

Characterization of polymer composites during autoclave manufacturing by Fourier transform Raman spectroscopy

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ABSTRACT

The superior engineering properties of fiber reinforced polymer matrix composites, primarily the high strength-to-weight ratio, make them suitable to applications ranging from sporting goods to aircraft components (e.g. helicopter blades). Unfortunately, consistent fabrication of components with desired mechanical properties has proven difficult, and has led to high production costs. This is largely due to the inability to monitor and control polymer cure, loosely defined as the process of polymer chain extension and cross-linking. Even with stringent process control, slight variations in the pre-polymer formulations (e.g. prepreg) can influence reaction rates, reaction mechanisms, and ultimately, product properties. In an effort to optimize the performance of thermoset composites, we have integrated fiber optic probes between the plies of laminates and monitored cure by Raman spectroscopy, with the eventual goal of process control. Here we present real-time measurements of two high performance aerospace composites cured within an industrial autoclave.

Keywords: composite cure, epoxy resin, polyester, polymer kinetics, Raman spectroscopy, real-time monitoring, autoclave

1. INTRODUCTION

The high strength-to-weight ratio of fiber reinforced polymer matrix composites make them ideal as structural support components for the aerospace industry.¹⁻³ Applications to automobiles, bridge supports, buildings, chemical reactor vessels, ships, and trains, are all known,^{4,5} but market growth remains below expectations. This is attributed to the inability to fabricate components within specifications that meet application guidelines. The difficulty arises from the complex chemistry associated with the composites.

The majority of composite components or products involve two manufacturing steps; preparing a prepreg and molding the part. Prepregs are prepared from a woven sheet of reinforcement fiber (carbon, glass or aramid) pre-impregnated (prepreg) with one or more matrix components (usually a partially cured thermoset polymer or thermoplastic). In the final product, the fibers with high strength and modulus carry the load, while the matrix provides toughness and protection. The chemical structure of a common prepreg thermoset resin is shown in Figure 1. Epoxy resins based on bisphenol A are widely used since thermosets containing substituted aromatic rings have high resistance to thermal degradation and chemical attack.

One of the most common methods of preparing a composite prepreg is to draw a sheet of woven fiber through a bath containing the base resin and the cross-linking agent in a solvent (Figure 2A). Nip rollers control the fiber-to-resin ratio, while a heating chamber removes the solvent through evaporation and partially cures the resin (B-staged, Figure 1). Ideally, the resin and cross-linking agent have reacted to form short polymer chains producing a viscoelastic solid, but has not cross-linked nor vitrified into glassy solid. The prepreg should be slightly tacky so layers do not slip over each other during layup, and it should be sufficiently pliable, such that it forms (drapes) to the mold plate (caul). Controlling the extent-of-cure is extremely important, and the prepreg sheets are often sealed in plastic film containing a release paper and stored at temperatures below 0 °C.

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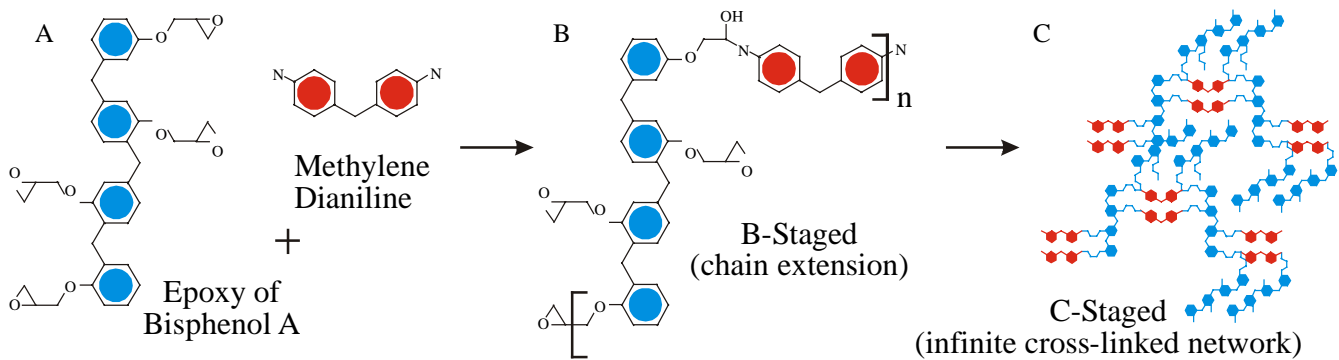


Figure 1. A) Chemical structures of an epoxy resin (bisphenol type, e.g. Novalac⁶) and an amine cross-linking agent (methylene dianiline), B) a B-staged resin used in prepregs (partially cured, simple chain extension $n = 2-5$), and C) fully cured resin of a composite (infinite network of cross-linked chains).

