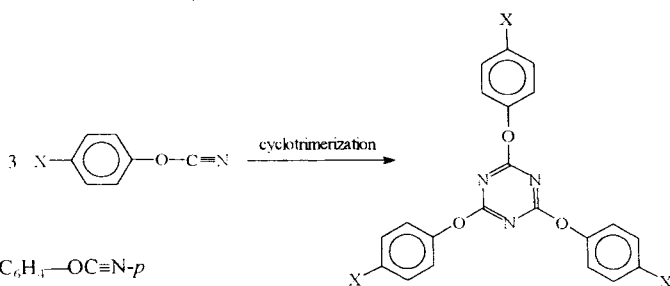
Received: 25 November 1996/Accepted: 23 January 1997

Summary

We report a study of the curing mechanism of ^{13}C labelled bisphenol A dicyanate ester in the presence of a electrolytically surface treated XAS carbon fibre using several techniques — solid state ^{13}C NMR, scanning electron microscopy (SEM) and diffuse reflectance FTIR. Comparison of the results obtained in pure matrices and solution shows that the resin undergoes the same reaction mechanism in both cases and forms the *sym*-triazine network structure in the composite.

Introduction

Over the last 20 years aromatic cyanate esters (CE) have become firmly established as a unique class of high-performance thermosetting resins, for use as prepreg matrices in both the electronic and aerospace industries.¹ The basic properties of CE resins, such as low moisture absorption, excellent electrical properties and good flammability characteristics, make them attractive composite matrices and differentiate them from standard epoxy resin (epoxide) and bismaleimides.² CE polymerise *via* a cyclotrimerisation reaction to form a polycyanurate network to a high degree of efficiency: the use of metallic or amine catalysts can reportedly achieve conversion of greater than 98%.³ In practice, commercial CE resins (commonly based on bisphenol A dicyanate ester) are usually cured by a transition metal carboxylate or chelate catalyst⁴ in the presence of an active hydrogen co-catalyst such as nonylphenol.⁵ Certain transition metal ions (e.g. zinc) show particularly high catalytic activity due to their low coordination number and high ligand mobility during the cure process.⁴ Characterisation has usually been carried out on bulk CE polymers by spectroscopic methods, e.g. NMR (both in liquid and solid forms)^{6–8} and FTIR.^{9,10}



X = $-\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_4-\text{OC}\equiv\text{N}-p$

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Advanced composite materials consist of a high strength reinforcing agent or fibre combined with a high performance matrix resin.¹¹ Of all current composites, carbon fibre reinforced plastics (CFRP) are the most important; with glass and aramid fibre reinforced epoxides fulfilling supporting roles. These together form in excess of 90% of all composites presently specified for aircraft construction. The combination of fibrous reinforcement in a matrix is the most common form of composite, but despite its importance, the nature of the interphase region in fibre reinforced composites remains largely unresolved. For the study of the interphase region several factors may be important. Wright considered carbon fibre surface treatment and its effect on fibre and composite properties, the use of sizes and polymer coatings and their effect on composite properties as well as various theoretical approaches and experimental techniques.¹²

In the present study, we have carried out an exploratory investigation of the cure of the ¹³C labelled CE resin at resin/fibre interphase and interface region, using high resolution ¹³C solid state NMR spectroscopy. Isotope enrichment was employed to minimise the contributions made by other nuclei in the resin in order to observe the chemistry of the principal reactive cyanate group ($\text{—OC}\equiv\text{N}$).

Experimental

Materials Acetone (Fisons, AR) was dried on NaOH and distilled before use. Bromine (Aldrich, 98%), K¹³CN (Aldrich, 99% ¹³C), triethylamine (Aldrich, 99%), Bisphenol A (Aldrich, 97%), phenol (BDH, AR), copper(II) naphthenate (Strem Chemicals, 77% in mineral), dichloromethane (Fisons, AR), talc (3MgO·4SiO₂·H₂O, Aldrich, approx. particle size 9 μm), XAS carbon fibres (Courtaulds Graphil, 100% surface treated, unsized) and XA carbon fibres (non-surface treated, unsized) were all used as received.

¹³C Labelled bisphenol A dicyanate ester ¹³C labelled bisphenol A dicyanate ester was prepared as a white crystalline material starting with K¹³CN based on the method described by Fyfe *et al.*⁷ In our procedure, dichloromethane was used to extract ¹³CNBr from the aqueous phase rather than employing distillation. The dichloromethane solution was then dried and used without further purification in the next step. ¹³C and ¹H NMR and IR data for the isotopically labelled cyanate ester are similar to their unlabelled counterparts: $\nu_{\text{max}}/\text{cm}^{-1}$, 2230 ($\text{—OC}\equiv\text{N}$ stretch). $\delta^1\text{H}(\text{CDCl}_3, 300 \text{ MHz})$, 7.43–7.32 (dd, 2H) 1.72 (s, 6H). $\delta^{13}\text{C}(\text{CDCl}_3, 75 \text{ MHz})$, 107.8 ppm (for $\text{—O}^{13}\text{C}\equiv\text{N}$).

