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In situ real-time monitoring of reactive systems by remote fibre-optic near-infra-red spectroscopy

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A remote fibre-optic near-infra-red (n.i.r.) spectroscopy set-up was recently assembled in our laboratory and successfully used for *in situ* real-time monitoring of various reactive systems. A disposable probe was designed and employed, enabling us to study processing of thermosetting polymers. A detailed description of our experimental set-up and several selected examples are presented in this communication.

(Keywords: *in situ* monitoring; near-infra-red spectroscopy; reactive systems)

Introduction

In situ real-time monitoring of chemical and physical changes during processing of reactive materials, polymer-forming and non-polymer-forming alike, continues to be an area of fervent research activity of both a fundamental and an applied nature. Information collected *in situ* by sensors is transmitted in real time to the process computer, whose task is to control the system parameters and guide the process along an optimum path.

The key elements of an *in situ* control loop are the source, the transmission line, the sensor and the detector. As a result of an unparalleled breadth and wealth of information on a molecular level contained in the infra-red portion of the electromagnetic spectrum (e.g. refs 1–6), Fourier transform infra-red (*FT* i.r.) spectroscopy offers fundamental advantages over other monitoring techniques[7].

The infra-red region is broad, though the vast majority of reported studies of reactive systems have been carried out in the mid-infra-red range (m.i.r.) which extends between about 4000 and $400\,\mathrm{cm}^{-1}$ (2.5–25 μm) and is replete with fundamental absorptions. Only a handful of investigations of reactive systems have been conducted in the near-infra-red range (n.i.r.), which extends from about 14 000 to $4000\,\mathrm{cm}^{-1}$ (0.7–2.5 μm) and contains weaker overtones of the fundamental absorptions (e.g. refs 8–15). One major advantage of the n.i.r. frequency range is that it can be transmitted through silica-type optical fibres, which are relatively inexpensive and are available in a variety of types and forms. As a result, there has been a recent surge of activity in the on-line use of remote n.i.r. spectroscopy. In the m.i.r. range, on the other hand, only exotic state-of-the-art chalcogenide and metal halide fibres have the required transmission capabilities, and even then usually over a limited frequency interval[16].

The principal objectives of this communication are: (1) to describe our recently assembled experimental set-up for remote fibre-optic n.i.r. spectroscopy of reactive systems, and (2) to present examples of our data obtained on several epoxy/amine systems. This study is part of an ongoing programme on *in situ* real-time characterization of reactive organic systems of both polymer-forming and non-polymer-forming type.

Experimental

FT i.r. spectroscopy was performed using a Nicolet Magna-IR System 750 Spectrometer with spectral range coverage from 15 800 to $50\,\mathrm{cm}^{-1}$ and the Vectra scanning interferometer with a better than $0.1\,\mathrm{cm}^{-1}$ resolution. N.i.r. data were obtained using a calcium fluoride beamsplitter, a white-light source and an MCT detector cooled with liquid nitrogen. All spectra were measured at $4\,\mathrm{cm}^{-1}$ resolution using 35 scans. A schematic presentation of our experimental set-up is given in *Figure 1A*.

A large core (600/630 μm), low –OH fused silica type multimode optical fibre (3M's specialty optical fibre) was used. The fibre was characterized by attenuation at 630 nm of less than $50\,\mathrm{dB\,km}^{-1}$ and a numerical aperture of 0.39 ± 0.02. Two 1.5 m lengths of the fibre were utilized as receiving and transmitting legs. An optical-fibre link containing reflective mirrors was used to couple the signal into the transmitting and out of the receiving leg. SMA connectors (supplied by Newark Electronics) were used to attach fibre legs to the fibre link. At the sample side, two distal fibre ends were axially centred and positioned to face each other. Depending on the type and size of sample, several disposable cell configurations were designed and successfully tested. All had an adjustable pathlength, enabling us to optimize the signal. In most instances, a pathlength of 2–3 mm was sufficient for excellent transmission and a clear n.i.r. absorption signal down to $4000\,\mathrm{cm}^{-1}$. The results shown in this communication were generated using the optical-fibre/capillary configuration, schematically shown in *Figure 1B*. A short length (less than 10 mm) of protective buffer was removed from the distal ends of fibres, which were then slipped into the capillary to a desired pathlength. The space between fibre ends was filled with the reactive mixture free of bubbles, and the whole assembly was inserted into a programmable temperature-controlled

