Thermal Curing of Glass-Epoxy Prepregs by Luminescence Spectroscopy

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ABSTRACT: In this study, we investigated the application of the luminescence spectroscopy technique in steady-state conditions to study glass fiber-epoxy F161 prepregs. We conducted this study by comparing the results obtained from the intrinsic fluorescence with Fourier transform near infrared spectroscopy. The extrinsic fluorescence of 9-anthroic acid (9-AA) was also used. Fourier transform infrared spectroscopy was also used to characterize the epoxide resin. The prepregs containing 9-AA and those that did not were heat-treated at 177°C (F161) for 1100 min at a 2°C/min heating rate. The results obtained by both methods indicated that the crosslinking reaction could be monitored by analysis of the spectral changes of the emission bands of the prepreg and 9-AA. The intrinsic emission at 320 nm was attributed to the fluorophore group containing the epoxy ring and was used to calculate the conversion degree. The photophysical behavior of the 9-AA probe indicated a reduction of free volume of the polymeric matrix with curing process. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 664–671, 2010

Key words: composites; curing of polymers; FT-IR; luminescence; photophysics

INTRODUCTION

Polymer-matrix composites are a combination of two or more components (reinforcing elements, fillers, and composite matrix binders) differing in form or composition on a macroscale. The reinforcing elements can be high-performance reinforcement glass, carbon, or polyamide fibers impregnated with a thermoplastic or thermosetting matrix binder. Epoxy resins, phenolic resins, and bismaleimide resins are commonly used thermosetting resins. Many advanced composites are constructed from thin laminating sheets known as *prepregs*, which is a shorthand expression for "preimpregnated." Prepregs consist of unidirectional or fabric fiber impregnated with a polymeric resin in the B stage that has been partially crosslinked at different points of the polymeric matrix. In this stage, the polymeric matrix is weak and susceptible to organic solvents. In the C stage, the crosslinking reaction is completed, with the material presenting high chemical and thermal resistance.[1–3]

The performance of the composite material depends on the reinforcement structure, fiber volume fraction, void content, resin-to-fiber bonding, and degree of resin cure. The degree of cure is crucial, especially at elevated temperature, to the achievement of high-performance applications, as, for instance, in primary aircraft structures.[4] However, the study of the curing process in the polymers and composites before, during, and after the fabric process is extremely important for reproducible processability and achievement of consistent mechanical properties.[5]

Some researchers have applied the luminescence spectroscopy technique in the study of moisture aging effects on composites and the resin curing process. Luminescence spectroscopy is a suitable nondestructive technique for the monitoring of the curing of resins. The technique's high sensitivity also allows one to study resins when an adequate molecular probe is located in the polymer matrix.[6,7]

Epoxy resins are thermosetting polymers synthesized through the reaction between epichloridrine and bisphenol A. In the crosslinking reaction or curing reaction, reactive molecules, called *hardeners* or *curing agents*, are used. Amines are one of the most important agents used for the curing of epoxide resins.[8] A significant spectral shift in the fluorescence emission maximum was observed during the curing process between the epoxide resin diglycidyl ether

of bisphenol A (DGEBA) and the aromatic diamine 4,4′-diaminodiphenylsulfone.[9,10] Sales and Dibbern-Brunelli[11] studied the curing process of the epoxy resin DGEBA with the curing agents 4,4′-diaminodiphenylmethane and 4,4′-diaminodiphenylsulfone. Two fluorescence methods were used: the intrinsic method, related to the polymeric matrix, and the extrinsic method, with the molecular probe 9-anthroic acid (9-AA). The results obtained by both methods indicated that the crosslinking reaction could be monitored by the analysis of the spectral changes of the emission bands of DGEBA, curing agents, and 9-AA.

The purpose of this study was to examine the effects of heat treatment on glass/epoxy prepregs through the application of the luminescence technique in the steady state with intrinsic and extrinsic fluorescence methods with the 9-AA molecular probe.

