Monitoring of Lamination Processes in an Autoclave with Fiber-Optic Infrared Spectroscopy

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SYNOPSIS

Curing reactions of certain laminates involve a series of chemical structure changes which occur with increasing temperature and/or pressure. This paper describes the use of a mid-infrared chalcogenide fiber to monitor the lamination of polymer prepregs in an autoclave. The fiber optic was used both as a wave guide and as a sensing element for acquiring evanescent wave spectra. The spectra were measured by embedding the fiber optic in a polymer prepreg package. The polymer prepregs studied include epoxy, polyimide, and bismaleimide triazine (BT) resins. The degree of cure and an understanding of the kinetic processes were obtained from the absorbance changes in specific bands. This *in situ* sampling technique demonstrates a new area of Fourier transform infrared (FTIR) spectroscopy for following the formation of polymeric bonds. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

During many lamination processes, there are a series of chemical structural changes with increasing temperature and/or pressure. Monitoring changes in these chemical structures during curing is very important in order to understand the reaction kinetics.[1-3] Fourier transform infrared (FTIR) spectroscopy has been used to study curing reactions[4-7] and, in recent years, fiber optics have also been applied to these investigations.[8-10] At the present time, lamination processes taking place in an autoclave under controlled temperatures and pressures have not been subjected to *in situ* monitoring. The major obstacle to on-line monitoring of lamination reactions is performing the measurements at high temperatures and pressures. Polymerization of resin prepregs during lamination processes is difficult to control precisely because key chemical parameters are not easily measured on-line. However, fiber optics offer a solution to many of the difficult problems encountered in on-line monitoring of these processes.

In situ infrared spectroscopic monitoring becomes practical through the use of fiber optics. A direct measurement of the curing kinetics can be obtained from the infrared spectra of reactants, intermediates, and products. Herein, we discuss results of the *in situ* monitoring of lamination processes by measuring evanescent wave (attenuated total reflection) spectra in the mid-infrared region.

The evanescent wave is generated in materials adjacent to the core of a fiber optic. Light launched into a high refractive index core is totally reflected at each interface with the lower refractive index of cladding or adjacent material; actually the light penetrates a short distance ($\sim 0.1\lambda$) into the adjoining material. During this short penetration, the light is attenuated at various wavelengths due to vibrational transitions of the chemical groups in the cladding or adjoining material. Thus, the light is not totally reflected at all wavelengths because of the attenuation. The resulting absorption spectrum is referred to as the evanescent wave or attenuated total reflection (ATR) spectrum of the cladding or adjoining material.

In this investigation, the fiber optic was used as a wave guide which directed the infrared (IR) beam from an FTIR spectrometer to a polymer prepreg inside an autoclave; it was also used as a sensor

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embedded in the polymer prepreg to obtain evanescent wave spectra of the polymer during the lamination. The evanescent wave spectra of polymers including epoxy, polyimide, and bismaleimide triazine (BT) were automatically collected every 15 min during lamination. The degree of polymerization was determined according to the absorbance changes at specific frequencies.

EXPERIMENTAL

Apparatus

A high temperature/high pressure autoclave was constructed by GRP (Atlanta, GA). The autoclave was ~ 0.5 m in diameter and ~ 1 m deep. Its temperature could be computer-controlled to ±10°F over the range of room temperature to 450°F (232°C), and its pressure controlled from atmospheric to 200 psi. The autoclave was interfaced to a BIO-RAD, Digilab Division FTS-40 (Cambridge, MA) spectrometer via a 1.5-m-long chalcogenide fiber optic. The fiber optic was coupled to the autoclave using Swage Lock quick-connects. About 40 cm of the fiber was placed in the autoclave; 15 cm of cladding in the middle of the fiber optic was removed with concentrated sulfuric acid. The unclad portion of the fiber optic was sealed in a polymer prepreg package which was placed in the autoclave as shown in Figure 1. One end of the fiber optic was connected to the spectrometer through a BIO-RAD fiber optic interface accessory, which consists of a three-dimensional translational stage for positioning the fiber optic. The other end of the fiber optic was directed to a liquid-nitrogen-cooled MCT detector (EG&G JUDSON Montgomeryville, PA; Model J15D14-M204-S01M-60), which was placed on the other side of the autoclave as displayed in Figure 1.