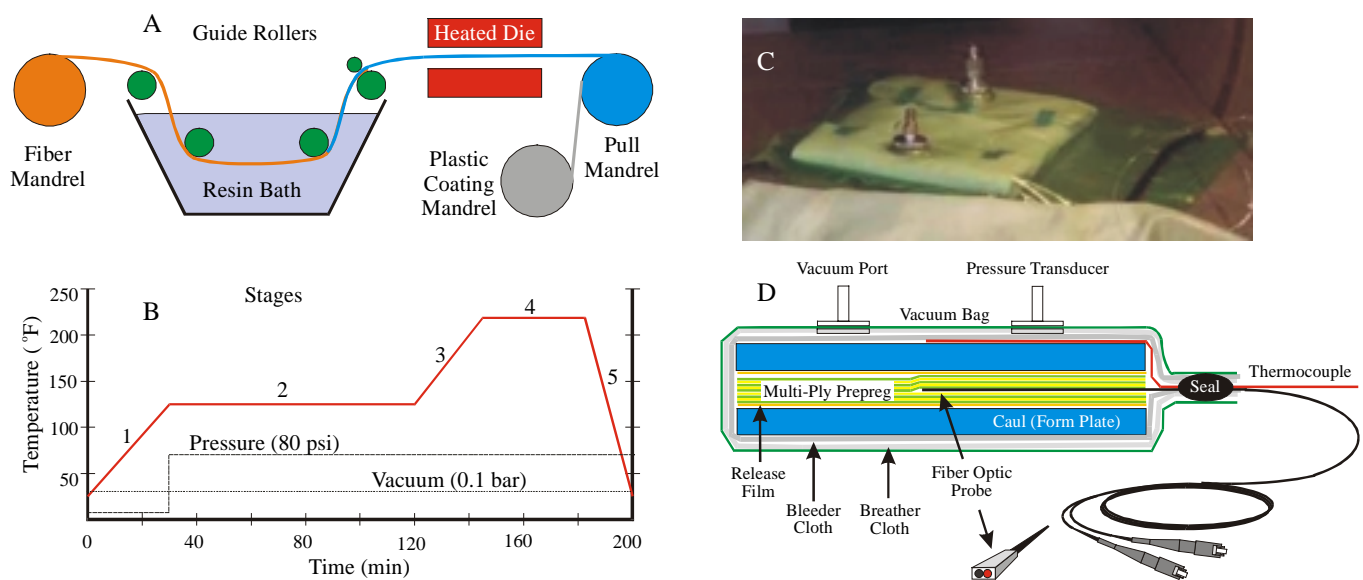


Figure 2. A) Illustration of prepreg manufacturing, B) diagram of typical manufacturers composite cure schedule, C) photograph of laminate prior to autoclave cure, and D) illustration of laminate components (including fiber optic probe).

The prepreg is then shaped and cured in a combination heat and molding device. For an autoclave, prepreg sheets are cut and layered on a metal form plate (caul) coated with a release film (Figure 2D). This is wrapped in a bleeder and/or breather cloth to absorb excess resin and/or volatiles. This is further enclosed in a vacuum bag and sealed. A thermocouple is usually placed between the bleeder cloth and caul plate, while a vacuum port and pressure transducer penetrate the vacuum bag or the caul plate. The vacuum bag is then placed into the autoclave and cured according to the manufacturer's temperature schedule.⁷ Typically five stages are used, two ramp temperatures, two hold temperatures, and a cool down. In the first stage, the prepreg softens and forms to the caul. The vacuum removes residual solvents and squeezes out excess resin. During the second stage, the resin and amine are cured isothermally. Initially, the reaction is kinetically controlled, and chain extension continues to the gel point. The third and fourth heating stages are designed to vitrify the resin through extensive cross-linking (diffusion controlled). In the last stage the composite is allowed to cool. This process defines the extent of the irregular three-dimensional molecular structure and ultimately determines the composite mechanical properties and useful temperature range.^{2,3,8,9}

Presently, autoclaves and similar devices, such as hot press molds are simply temperature and pressure controlled according to the manufacturer's schedule. This schedule is based on pre-determined, off-line measurements such as dynamic mechanical rheology. For example a series of isothermal cures of a resin system can be performed to determine the gel and vitrification

points. The gel point has been defined as the time during cure when the measured elastic (storage) and viscous (loss) moduli crossover (have equal value), whereas vitrification has been defined as a maximum in the phase angle (the loss modulus divided by the storage modulus).¹⁰ It is accepted that these macroscopic properties can not define molecular structure. Although, researchers have recently applied nuclear magnetic resonance spectroscopy and Raman spectroscopy to develop correlations.¹¹⁻¹³

The ability to monitor the cure reaction of polymers, particularly epoxy resins, by optical spectroscopies has been practiced for at least thirty years.¹⁴ Recently, fiber optics have been used to access reactions and processes in-situ to monitor epoxy cure by fluorescence,^{15,16} near infrared,¹⁷ infrared¹⁸ and Raman spectroscopies.^{19,20} Although several of these studies demonstrated the potential of measuring composite cure during manufacture, only one study actually performed measurements within a composite.¹⁸ The work presented here may represent the first measurements performed within an industrial autoclave. Autoclave driven cure was measured by Raman spectroscopy within two thermoset resin composites, Hexcel 8552 (epoxy based) and Cytec Cycom 4102 (polyester based). These composites are used to prepare high performance components in helicopters and ground combat vehicles.