EXPERIMENTAL

Preparation of the samples

A unidirectional glass fiber/epoxy resin prepreg, F161 (Hexcel Composites Ltd., Livermor, CA), with a nominal size (30×20 mm^2) was used. 9-AA (Aldrich Chemical Co., Inc.) was incorporated into the prepreg samples through the addition of 0025 mL of a 0.1 mol/L solution of the molecular probe in *n*-butanol (Aldrich). The prepreg samples, with and without 9-AA, were heat-treated to 177°C (F161) for 6 h at a 2°C/min heating rate with an oven (EDG3000-EDGCON3P, São Carlos, Brazil). The samples were removed from the oven at every 1 h for analysis and were allowed to cool to room temperature for 20 min.

Fourier transform infrared (FTIR) spectroscopy

FTIR analyses were performed in a Spectrum One PerkinElmer spectrometer (Shelton, CT) with a universal attenuated total reflectance (UATR) accessory with acquisition parameters as follows: (1) 4000–400-cm^{-1} spectral width (midinfrared) and (2) 8000–4000 cm^{-1} [near infrared (NIR)], 4 cm^{-1} resolution, 1 gain, and 40 accumulations.

The samples were analyzed by FTIR transmission techniques: liquid film and controlled pyrolysis-FTIR (CONTROLPIR/FTIR).[12] In CONTROLPIR/FTIR, a prepreg sample was pyrolyzed in a Spectra-Tech PY-2 (Stamford, CT) at 600°C for 5 min, and the products were analyzed as liquid film.

The epoxy conversion (α_{NIR}) was calculated with eq. (1) with the NIR absorption peaks:

$$\alpha_{NIR} = 1 - \frac{\left[\left(A_{E,t} \right) \left(A_{R,0} \right) \right]}{\left[\left(A_{E,0} \right) \left(A_{R,t} \right) \right]} \quad (1)$$
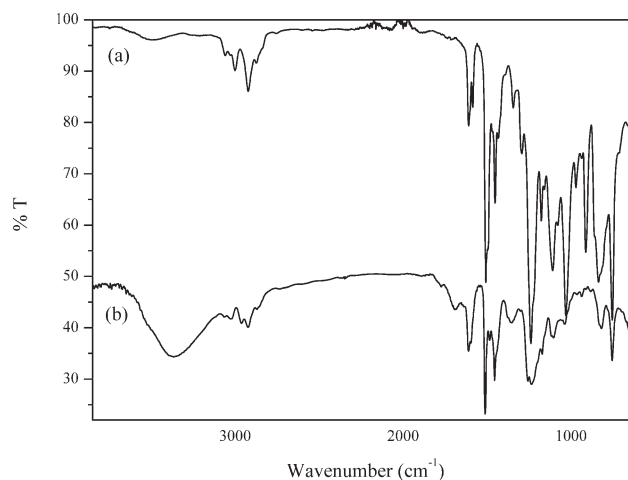

Figure 1 (a) F161 sample and (b) control pyrolyzed sample of F161 at 600°C/5 min.

where A_{E0}, and A_{R0}, are the initial areas of the bands at 4530 and 4623 cm^{-1}, attributed to the epoxy and phenyl groups (internal reference), respectively, and $A_{E,t}$ and $A_{R,t}$ are their corresponding values at a given time t.[13–16]

Emission and excitation spectra

Fluorescence spectra were measured with a steady-state luminescence spectrometer (FS920-Edinburgh Analytical Instruments, Edinburg, Scotland) in the photocounting mode with a xenon arc lamp 450 W (Osram Co.) and double holographic grating monochromators of excitation and emission (Czerny-Turner configurations).