The polymer package was made of ten 20 × 15-cm resin prepreg sheets placed in a polyethylene package. The polymer prepreg sheet is composed of the resin prepreg partially cured over a layer of glass fiber. The 15-cm-long unclad portion of the fiber optic was placed between the polymer prepreg sheets. It was found that the uncoated length of the 15-cm fiber optic gave a reasonable level of infrared absorbance when brought into contact with the resin prepregs. The package was sealed in a polyethylene "turkey bag" with APIAZON Q (sealing) wax and connected to a vacuum pump on the top of the autoclave with Swage Lock quick-connects as shown in Figure 1. A thermocouple was attached to the package in order to detect and control the temperature. During the curing process, the pressure was varied from ambient to 150 psi and the temperature from ambient to 405°F (207°C) by computer control, as shown in Figure 2. Completing a lamination process took ~ 5 h. The package was evacuated for 30 min prior to the first application of temperature and pressure, and it was kept under vacuum throughout the entire process. The autoclave was filled with ni-

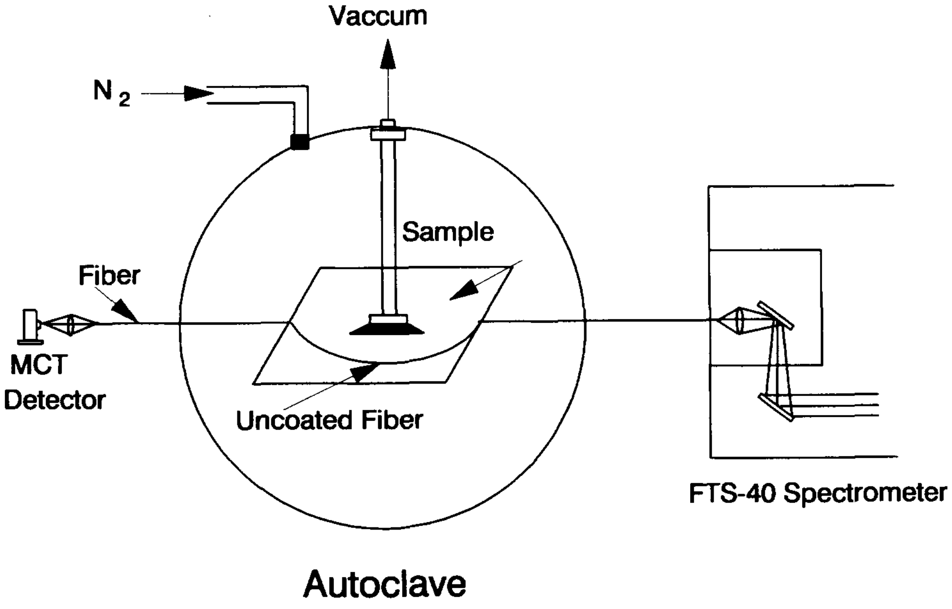

Figure 1 A system for monitoring lamination processes in an autoclave with fiber optic infrared spectroscopy.

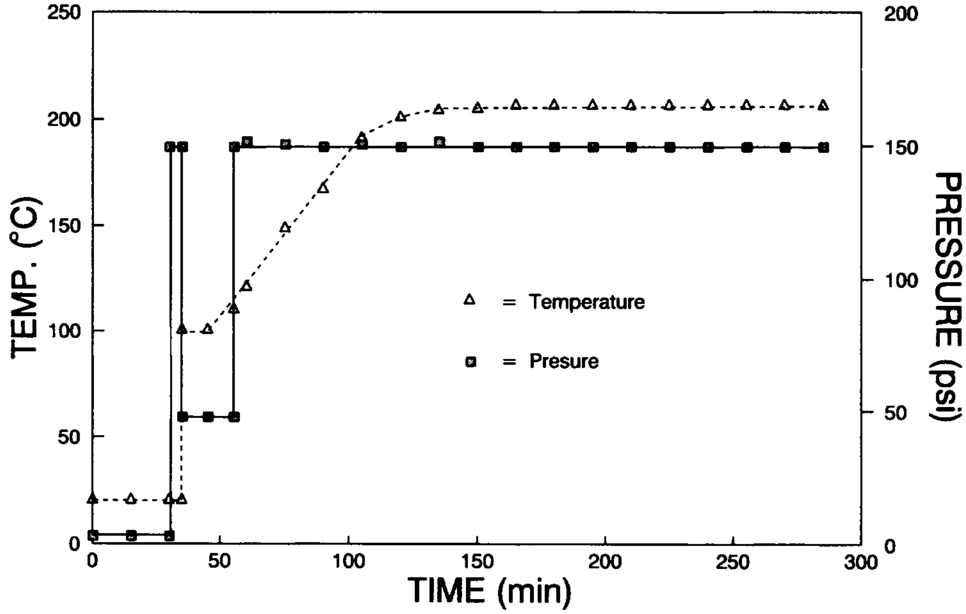

Figure 2 Time dependence of temperature and pressure during lamination processes: △ – – △ – –: temperature; ■ — ■ — ■: pressure.

trogen gas to compress the package, in order to further shape the fiber–resin combination as it cured. Analog Connection Jr. (Strawberry Tree Computer, Sunnyvale, CA) software was used for process control and monitoring; it measured the temperature and pressure, and controlled heaters, fans, pumps, and solenoid valves.