2. EXPERIMENTAL

Two glass reinforced thermoset composite prepregs were used to prepare 1 foot square test laminate plates. One consisted of an amine cured epoxy resin, Hexcel 8552 (Pleasanton, CA) with S2-glass reinforcement (2x2 plain weave), and one consisted of a polyester, Cytec Cycom 4102 (Havre de Grace, MD) with S2-glass (5x5 plain weave). The prepregs, which were stored in polyethylene bags in a freezer at -10 °F, were removed for thawing overnight to remove any condensation prior to autoclave processing. The prepregs were cut into 1 foot square plies. The epoxy laminate consisted of 20 plies, while the polyester consisted of 10 plies. In both cases, the plies were layered on 1/2 inch aluminum caul plates coated with Wrightlon 4500 halohydrocarbon release film (Airtech International, Huntington Beach, CA). The fiber optic probes were placed between the middle plies (see below). A second caul plate coated with release film was placed on top of the plies to complete the sandwich assembly. A thermocouple for temperature control was attached to this plate. The assembly was first wrapped in two plies of nylon bleeder-release peel-ply, then wrapped with an Airweave nonwoven polyester breather cloth (Airtech). A Wrightlon 5400 nylon vacuum bag was then heat sealed to fit the finished sandwich assembly. Vacuum and vacuum transducer attachments were made through the top surface of the bag, while the thermocouple and fiber optic probes were fed through one side of the bag and sealed with AT-200Y sealant tape (Airtech).

The laminate plates were cured in a programmable 3 foot diameter by 6 foot long horizontal autoclave capable of 800 °F and 450 psi (Figure 3, Thermal Equipment Corp., Torrance, CA). The computer operated system used PID controllers (Leeds & Northrop, Philadelphia, PA) to achieve desired pressures and temperatures. The Hexcel epoxy composite was cured according to a five stage schedule (as in Figure 2). The temperature was first raised to 225 °F (107 °C) at 5-7 °F/min, then held constant for 90 min, raised again at 5-7 °F/min to 350 °F (177 °C), again held constant for 60 min, and finally cooled. The polyester composite was cured through three stages, first heated at 7-10 °F/min, held at 250 °F (121 °C) for 1 hour, and cooled. The only pressure applied was the ~ 30 psi obtained from the applied vacuum.



Figure 3. Photograph of Thermal Equipment Corp. Autoclave.

In each test laminate, three side-by-side fiber optic probes were placed between the center plies at roughly 2, 4 and 8 inches in from the center of one edge (Figure 2). All three probes were 3 meters long and employed a 200 μm diameter source fiber optic. The collection fiber optics employed were a 550 μm diameter fiber for the short probe, a 365 μm diameter fiber for the long probe, and two 365 μm diameter fibers for the middle probe. The fiber optic probes were fixed parallel with epoxy resin (ND 353, Epotek, Billerica, MA) and polished smooth with 0.5 μm alumina paper (Buehler, Lake Bluff, IL). The probes

were threaded through an existing vacuum line opening in the autoclave wall and sealed. Prior to insertion of the probes into the laminate, the throughput of each source fiber was measured. This was accomplished by manually changing of the ST (bayonet type) fiber optic connectors at the laser exit port and the FT-Raman interferometer entrance port. In all experiments ~ 70% of the 1W laser source entry power reached the sample. The collection efficiency of each return fiber was measured by placing a sealed glass vial of toluene at the probe tip. Each probe geometry yielded Raman spectra of similar intensity.

A prototype Fourier transform Raman spectrometer (Real-Time Analyzers, RTA, East Hartford, CT) was used for these measurements.²¹ The system consisted of a Nd:YVO₄ laser (Spectra Physics, Palo Alto, CA) for excitation at 1064 nm, an interferometer built by On-Line Technologies (OLT, East Hartford, CT) for frequency separation, an uncooled InGaAs detector for signal detection (RTA), and an Intel 400 MHz Pentium II based laptop computer (Dell, Round Rock, TX) for interferometric control, data acquisition (OLT), and analysis (LabVIEW by National Instruments, Austin, TX). Additional components included a Notch filter (Kaiser, Ann Arbor, MI) and interferometer entrance and exit optics (Edmund Scientific, Barrington, NJ). This design allowed spectral acquisition from -950 (anti-Stokes) to 3500 cm⁻¹ (Stokes) per scan. A shutter was included to chop the laser synchronously with the scanning of the interferometer mirror (Uniblitz model VS25, Vincent Ass., Rochester, NY), such that sequential forward and backward scans could be separately co-added.²² Subtraction of thermal emission spectra (laser blocked) from thermal emission plus Raman spectra (unblocked) allowed observing high temperature Raman spectra. Silicon oxide modes generated in the source fiber were simply subtracted when necessary.