The fluorescence spectra of the solid samples were obtained through a front-face illumination. The excitation wavelengths were carefully chosen because the epoxy resin presented many emission bands in the 290–380-nm range.[11]

The conversion degree through the intrinsic luminescence technique (α_I) was calculated with eq. (2):

$$\alpha_I = \frac{(I_t - I_0)}{(I_\infty - I_0)} \quad (2)$$

where I_t, I_0, and I_∞ are the relative intensities of the 320-nm emission band at time $t = t$, $t = 0$, and $t = \infty$, respectively, during the curing process.[13,17]

RESULTS AND DISCUSSION

Infrared spectroscopy of the F161 prepreg

FTIR of F161 prepreg

F161 prepreg was characterized by means of FTIR. Figure 1 shows the FTIR spectra of the F161 prepreg sample as received, and the products of the controlled pyrolyzed samples. A remarkable similarity

TABLE I
Band Assignments of the FTIR Spectra of Prepreg
F-161[17–25]

Wave number (cm^{-1})	Band assignment
3496	νOH free
3228	ν_sN—H
3062	Combination band of νCOC epoxy and ν_sCH$_3$
3027	νCH aromatic stretching
2999	νCH aromatic ring
2923	ν_aCH$_2$, νCH
2874	ν_sCH$_3$
1609	νC=C aromatic ring buckle
1584	νC=C aromatic ring buckle
1507	νC=C aromatic ring buckle
1453	δ_sCH$_2$
1432	
1345	δ_sCH$_3$
1293	νC—O aromatic ethers with alkoxy groups
1237	νCOC epoxy
1177	νAr—H symmetrical axial deformation
1158	νC—O
1110	νC—O
1078	δ_aC—N symmetrical axial deformation
1031	νC—O
972	νCOC epoxy
913	νCOC epoxy
835	δ phenyl—H
756	δCCN

*, vibrations; ν, stretching; ν_a, asymmetric stretching; ν_s, symmetric stretching; δ, deformation; δ_a, asymmetric deformation; δ_s, symmetric deformation.

was observed between the F161 spectrum [Fig. 1(a)] and the spectrum of the poly(glycidyl ether) of phenol formaldehyde novolac of the literature;[1] this indicated that this epoxide resin was used. The great advantage of this type of epoxide resin is the considerable number of epoxide groups in relation to DGEBA.[1] Table I shows the wave numbers of the bands and their respective assignments.[18–26]

The FTIR spectrum of the F161 sample [Fig. 1(a)] showed an absorption band at 3496 cm^{-1} due to the hydroxyl group. Delor-Jestin et al.[19] assigned the bands at 1610, 1585, and 1510 cm^{-1} to the C=C vibration of the phenyl groups. The absorption bands at 1237, 930, and 913 cm^{-1} were assigned to the stretching vibrations of the epoxide groups and decreased along the curing process.[27,28] The absorption bands at 1295, 1158, and 1110 cm^{-1} were attributed to stretching vibrations of the aromatic ethers with alkoxy groups.

There were also additional bands in the spectrum that were not related to the epoxide resin. A low-intensity band was observed at 3228 cm^{-1} and an absorption peak was observed at 1078 cm^{-1} that were attributed to the N—H stretching vibration[29] and axial bending of the C—N linkage, respectively. This suggested that the last two bands might have been related to functional groups of the curing agent.

The curing agents commonly used in epoxide resins are aliphatic and aromatic amines, aromatic amides, and compounds containing anhydride groups. Delor-Jestin et al.[19] observed absorption bands at 1860 and 1740 cm^{-1} related to anhydride carbonyl groups of the DGEBA-anhydride mixture. Tanaka et al.[30] observed that the absorption spectra of films of polyamideimide and bisphenol A epoxide resin presented bands at 1664 and 1531 cm^{-1}, which were assigned to carbonyl stretching and amide N—H bending, respectively. Because no absorption peaks were observed in this region of the spectrum, we presumed that the curing agent of the F161 prepreg did not contain amide and anhydride groups.