Spectra Measurement and Processing

Spectra were automatically measured every 15 min with 128 scans at 4 cm^{-1} resolution during the lamination processes. Three different kinds of resins, including epoxy, polyimide, and BT, were studied in this research. All laminated packages were formed under the same temperature and pressure conditions as described in Figure 2. The absorbances at specific frequencies, reflecting the progress of the lamination process, were measured and plotted as functions of curing time. All of the spectral processing were performed in LAB CALC (Galactic Industries Co. Salem, NH) software.

RESULTS AND DISCUSSION

Fiber Optic Spectra

A mid-infrared transmitting chalcogenide fiber optic (Galileo Electro Optics Co., Sturbridge, MA) was used in this study. The fiber optic has a 300-μm core of an arsenic, germanium, tellurium, and selenium glass, coated with a 15-μm thickness of epoxy acrylate cladding. The attenuation loss of the fiber is about 10 dB per meter, which restricts the useful length of the chålcogenide fiber to ~ 3 m.

Figure 3 is a single-beam spectrum of the chalcogenide fiber measured at room temperature. It was used as a background reference for the spectra of resins during the lamination process in order to cancel out absorptions due to the chalcogenide fiber. The spectra of the chalcogenide fiber heated for 30, 60, and 270 min, corresponding to temperatures of 70°F (21°C), 250°F (121°C), and 405°F (207°C), respectively, are shown in Figure 4. Most of the spectral changes are due to changes in the acrylate cladding. The only major absorption change is at 1080 cm^{-1}; the other changes are relatively small. Since the absorptions used for detecting the changes during the lamination process are in the region of 1200–1800 cm^{-1}, and one-third of the exposed cladding inside the autoclave was removed, the changes in the cladding spectrum as a function of temperature were not considered in this research.

Epoxy Resin Prepreg Lamination

Epoxy resins are useful composite materials for a variety of demanding structural applications. The chemistry involved in the applications of epoxy resins is the key to their outstanding performance. The

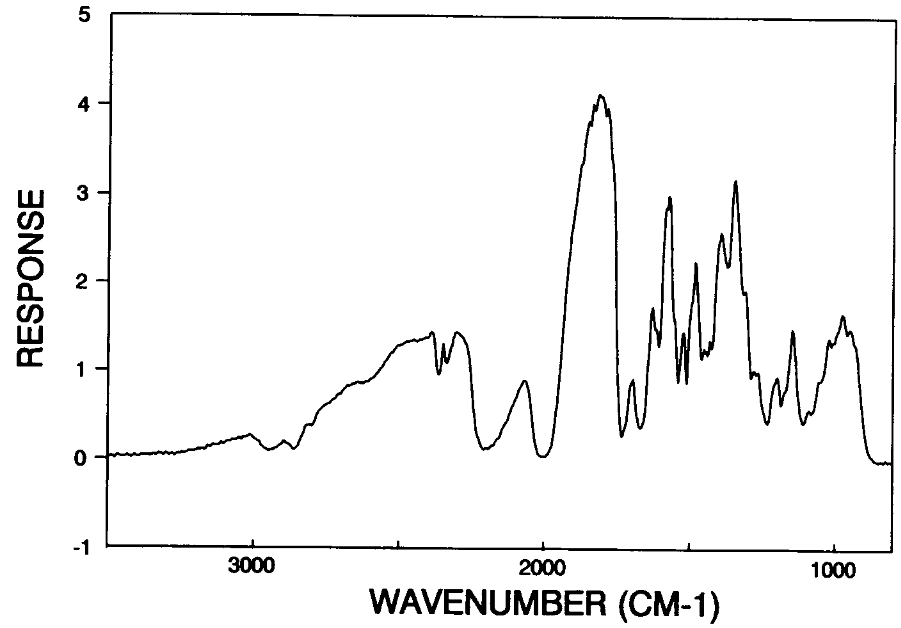

Figure 3 Single beam spectrum of chalcogenide optic fiber at room temperature.