¹³C Labelled bisphenol A dicyanate ester/carbon fibre composite A variety of composite processing techniques are employed of which prepreg formation is the most widely used to study epoxy composite fabrication technique.¹¹ Prepregs are made by impregnating fibres with resin either in the molten state or in solution, followed by evaporation of the solvent, or by using a film forming technique. The latter applied on the samples used in this work. The resin solution contained ¹³C labelled bisphenol A dicyanate ester (0.35 g), phenol (13 mg), copper(II) naphthenate (77% in mineral, 0.2 mg) and acetone (3 cm³). In a specially designed boat-shaped glass tube with a narrow mouth, XAS carbon fibres were pulled through the resin solution. This ensured that all the fibres were wet by the solution. The coated fibres were then cut to a length of 15 cm, and dried in an oven. The coated fibres were treated at 100 °C (one hour) to evaporate the solvent, 170 °C (two hours) and 225 °C (six hours) to cure the resin. It was then cooled for a period of 10 hours to avoid thermal shock and to yield stiff black strips of unidirectional composite.

Spectroscopic methods ^{13}C Labelled bisphenol A dicyanate ester/carbon fibre composite samples were powdered under liquid nitrogen in a Glen Creston 6700 freezer/mill, then mixed with talc (80% w/w). ^{13}C Solid state NMR spectra were obtained using a Varian UNITYplus 300 spectrometer with a 7 mm Doty Scientific MAS probe operating at 75.43 MHz. The spectra were obtained at a spectral width of 30007.5 Hz, frequency relaxation delay 1.0 sec, spin rate 7950 Hz and acquisition time 9.6 ms. The spectra were referenced to an external sample of TMS (in practice a secondary reference adamantane was used with Hartmann-Hahn match condition). The ambient probe temperature was 25 °C. Diffuse reflectance FTIR were recorded on a Perkin Elmer (PE) 1700 FTIR spectrometer, with PE diffuse reflectance unit continuously purged with nitrogen gas. The XA carbon fibre was used to acquire the background spectra. Scanning electron micrographs (SEM) were taken using a Cambridge Stereoscan 250 scanning electron microscope at 20 kev. A carbon fibre/bisphenol A dicyanate ester composite strips were cut with a blade and fractured. The surfaces were sputter-coated with a layer of gold film before analysis.

Results and Discussion

Scanning electron microscopy (SEM) examination of the carbon fibre/ ^{13}C labelled bisphenol A dicyanate ester composite showed that the carbon fibres were covered fairly uniformly by a thin layer (1-2 μm) of resin matrix (see Fig.1). This layer is deeper than the interphase area, but much smaller than in a normal composite sample. The resin fraction used was very low (less than 15% W/W in solution). Most of the fibres were either still separated from each other, or attached only by small amount of the resin. Good interfacial adhesion can be clearly identified in those parts of the fractured sample.

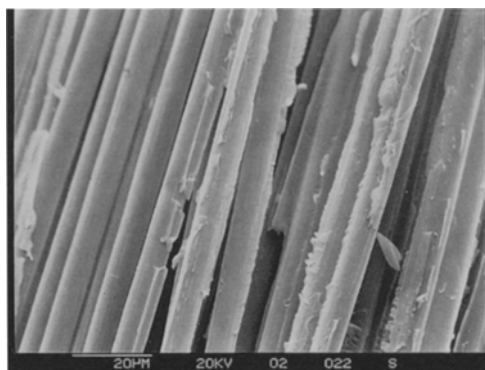


Fig. 1 SEM micrograph of the carbon fibre/ ^{13}C labelled bisphenol A dicyanate ester composite.

NMR spectra have been obtained previously only on composites reinforced with fibres other than carbon fibres. In a carbon fibre composite electrical conductivity of the continuous carbon fibres severely attenuates the rf magnetic fields being applied and being detected in an NMR experiment.^{13,14} The ^{13}C solid state NMR spectra of the

composite sample containing carbon fibres and ^{13}C labelled bisphenol A dicyanate ester are shown in Fig.2. The problem caused by the carbon fibre's conductivity was overcome by grinding the composite to a powder and diluting the sample with talc. The characterisation using ^{13}C NMR spectroscopy was greatly improved through the specific labelling of ^{13}C in the $-\text{O}^{13}\text{C}\equiv\text{N}$ group. Two experiments, the direct excitation of carbon (with proton decoupling) and the cross polarisation from protons (also with proton decoupling), were undertaken. The only observable resonance in both spectra is located at 173.4 ppm. This finding represents strong evidence for the formation of a *sym*-triazine ring. The signals from the cross polarisation experiment were much less intense, but do confirm the presence of a resonance at 173 ppm, no other resonances were observed.