To try to characterize the curing agent, we performed a controlled pyrolysis of the F161 prepreg and obtained an FTIR spectrum [Fig. 1(b)] of the oxidation products as a liquid film. A broad band was observed at 3300 cm^{-1} and a low intensity band was observed at 1380 cm^{-1} due to the stretching of OH—H bonds and in-plane angular bending O—H, respectively. The spectrum also showed C—H stretching bands at approximately 3000 cm^{-1} overlapped with a broad band assigned to different contributions of the hydroxyl groups linked by hydrogen bonds and protonated primary amines.[31]

The absorption of the carbonyl group appeared at 1775 and 1691 cm^{-1}. Additionally, an enlargement of the bands assigned to the ether aromatic bonds in the 1100 cm^{-1} region was verified. It was established that polymer degradation in the presence of oxygen leads to the formation of a complex mixture of products, such as alcohols, hydroperoxides, lactones, esters, carboxylic acids, and ketones. The hydroxyl and carbonyl bands were attributed to the numerous oxidation products.[19] The epoxide groups were not observed because the band at 913 cm^{-1} did not appear, but the bands at 940, 884, and 822 cm^{-1} indicated substitution in the epoxide ring. This suggested that the uncured resin did not appear in the oxidation products, but the pyrolytic process formed small fractions of the epoxide resin.

Finally, absorption peaks were observed at 1596, 1485, and 1358 cm^{-1}; these were attributed to the bending modes of N—H bonds in secondary and primary amines. Although it was not possible to exactly identify the curing agent, this suggested that it contained amine groups. This information was very useful for the attribution of the intrinsic luminescence of the F161 spectra.

Fourier transform near infrared (FT-NIR) spectroscopy

Shown in Figure 2 are the NIR region absorption spectra of the uncured sample and samples submitted to heat treatment for the following periods of
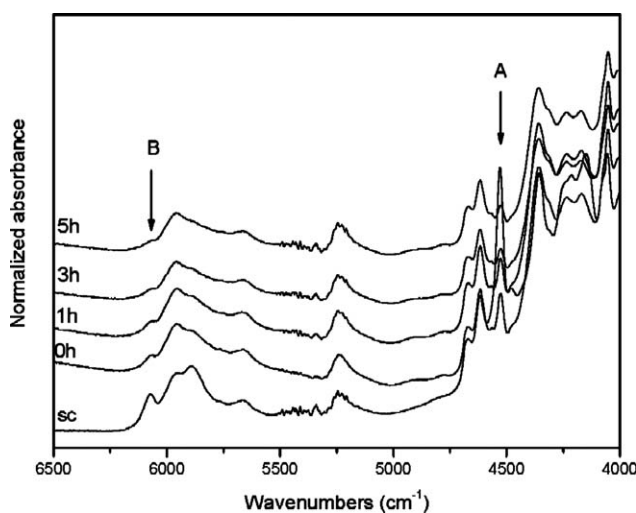
Figure 2 FT-NIR spectra of the uncured prepreg F-161 and samples submitted to the thermal treatment at 177°C.

Figure 3 FT-NIR spectra of prepreg F-161 during the curing reaction.

time: 0, 1, 2, 3, 4, 5, and 6 h at 177°C. The main absorption bands, including epoxy, methylene, and phenyl groups, agreed with those reported in the literature[24] for the epoxide resin.

According to Musto et al.,[16] the peaks at 6064 cm^{-1} [Fig. 2(B)] and 4524 cm^{-1} [Fig. 2(A)] are related to the epoxy ring. These peaks could be attributed to the first overtone of the terminal CH_2 stretching mode and to a combination band of the second overtone of the epoxy ring stretching at 916 cm^{-1} with the fundamental C—H stretching at about 2725 cm^{-1}, respectively.[16,32] The relative intensities of both absorption bands were considerably reduced with heat treatment and after the postcuring process, with the bands almost completely disappearing (Fig. 2).