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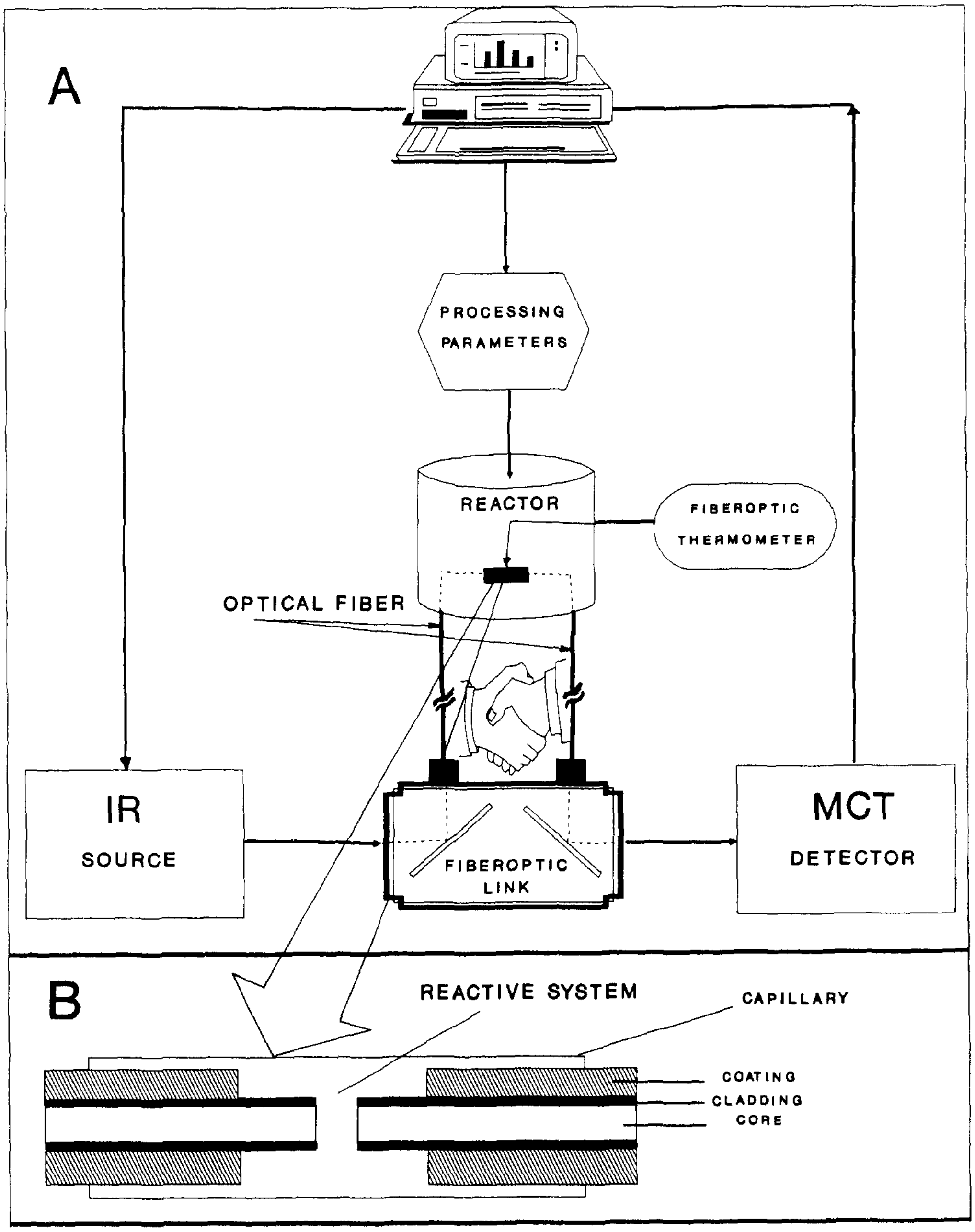