epoxide functional group is a 1,2- or α-epoxide called the glycidyl group. Curing of the epoxy resins from the reaction of this group with compounds containing reactive hydrogen atoms, such as a molecule with —OH, —NH, or —COOH groups, results in a glycidyl ether, glycidyl amine, or glycidyl ester.[11]

Preliminary studies demonstrated that a fiber optic coupled to an FTIR spectrometer could be used to measure the mid-infrared spectra of a commercial epoxy resin during curing reactions after the resin was mixed with a hardener. The fiber optics in those experiments were covered with the epoxy resin; evanescent wave spectra were recorded periodically to monitor the curing process after the hardener was added and mixed with the resin. Four evanescent wave spectra of the epoxy resin at 0, 2, 10, and 68 min after the addition of the hardener are shown in Figure 5(a) and 5(b). Obvious intensity changes and band shifts are detectable in the spectra as a function of curing time.

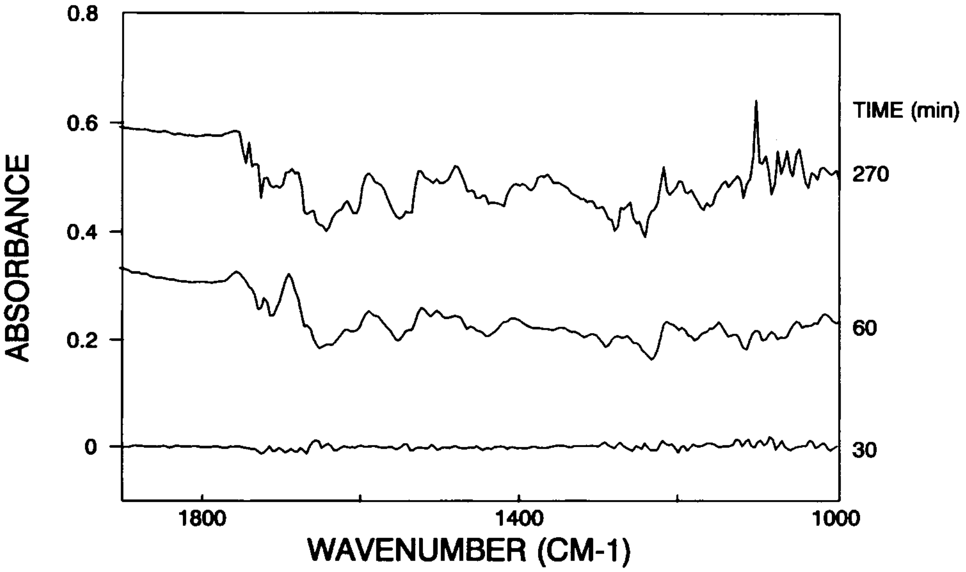

Figure 4 Spectra of chalcogenide fiber during lamination processes.

The spectral results of the curing reaction of an epoxy prepreg are shown in Figure 6, in which the spectra for 30, 60, and 270 min, corresponding to temperatures of 21°C, 121°C and 207°C, are displayed. The bands at 1670 and 1728 cm^{-1} due to carbonyl C=O stretching vibration are shifted to higher wave numbers of 1690 and 1759 cm^{-1} at higher temperatures. Other bands increase in intensity during the lamination cycle. The absorbance increases at 1215, 1504, and 1593 cm^{-1} are plotted as functions of the lamination time in Figure 7. The band at 1593 cm^{-1} due to aromatic C=C stretching vibration reaches a maximum at 75 min, whereas the other two bands continue to increase up until 120 min and have slight fluctuations after that time. The band at 1215 cm^{-1} is due to the epoxide C—O stretching vibration in the polymer. The band does not become stable (constant intensity) until ~ 225 min. Thus, it appears that epoxide bands continue to form after other groups have stabilized.

Polyimide Prepreg Lamination

Polyimides are synthesized through a dehydrocyclization reaction of polyamic acids. Generally, the curing reaction includes loss of the amide structure with an increase of imide structure.[7,9] Figure 8 shows spectra of polyimide cured for 30, 60, and 270 min. Comparing the spectra during the lamination process reveals that the band at 1666 cm^{-1} (due to amide C=O stretching vibration) is observed at 21°C, but disappears after being heated to 121°C; bands associated with the imide functions at 1380 cm^{-1} (C—N stretching vibration in the imide), 1713, and 1771 cm^{-1} (imide I and imide II C=O stretching vibration) are present in the spectra recorded at the higher temperatures. The band near 1380 cm^{-1} is also shifted to a lower wave number with the temperature increase, which is consistent with configuration changes of the imide ring. The complexity of the curing reaction also leads to some ambiguities in the observed spectral data. For example, both the aromatic amide and aniline have an absorption at 1510 cm^{-1}; this absorption should decrease with the decrease of the amide and aniline concentrations with increasing temperature. Thus, the absorption increase at 1510 cm^{-1} is due to other functional groups, such as benzene ring stretching, which may change with the configuration changes of the adjoining groups.