A LabVIEW program was written that displayed each spectrum as it was collected and a false intensity color scale of sequential spectra that was continually updated (Figure 4). The program also allowed selecting a spectral feature (peak height, integrated area, or region), normalizing it to another feature, correcting for baseline offsets, and plotting it as a function of cure time. Once several data points were collected, it could also be fit to determine a projected or final rate constant. The acquired spectra could also be continually displayed (movie mode) to monitor trends in real-time. All these operation could be performed simultaneous to the collection of data.

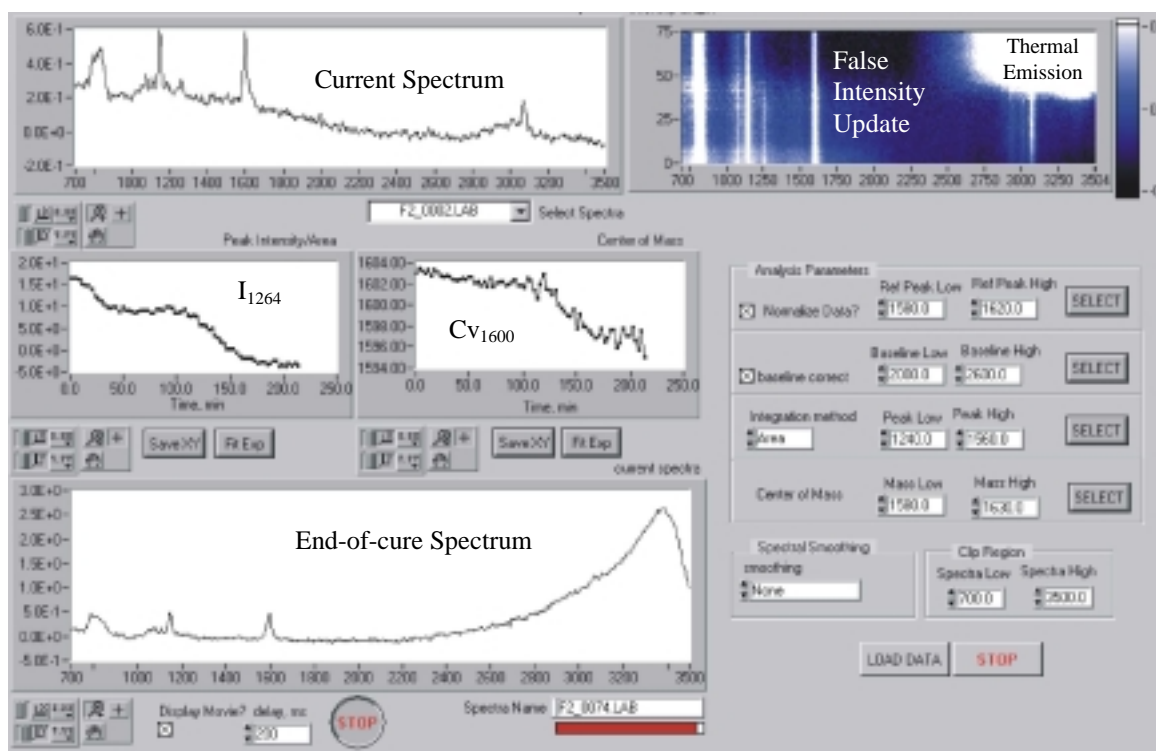


Figure 4. Display of Cure Rate program. Top row shows active spectral acquisition, and false intensity color scale of spectra already collected (large white region corresponds to thermal emission). Middle row shows peak/area intensity and center-of-mass (spectral region) as a function of cure time (note epoxide band decays in two steps, the 1600 band shifts mostly in the second step). Bottom row shows continuous display of collected spectra (movie, end of cure spectrum displayed). All parameters and features can be selected and displayed simultaneous to the collection of data.