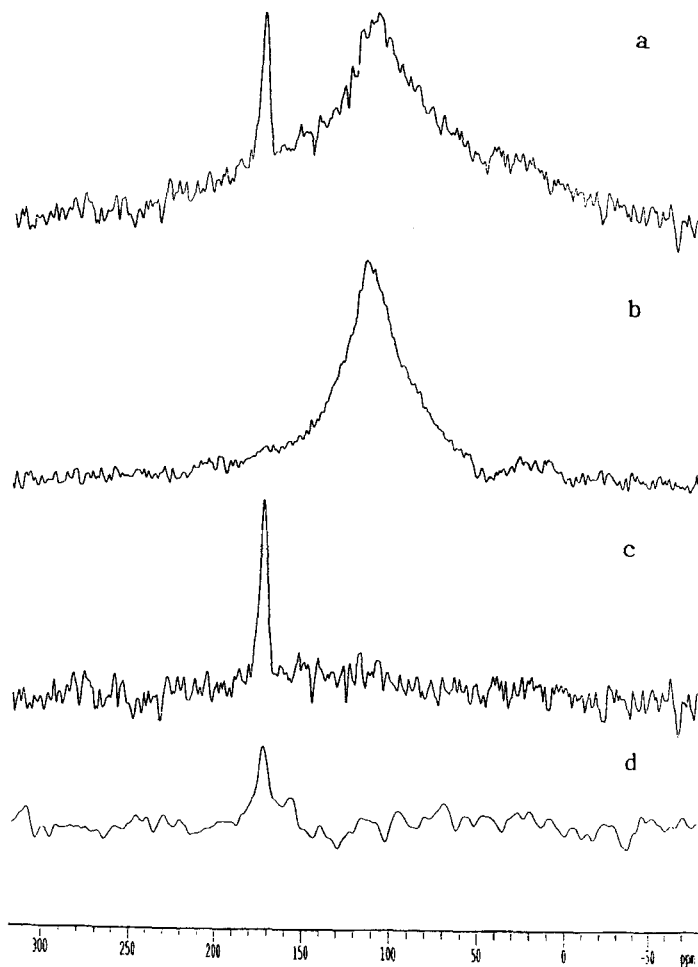


Fig. 2 Solid state ^{13}C MAS NMR spectra of (a) the carbon fibre/ ^{13}C labelled bisphenol A dicyanate ester composite and talc mixture, (b) pure talc, (c) a-b and (d) CP-MAS spectrum of the same sample in (a).

Fyfe *et al.* employed high resolution ^{13}C and ^{15}N NMR spectroscopy in both solution and the solid state, to investigate the curing reaction of CE resins.⁷ It was found that in methyl ethyl ketone (MEK) solution, the reaction proceeded at 60 °C to form triazine rings as well as the carbamate ($-\text{OCONH}_2$) functionality. The ^{13}C NMR spectrum of bulk cured CE resin gave a peak at 174 ppm, with no indication of substantial amounts of the unreacted monomer or carbamate arising from side reactions. By comparison with Fyfe's results, obtained in pure polymer matrices and solution, our work suggests that the resin undergoes the same reaction mechanism and presumably forms the same network structure in the interphase region of the carbon fibre reinforced composite.

Many workers have used FTIR to study the curing of dicyanate esters. Peaks around 2230-2270 cm^{-1} ($-\text{OC}\equiv\text{N}$) are distinctive and well separated from the rest of the IR spectrum.¹⁵ FTIR analysis of carbon fibres has been difficult due to the severe scattering phenomena and the high absorptivity of the material. However FTIR techniques such as attenuated total reflectance (ATR)¹⁶⁻¹⁸ and diffuse reflectance¹⁹ FTIR have been successfully used to investigate carbon fibres or carbon fibre reinforced composites at the interface or interphase area. Diffuse reflectance FTIR was used, for its ability to differentiate the near-surface region of a sample from the bulk and to complement the solid state NMR study. By operating under a nitrogen atmosphere, the effect of any carbon dioxide and moisture was minimised. However, owing to the setting of the diffuse reflectance accessory, and severe scattering effect of the carbon fibres, only approximately 3-4% of the energy can reach the detector, and consequently the signals were weak.

The FTIR spectrum of pure carbon fibres comprised a noisy baseline. The FTIR spectrum of carbon fibre/ ^{13}C labelled bisphenol A composite displayed more features with improved signal/noise ratio. The absence of any absorption in the latter between 2230-2270 cm^{-1} (for $-\text{OC}\equiv\text{N}$) supports the NMR result, indicating complete CE conversion from monomer. There are peaks in the 1580-1520, and 1360-1340 cm^{-1} regions, which are presumably due to the $\text{C}=\text{N}$ stretch. However, these peaks occur about 20 cm^{-1} lower than the corresponding absorptions in the bulk cured polycyanurate (1565 cm^{-1})¹⁰. Several factors may affect the shift and are currently being investigated. Whilst the ^{13}C NMR spectrum showed no signals from the aromatic rings, they could be identified from the FTIR spectrum *viz.* bands at 1600 and 1495 cm^{-1} .

Acknowledgement

We wish to thank the EPSRC for funding (Grant Number GR/H95891) a postdoctoral research fellowship (S.Y.L). We would also like to thank Mr. R. Whattingham in the materials chemistry laboratory for assistance, and Dr. D. C. Apperley at the EPSRC solid state NMR service, University of Durham, for obtaining the ^{13}C NMR spectra.

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