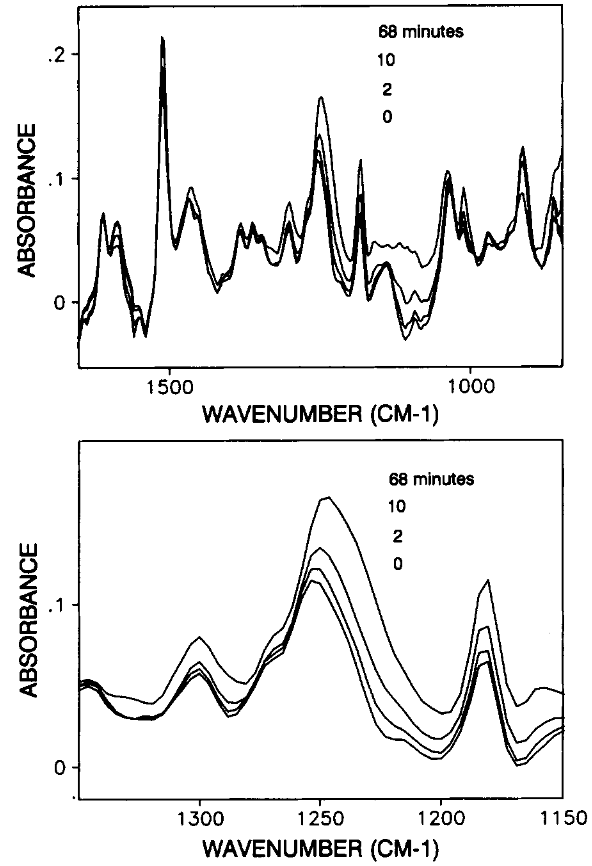

Figure 5 Spectra of a commercial epoxy resin during curing reaction.

The absorbances at 1380, 1713, and 1771 cm^{-1} are plotted as the functions of the lamination time in Figure 9. The absorbances at 1380 and 1713 cm^{-1} increase rapidly at the beginning of the lamination cycle and reach the maximum in 75 min. The absorbance at 1713 cm^{-1} decreases to a lower intensity at 105 min and shows slight fluctuations after that time. The rapid increase followed by a decrease in the production of imide I (1713 cm^{-1}) would seem to indicate that the initial temperature might be reduced to slow down the curing process and avoid the over-production of imide I during the early part of the lamination cycle. The absorbance at 1771 cm^{-1} increases more slowly than the other two bands. All of the bands reach a steady state in ~ 120 min, which suggests that the lamination process should be concluded at that time.

BT Resin Prepreg Lamination

BT resin is a general term for the highly heat-resistant thermosetting polyimide resins with two main constituents of bismaleimide (B) and triazine (T). Generally, BT resin is cured by heating bismaleimide and triazine prepreg without the addition of hardening agents to form triazine rings, triazine-imidazole rings, and oxazole rings.[12] BT resin is a highly regarded material in microelectrical industries.