The band at 4534 cm^{-1} was attributed to a combination of the stretching fundamental (3050 cm^{-1}) with the CH_2 deformation fundamental (1460 cm^{-1}) of the epoxy ring.[14,15,33] The FT-NIR spectra of the heat-treated prepreg with time are shown in Figure 3. A relative intensity decreasing of the band at 4534 cm^{-1} with heat treatment was observed. The band at 4625 cm^{-1}, attributed to the normal mode vibration of the phenyl groups, did not show any dependence on the reaction time and was used as an internal standard.

The first step of the epoxy curing reaction through diamine curing agents consisted of epoxy ring opening by the amine group forming the secondary amine and hydroxyl groups. In the second step, there was a subsequent reaction of the secondary amine and another epoxy ring generating a tertiary amine group.[5]

Fluorescence spectroscopy of the F161 prepreg

Intrinsic fluorescence

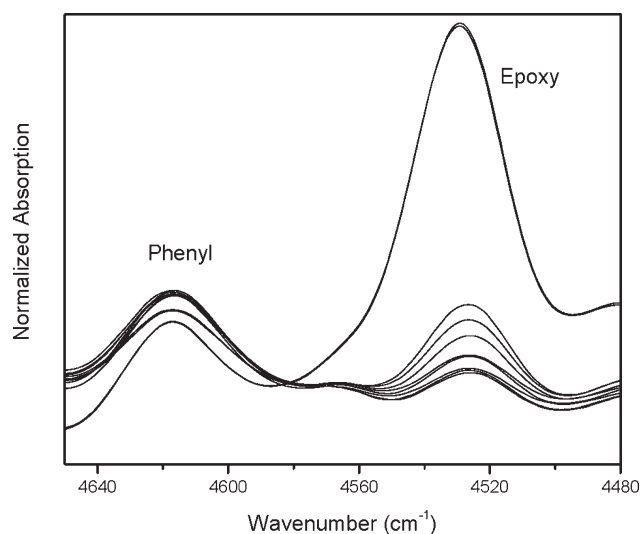The intrinsic fluorescence emission spectra of the prepreg samples were analyzed to estimate the

curing process of the samples and to compare them with results obtained through the FT-NIR technique. Because these emission spectra had a strong dependence on the excitation wavelength,[11] the excitation wavelength at 290 nm was selected, which was more adequate for the study.

Figure 4 shows the emission spectra of the uncured and heat-treated prepreg samples. The uncured sample presented a broad and unstructured band at 320 nm, which decreased, whereas the intensity of the three shoulders at about 420, 450, and 470 nm increased with curing time. The FT-NIR analysis of the prepreg samples revealed that the most significant spectral change was related to the substitution reaction in the oxirane ring. We presumed that the emission band at 320 nm was related to the fluorophore group that contained this group.
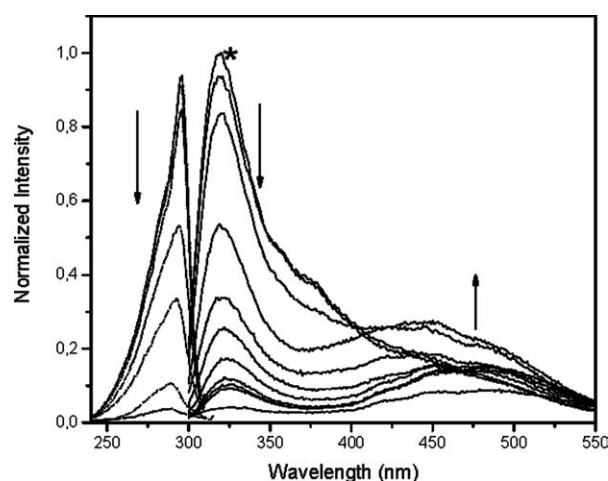