3. RESULTS AND DISCUSSION

Prior to the addition of heat to initiate composite cure, pre-cure spectra were collected to establish that each fiber probe survived the vacuum, to select the fiber probe that yielded the best signal to noise (S/N), and to set the number of scans to achieve a S/N of 30 or greater. For both cures the single 365 μm fiber inserted 8 inches into the laminate yielded a slightly better S/N and was used to collect spectra. Each epoxy cure spectrum represents 100 averaged scans (3 min), while each polyester spectrum represents 220 scans (6.66 min). Figure 5 shows the first epoxy cure spectrum collected at 30 $^{\circ}\text{F}$ and the last spectrum collected at 350 $^{\circ}\text{F}$ (200 min after cure was initiated). The initial spectrum contains the following spectral bands associated with bisphenol A type epoxies²³ (see Figure 1). The aromatic C-H bends occur at 835 cm^{-1} (superimposed on a fiber optic band centered at 820 cm^{-1} , subtraction shown in figure), 1108 and 1193 cm^{-1} . The characteristic epoxide C-O-C stretch occurs at 1264 cm^{-1} , while a weak intensity epoxide C-H bend occurs at 1442 cm^{-1} . A weak aromatic C=C stretch occurs at 1508 cm^{-1} , and a strong aromatic C=C ring (phenyl) stretch occurs at 1600 cm^{-1} . A CH_2 stretch occurs at 2932 cm^{-1} , an epoxide CH_2 stretch occurs at 3012 cm^{-1} , and an aromatic ring C-H stretch occurs at 3074 cm^{-1} . In addition to these bands a medium intensity band appears at 1077 cm^{-1} , and strong band at 1150 cm^{-1} . The latter may be due to the amine curing agent or more likely indicates the formation of an alkane backbone due to chain extension of the partially cured prepreg resin (e.g. $n > 5$ Figure 1). The extent of the partial cure is substantial, in that the intensity of the epoxide band (1264 cm^{-1}) is only 1/10th the phenyl ring stretch (1600 cm^{-1}), and they are approximately equal when the reactants are initially mixed in equimolar concentrations. Also a shoulder at 1615 cm^{-1} is apparent on the 1600 cm^{-1} band, possibly due to a second phenyl ring with different substitution (e.g. aniline). Although the Hexcel resin is proprietary, the pre-cure spectrum suggests a B-staged resin similar to that formed from a Novalac cured with methylene dianiline (Figure 1).

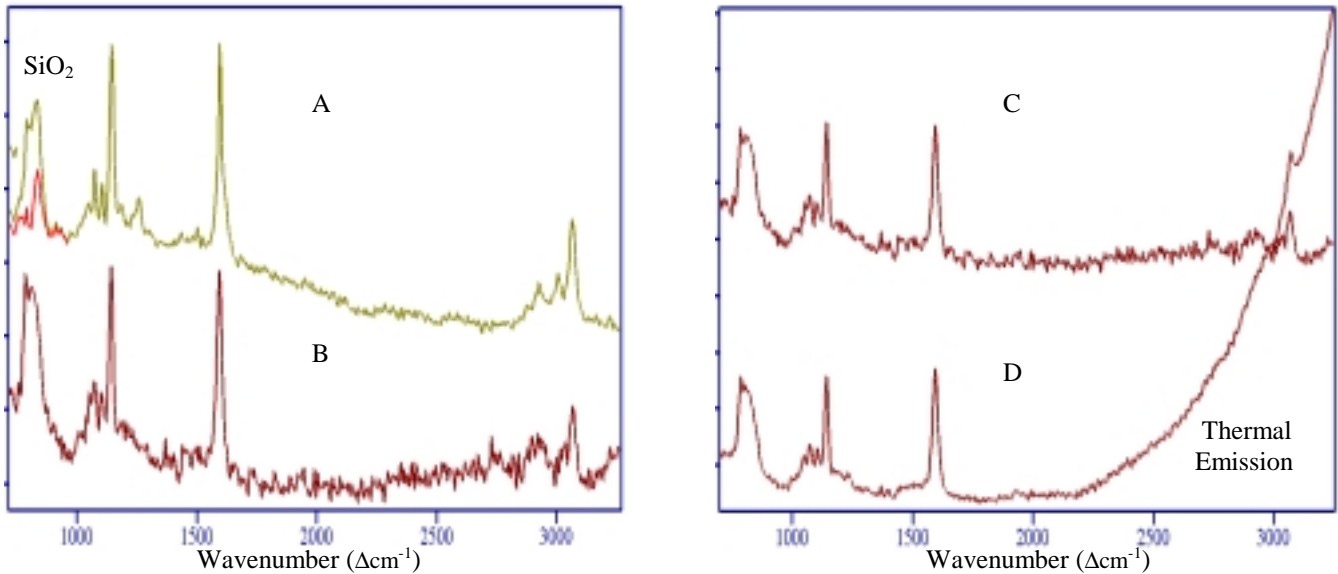


Figure 5. FT-Raman spectra of Hexcel 8552 composite at the A) onset (1.5 min, 30 $^{\circ}\text{F}$), B) and C) after cure (200 min, 350 $^{\circ}\text{F}$) in a TEC autoclave. Spectra obtained via a 3 m fiber optic probe consisting of a 200 μm source fiber optic and a 365 μm collection fiber optic. Spectral conditions: 700 mW of 1064 nm excitation, 100 averaged scans (3 min), 8 cm^{-1} resolution. Spectrum A) includes subtraction of 820 silica peak from the fiber optic probe to reveal 835 cm^{-1} peak. Spectrum B and C) obtained by spectral subtraction of the thermal emission from spectrum D).