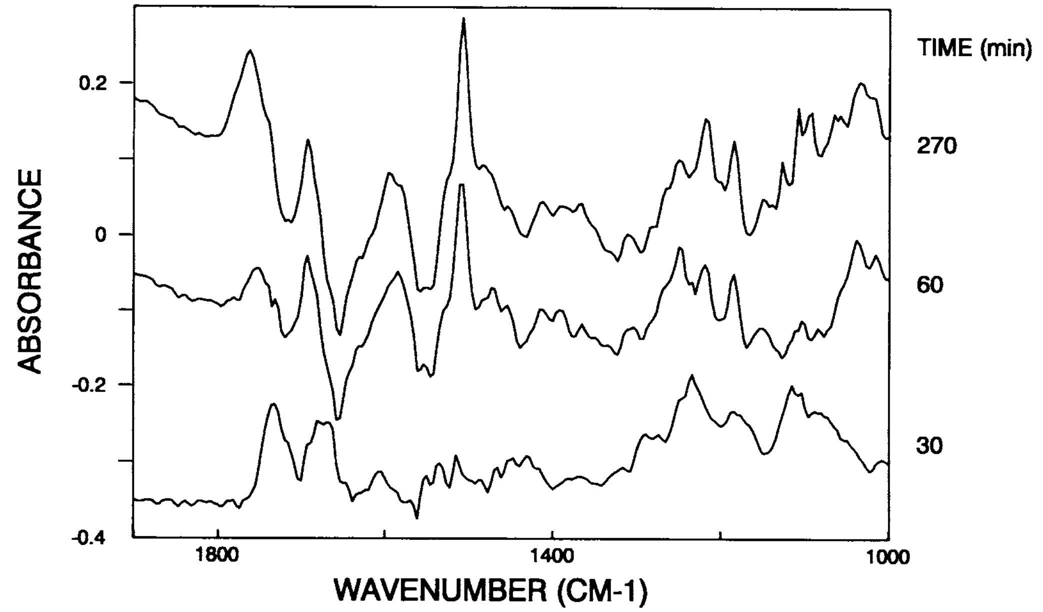

Figure 6 Spectra of epoxy prepreg during lamination process.

Figure 10 displays spectra of BT resin cured for 30, 60, and 270 min under the same conditions as discussed for epoxy and polyimide laminations. It shows obvious changes in the bands at 1366, 1504, 1686, and 1771 cm^{-1}. The band at 1366 cm^{-1} due to the triazine ring stretching vibration has higher intensity in the spectrum at 60 min than that at 270 min. The absorption at 1504 cm^{-1} due to the benzene and the oxazole ring stretching vibrations increases with temperature. The absorbance increase in the band at 1686 cm^{-1} is due to $C{=}N$ stretching vibration of the oxazole rings, and the band at 1771 cm^{-1} is due to imide $C{=}O$ stretching vibration of the triazine–imidazole ring.[12,13] Figure 11 displays these absorbance changes vs the curing time. The intensity at 1366 cm^{-1} increases in the first 75 min,

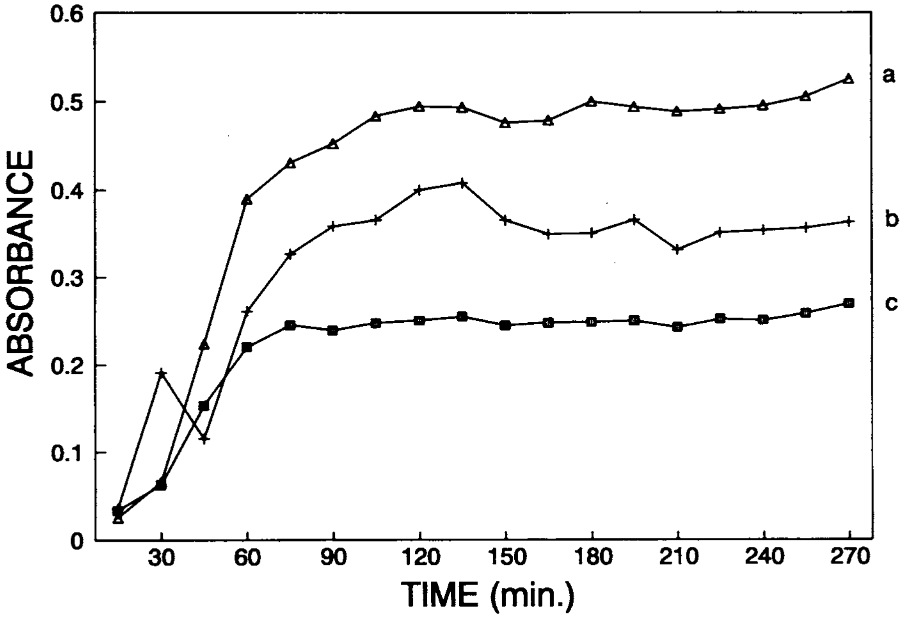

Figure 7 Absorbance changes of epoxy prepreg during lamination process: (a) 1504 cm^{-1}; (b) 1215 cm^{-1}; (c) 1593 cm^{-1}.