Figure 1 (A) Schematic of remote fibre-optic n.i.r. spectroscopy assembly; (B) schematic of disposable optical-fibre/capillary cell configuration

chamber. Highly accurate measurement of the sample temperature is essential in kinetic studies, and that places a premium on the experimental precision. During reaction, temperature was monitored with Luxtron's 750 Multichannel Fluoroptic Thermometer, by placing its optical-fibre probe in direct contact with the portion of capillary filled with the reactive mixture. This experimental procedure is very attractive; it features a simple design, low cost, small sample size, short preparation time, *in situ* real-time response, and remarkable reproducibility and reliability of data. Most importantly, however, the cell is disposable, in contrast to several recently marketed and quite expensive fibre-optic probes that are non-disposable and hence cannot be used to monitor processing of thermoset polymers and composites. We believe that the information provided in this communication is sufficient to enable interested researchers to assemble their own remote fibre-optic n.i.r. set-ups at a minimal cost. After curing of our sample, a small length of the fibre embedded in the cured resin is cleaved, and the new ends polished to a clean, mirror-flat surface for the next run. Selected examples of results presented in this communication were chosen from studies of an epoxy/amine model system composed of 1,2-epoxy-3-phenoxypropane (also known as phenyl glycidyl ether or PGE) and aniline, and a multifunctional epoxy/amine formulation composed of diglycidyl ether of bisphenol F and methylene dianiline (DGEBF/MDA). The reactants were mixed in stoichiometric proportions and immediately tested under isothermal conditions at a series of selected temperatures.