The final spectrum, obtained by subtracting a thermal spectrum (laser off, Figure 5B), shows the expected disappearance of the epoxide modes at 1264, 1442 (less obvious) and 3012 cm^{-1} . The intensities (peak height or integrated peak area) of all three bands, normalized to the 1600 cm^{-1} band decrease in intensity at the same rate. Figure 6A shows the normalized spectral intensities for the 1264 cm^{-1} epoxide band as a function of cure time, the established method of monitoring cure rate by Raman spectroscopy.^{19,20} It is clear from the data that the reaction proceeds in two stages. Inclusion of the heat schedule in the figure shows that the reaction of the epoxide tracts the two ramp and hold heating stages. Each segment of the reaction was fit by a first order rate equation, viz: $\alpha_t = Ae^{-Bt}$, where α_t is the rate that the 1264 cm^{-1} epoxide band intensity decreases, t is time, A is a constant (1 for normalized data), and B is the rate constant. In Figure 6, $B = 4.3 \times 10^{-2}$ and $3.7 \times 10^{-2} \text{ I}_{1264}/\text{min}$

(normalized) for the first and second reaction segments, respectively. The errors in the fit to the data for each curve, R^2 (the coefficient of determination), were 0.96 and 0.97, respectively. Although the reaction rates are very similar, they represent different reaction mechanisms, in that, according to the Arrhenius equation ($k=AE^{-E/RT}$, E is the activation energy, R is the gas constant, and T is absolute temperature), the first reaction rate would have had to been 1.2×10^{-2} to correspond to the same reaction with the same activation energy.

Originally, the cure rate was to be determined by monitoring the shift of CH stretching bands as a group to lower wavenumbers by calculating the center-of-mass (or wavenumber, C_v) of the bands from 2800 to 3200 cm^{-1} , i.e. $C_v = \Sigma(v_i I_i) / \Sigma I_i$, where I is the intensity of the i th wavenumber element. This method had previously proven quite successful for monitoring diglycidyl ether of bisphenol A cured with triethyl tetramine by fiber optic Raman in a rheometer.^{13,23} However, the thermal emission at higher temperatures generated significant scatter in the data. Nevertheless, this approach was applied to the disappearance of the 1615 cm^{-1} weak shoulder of the intense 1600 cm^{-1} band. Since it is difficult to plot the decay of this indistinct band with any precision, the frequency weighted center of the entire 1600 region was plotted (Figure 6B). Again the data changes in two distinct regions corresponding to the two ramp and hold temperatures. The band center shifted slightly, 1603.5 to 1602 cm^{-1} , until the second temperature plateau, and then shifted rapidly to 1597 cm^{-1} . This data was also normalized from 0 to 1 (Figure 6) to allow comparing reaction rates. The first order rate constants, B , where 1.6×10^{-2} and $3.9 \times 10^{-2} C_{v1600}/\text{min}$, and R^2 where 0.88 and 0.86, respectively. According to the Arrhenius equation these rates probably represent the same reaction at different temperatures.

Since the exact chemical structures of the Hexcel resin reactants are unknown to us, it is not possible to identify the reaction mechanisms with certainty. However, the following can be stated regarding the kinetic data. The epoxide group is involved in two separate reaction mechanisms associated with the two ramp and hold temperature stages. The chemical group responsible for the 1615 cm^{-1} band is most likely involved in one reaction mechanism. This chemical group reacts at the same rate as the epoxide group at the higher temperature and is probably part of the same reaction mechanism. If it is assumed that the manufacturer's heat schedule is intended to initiate the expected reactions for epoxy resins, i.e. chain extension at the first temperature plateau and cross-linking at the second plateau, then it is reasonable to conclude that the 1264 cm^{-1} data represents these epoxide reaction mechanisms. Furthermore, the 1615 cm^{-1} data probably represents the cross-linking reaction. The spectral position of this band also suggests an aromatic $C=C$ assignment, and if it is in fact due to an aniline cross-linking agent, then the 1615 cm^{-1} band may represent secondary amine reactions, *viz.*: $-\text{Ar}-\text{NH}- \rightarrow \text{Ar}-\text{N}-$.