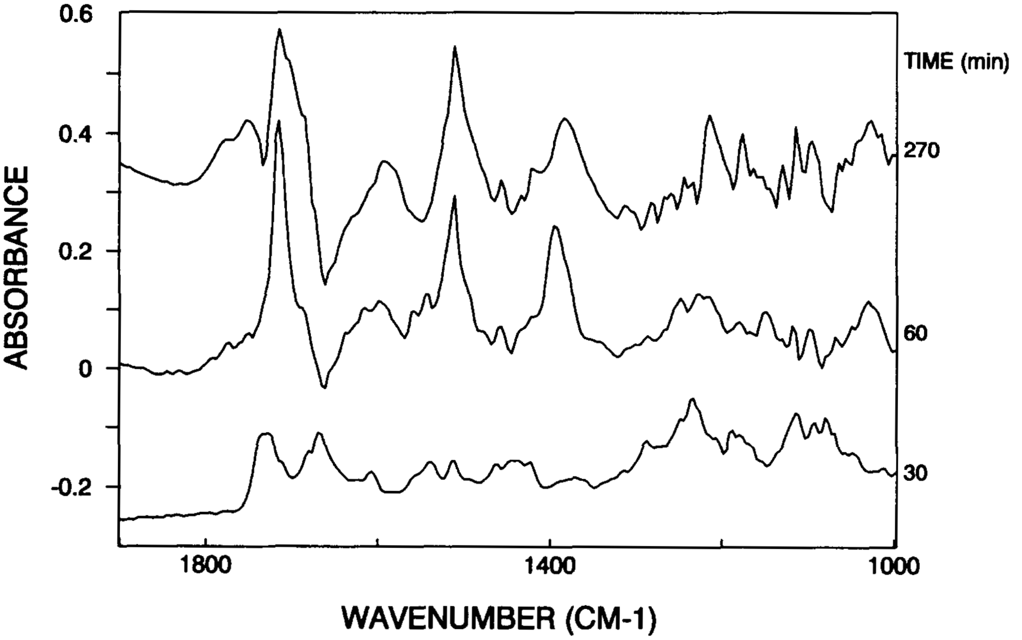

Figure 8 Spectra of polyimide prepreg during lamination process.

and then decreases to a constant level at ~ 120 min; this rapid increase followed by a decrease would also suggest an over-production of the triazine ring during the early part of the curing process. The absorbances at 1504 and 1686 cm^{-1} increase rapidly in 60 min and show slight fluctuations after that time. The absorbance at 1771 cm^{-1} increases slowly until ~ 120 min. The curing reaction reaches its stable level at ~ 120 min, which suggests that the curing could be concluded at that time.

CONCLUSION

The possibility of using a mid-infrared transmitting chalcogenide fiber optic as an evanescent wave

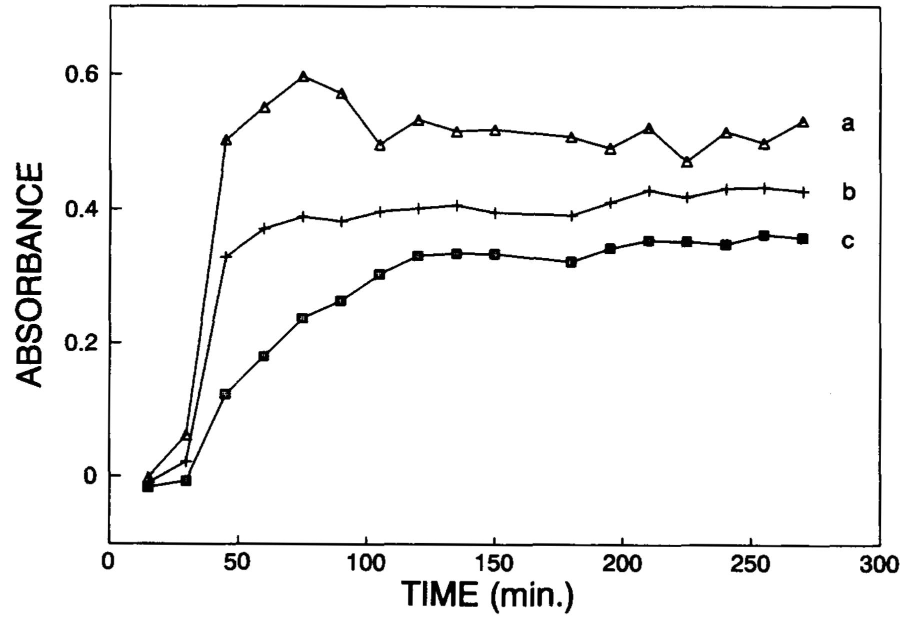

Figure 9 Absorbance changes of polyimide prepreg during lamination process: (a) 1713 cm^{-1}; (b) 1380 cm^{-1}; (c) 1771 cm^{-1}.