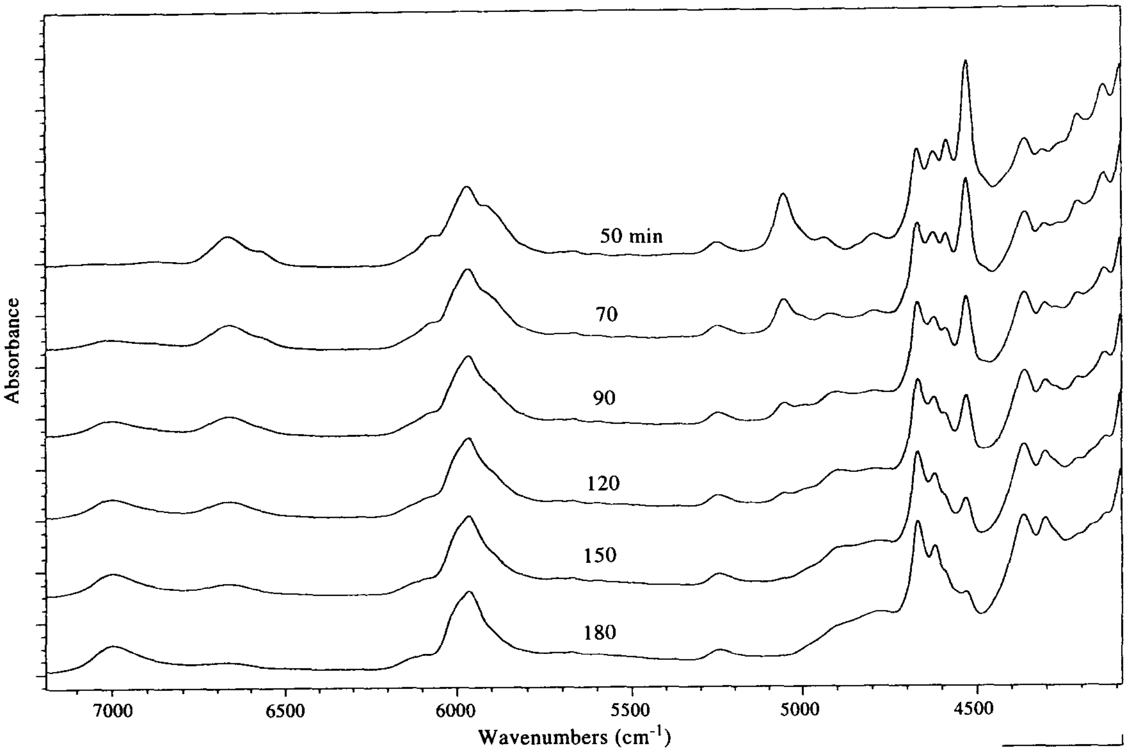

Figure 2 N.i.r. spectra of PGE/aniline system during reaction at 100°C, with reaction time in minutes as a parameter

Results and discussion

Figures 2 and *3* show series of spectra obtained with our fibre-optic probe during PGE/aniline (non-polymer-forming) reaction at 100°C and DGEBF/MDA (polymer-forming) reactions at 84°C, respectively. Spectra are very 'clean', free of noise, completely reproducible, with sharp peaks and, as a rule, superior to those obtained by using standard sample configuration. The progressive changes in spectra were systematic and conducive to precise quantitative analysis. The trends

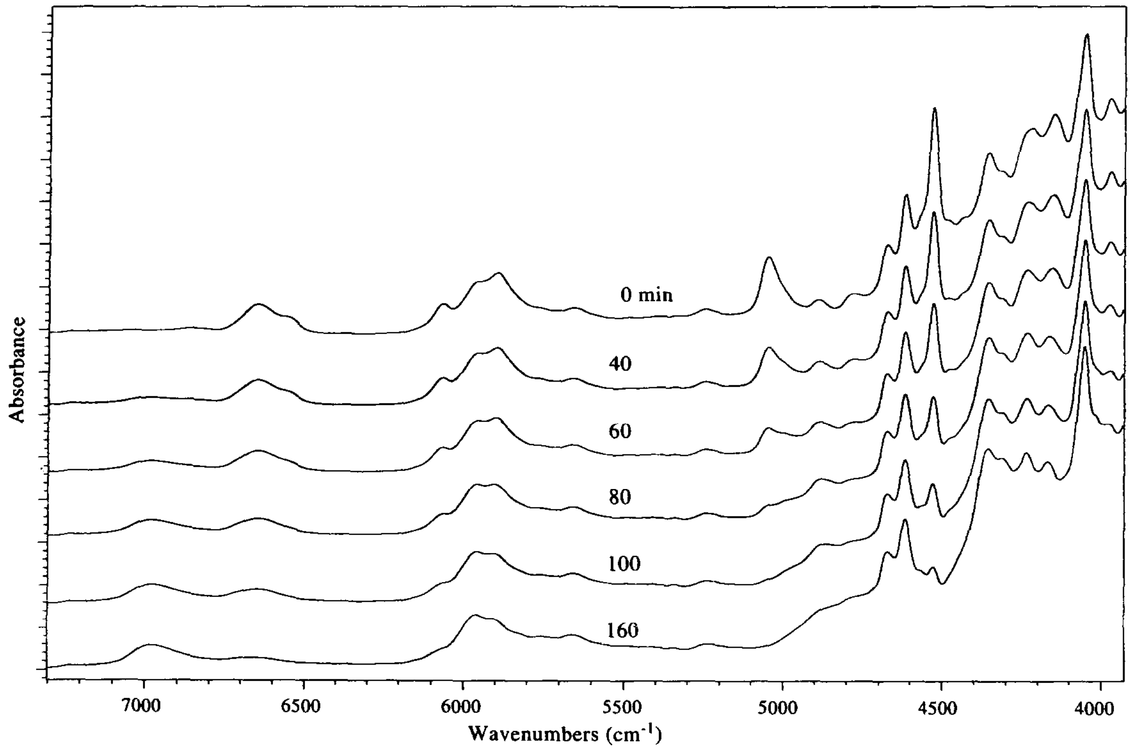

Figure 3 N.i.r. spectra of DGEBF/MDA system during reaction at 84°C, with reaction time in minutes as a parameter