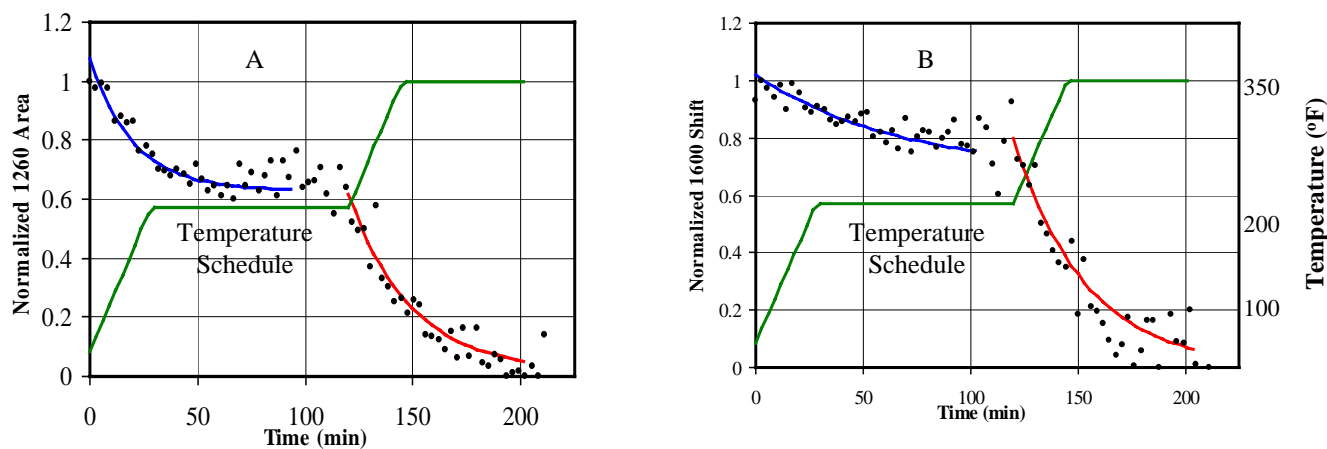


Figure 6. A) Plot of spectral intensities for the 1264 cm^{-1} epoxide band (I_{1264} , integrated area) normalized to the intensity of the 1600 cm^{-1} phenyl band (height) as a function of cure time (\bullet). B) Plot of the shift of the 1600 cm^{-1} center-of-mass (C_{v1600} , normalized to 1) as a function of cure time (\bullet). First order decay equations fit to the data illustrate that both spectral features change in two distinct steps associated with the heat schedule ($-$). The heat schedule is superimposed for comparison.

Finally, the real-time cure monitoring data suggests that little if any reaction occurs in the second hour. The Raman data suggests that the majority of the first reaction, presumably chain extension, is complete after 60 to 70 minutes. The second reaction could be initiated at this time, reducing the 4 hour manufacturing time to 3 hours. This could lead to substantial savings in energy, as well as an increase in production.

Figure 7 shows the first polyester cure spectrum collected at 30 °F and the last spectrum collected at 250 °F (80 min after cure was initiated). Again, the chemical structure of this prepreg is unknown to us, but many bands can be assigned. The two bands that are associated with polyester polymerization are the C=CH deformation mode at 1303 cm⁻¹ and the intense C=C ester stretching mode at 1650 cm⁻¹.²⁴ Other polyester bands include the C-O-C stretching modes observed at 873, 1075 (shoulder) and 1277 cm⁻¹, and the C=O stretch at 1735 cm⁻¹. Additional bands at 1460 and 2950 cm⁻¹ are assigned to CH₂ deformation and stretch, respectively. The intense bands at 1041 and 1606 cm⁻¹ are assigned to aromatic C=C ring stretching (phenyl groups). Similarly, the 3078 cm⁻¹ is assigned to an aromatic ring C-H stretch. Except for the 1041 cm⁻¹ band, all of these additional bands appear in the epoxy resin spectra and suggest similar functional groups, i.e. an alkane backbone with substituted phenyl groups. In fact most polyesters are cured by styrene,¹ which may be responsible for the phenyl bands observed.

The polyester cure reaction was monitored by normalizing the 1650 cm⁻¹ band to the 1606 cm⁻¹ band and plotting the intensity as a function of time (Figure 8). Again, the reaction rate closely trends the heating schedule. After an initial linear decay during the temperature ramp to 250 °F, the reaction becomes first order, with $B = 4.0 \times 10^{-2} I_{1650}/\text{min}$. The 1303 cm⁻¹ band height disappears at the same rate.