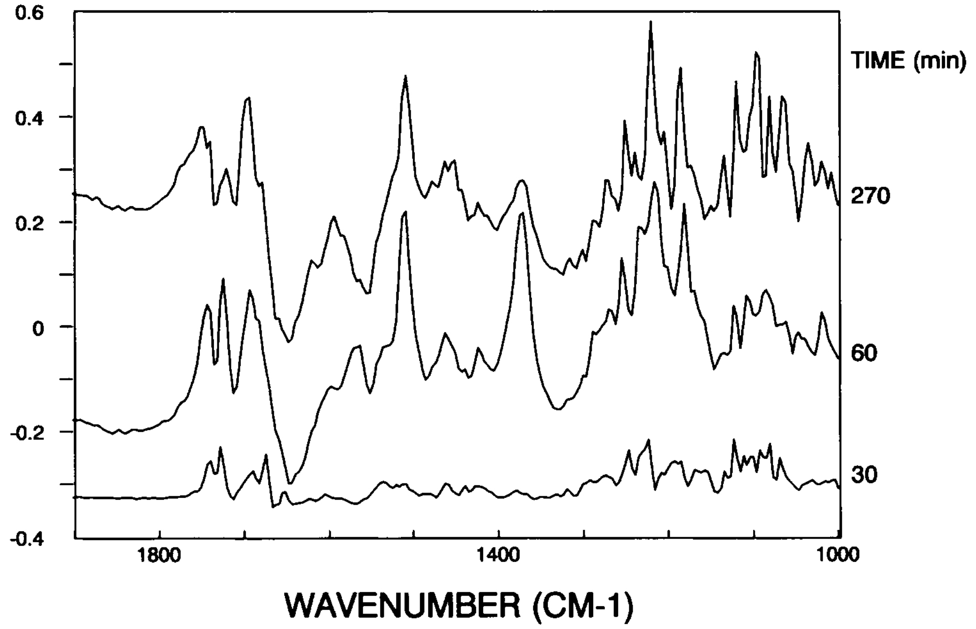

Figure 10 Spectra of BT prepreg during lamination process.

spectroscopic sensor to monitor lamination processes of epoxy, polyimide, and BT resins at high temperatures and pressures has been demonstrated. By removing the cladding of the chalcogenide fiber over a short portion in the middle of the fiber optic, and sealing this portion into contact with a resin prepreg package in an autoclave, we can conveniently obtain the evanescent wave spectra of a resin during the lamination process. The fiber optic was also used as a wave-guide interface between the spectrometer and the autoclave.

The *in situ* monitoring of lamination processes leads to very useful information. Major bands due to the various starting reactants, the intermediates, and the final products can be identified and used to determine yields of polymerization. The sampling

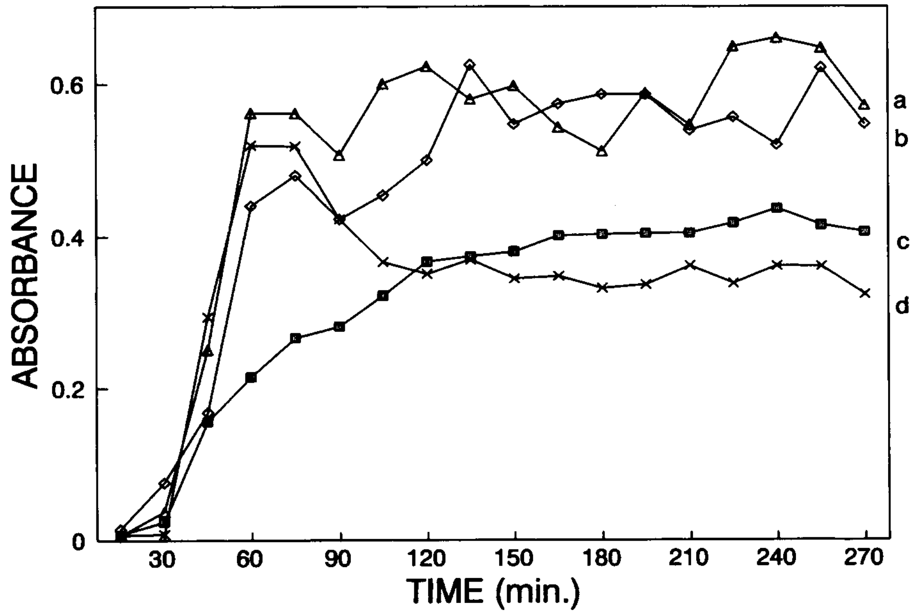

Figure 11 Absorbance changes of BT prepreg during lamination process: (a) 1504 cm^{-1}; (b) 1686 cm^{-1}; (c) 1771 cm^{-1}; (d) 1366 cm^{-1}.

technology used in this study makes it practical to obtain real-time, on-line information about the curing process. One drawback of this study is that the chalcogenide fiber optic is fragile and expensive. However, the last few years have brought improvements in the fiber optic fabrication process and decreases in cost. This *in situ* monitoring technique shows considerable potential for understanding and improving lamination processes.

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