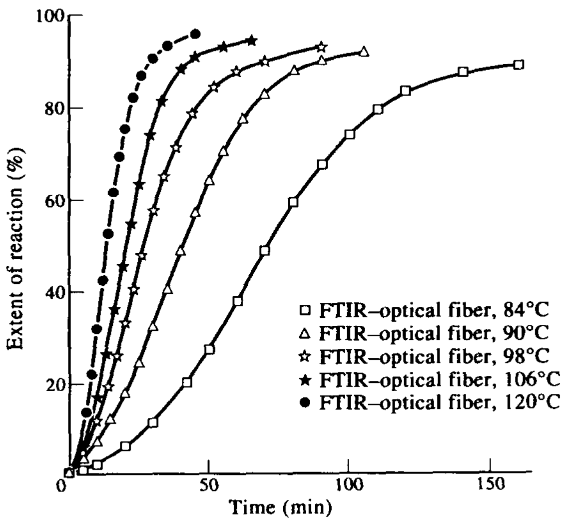

Figure 4 Extent of reaction of DGEBF/MDA system as a function of time, with temperature as a parameter

displayed by major peaks of relevance in epoxy/amine reactions were evident; a decrease in epoxy absorption (4530 and 6080 cm^{-1}), a decrease in amine absorption (5056 and 6670 cm^{-1}), and an increase in hydroxyl absorption (7000 and 4800–4900 cm^{-1}). A comprehensive account of the origin, location and shifts of all n.i.r. peaks during epoxy/amine reactions is given in a recent paper from our group[17], and is beyond the scope of this communication.

Spectral data of the type shown in *Figures 2* and *3* were used for quantitative determination of reaction kinetics. The use of *FT*i.r. spectroscopy to study reaction kinetics has been documented in the literature (e.g. refs 18, 19). The extent of reaction (α) at any time t is calculated from the initial areas of epoxy and reference peaks, $A_{\mathrm{epoxy},0}$ and $A_{\mathrm{ref},0}$, respectively, and their corresponding values at time t, $A_{\mathrm{epoxy},t}$ and $A_{\mathrm{ref},t}$, according to the following equation:

$$\alpha = 1 - [(A_{\mathrm{epoxy},t})(A_{\mathrm{ref},0})]/[(A_{\mathrm{epoxy},0})(A_{\mathrm{ref},t})] \qquad (1)$$

In this study, the peak at 4530 cm^{-1} was used to monitor the disappearance of the epoxy group. Various reference peaks were examined, and the most reproducible results were obtained using the peak due to the C–H stretching vibration of the benzene ring at 4673 cm^{-1}. An example of quantitative kinetic results is shown in *Figure 4*, where the extent of reaction of DGEBF/MDA multifunctional formulation, calculated from equation (1), is plotted as a function of reaction time, with reaction temperature as a parameter. Caution must be exercised, however, in that a direct comparison of results in *Figure 4* with kinetic information generated on a sample of different size must first account for the difference in heat transfer characteristics and hence can be made only when the sample have identical thermal histories.

Conclusions

An *in situ* real-time monitoring set-up, containing a remote fibre-optic sensor and an *FT*i.r. spectrophotometer operable in the n.i.r. frequency range, was assembled and successfully tested in our laboratory. Several non-polymer-forming model systems and polymer-forming multifunctional formulations were studied. An investigation of the latter group was made possible by designing and utilizing a disposable sample cell. The results were characterized by a strong, clean signal and superb reproducibility. Quantitative treatment of spectra generated via the fibre-optic sensor was used to evaluate the reaction kinetics. Owing to low signal attenuation and a fundamental molecular nature of the collected information, remote fibre-optic n.i.r. spectroscopy is expected to become the foremost diagnostic tool for *in situ* real-time monitoring in the chemical processing industry.

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