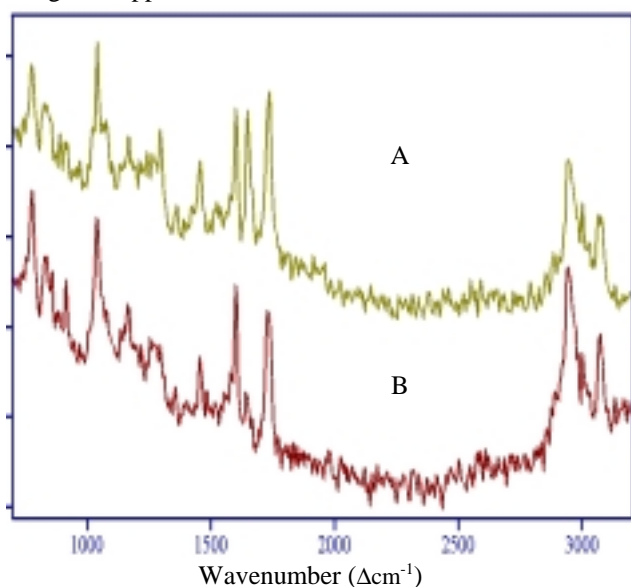


Figure 7. FT-Raman spectra of Cytec Cycom 4102 glass reinforced polyester composite at A) the onset (3 min, 30 °F) and B) after cure (80 min, 250 °F) in a TEC autoclave. Sample and spectral conditions as in Figure 5, except: 220 averaged scans (6.66 min), and subtraction of thermal emission was not required.

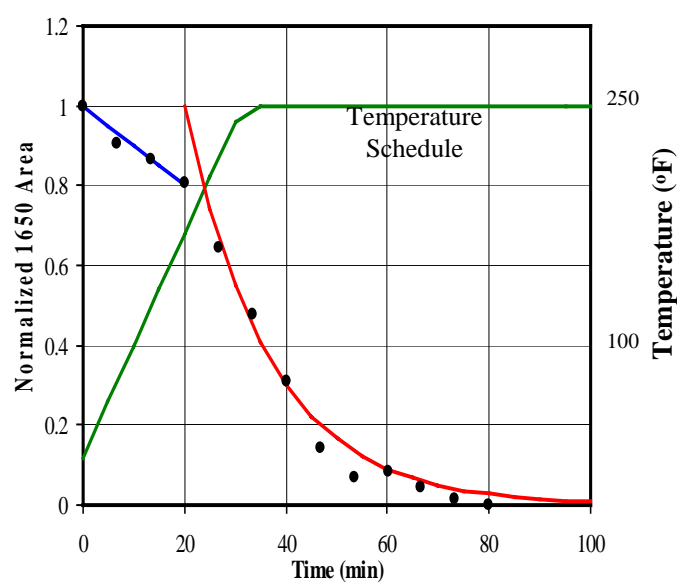


Figure 8. Plot of spectral intensities for the 1650 cm⁻¹ C=C band (integrated area) normalized to the intensity of the 1606 cm⁻¹ phenyl band (height) as a function of cure time (•). After an initial linear decay, the C=C band decays according to first order kinetics (-). The heat schedule is superimposed for comparison.

4. CONCLUSIONS

The cure of two high performance composites was measured in real-time within an industrial autoclave at temperatures up to 350 °F. The polymerization reactions of an epoxy and a polyester based composite were monitored by Raman spectroscopy (disappearance of the epoxide band at 1264 cm⁻¹, and the C=C band at 1650 cm⁻¹, respectively) via simple side-by-side fiber optic probes placed between the central ply layers. The cure rates of both composites tracked the temperature schedule and could be fit with first order rate equations. The epoxy was cured according to two ramp-and-hold temperatures and yielded the following information and interpretation. At each temperature plateau, the epoxide band decreased in intensity at similar rates. However, the relative activation energies are considerably different and indicate two different reaction mechanisms, possibly chain-extension and cross-linking. Different reaction rates for a second band at 1615 cm⁻¹ for each plateau corresponded to near identical activation energies (within experimental error). In addition, the rate of decay for this band closely matched the epoxide band at the higher temperature, and probably represents the same reaction mechanism.

Furthermore, the spectral position of the 1615 cm⁻¹ band indicates an aromatic C=C assignment, this coupled with the matching reaction rates, suggests assigning the higher temperature mechanism to the reaction of secondary amines plausible.

In addition to real-time process monitoring, the data suggests methods to control and improve autoclave processes. The Raman cure rate data for the epoxy composite indicate that the second reaction, initiated by an increase in temperature, is delayed 1 hour after the first reaction is complete. A substantial savings in energy, as well as an increase in productivity, could be realized if this delay is unnecessary. Also, the intensity of the bands associated with the polymerization reactions could also be compared to non-reacting bands (e.g. the 1600 cm⁻¹ phenyl ring band) prior to cure to estimate the extent-of-cure for the prepreg. This data could be used to adjust the cure schedule, not only to optimize energy and time usage, but to optimize material properties. Although these conclusions are based on limited data, the rich molecular information provided by Raman spectroscopy, strongly suggests that this analytical technique would be invaluable to monitoring and controlling composite processing.

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