Figure 4 Intrinsic excitation (λ_{em} = 320 nm) and emission spectra (λ_{exc} = 290 nm) of the F161 prepreg samples.
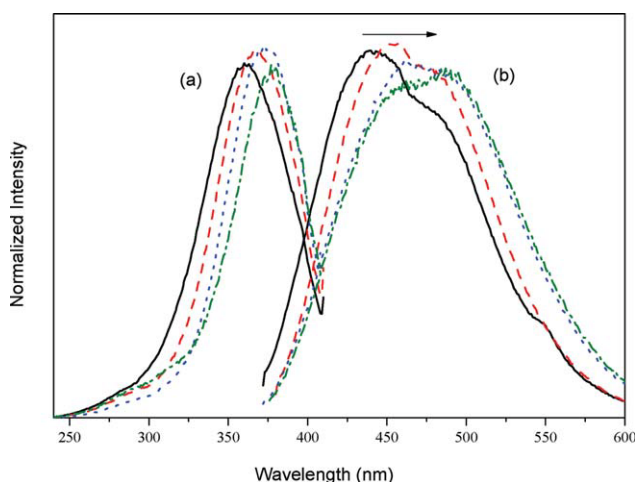
Figure 5 Intrinsic excitation (λ_{em} = 420 nm) and emission spectra (λ_{exc} = 360 nm) of the F161 prepreg samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The decrease in the epoxy group intensity was confirmed through the analysis of the sample's excitation spectra at an emission wavelength of 290 nm (Fig. 4). The reactivity of the epoxide resin was related to the cyclic ether bond (epoxy group). The epoxide ring could be easily opened during the curing process.[1] Bands located in the red region were attributed to the secondary and tertiary amines that were formed through the curing reaction. An increase in the band relative intensity was observed at 450 nm.[5,9,34,35]

To analyze the photophysical behavior of the fluorophore in the red region of the spectrum, the excitation (λ_{em} = 420 nm) and emission (λ_{exc} = 360 nm) spectra of the prepreg samples were obtained. The emission spectrum of the F161 prepreg at the beginning of the heat treatment [Fig. 5(a)] showed a 440-nm band and a shoulder at about 477 nm. The following spectral changes, dependent on the heat treatment time, were observed: (1) a continuous band redshift of 15 nm, (2) a decrease in the shoulder maximum intensity at 456 nm, and (3) an increase in the shoulder maximum intensity at 480 nm. These spectral changes observed after heat treatment were associated with the crosslinking reaction and conversion of primary amines into secondary and tertiary amines because it was suggested that the curing agent contained amine groups through the FTIR spectroscopy.[9,36,37] The beginning of the crosslinking process occurred when the primary amino hydrogens reacted in the first step to form linear oligomers; then, network structures were formed in the second step through the reaction of the secondary amino group with the epoxy group. The networks contained rigid structure units of the

epoxy compound and the crosslinker and short aliphatic chains resulting from glycidyl groups.[37]

Figure 5(b) shows the excitation spectra of the F161 prepreg at an emission wavelength of 420 nm before and after heat treatment and reveals a broad band before the heat treatment with a maxima at 361 nm. After the heat treatment, the excitation spectra showed a similar trend as in the emission spectra as a function of the curing time;[38] the excitation maximum showed a redshift up to 13 nm, related to the crosslink process.[5]

Table II summarizes the most important bands that allowed the characterization of the F161 prepreg through the FTIR, FT-NIR, and intrinsic luminescence techniques.

Extrinsic fluorescence

Figure 6 shows the emission spectra of prepreg samples containing 9-AA. A decrease in the relative intensity and a redshift in the fluorescence maxima were observed with heat treatment. The photophysical behavior of the 9-AA probe was strongly dependent on the medium polarity and concentration.[39,40] The carboxylic group of 9-AA in the monomeric form had a perpendicular plane in relation to the anthracene ring in the ionized form in both electronic states, ground and excited; this resulted in an anthracene-like emission.[39–43] The 9-AA broad emission band was attributed to the 9-AA protonated form,[4,41,44] which presented a rotation of the carboxyl group in the excited state into a position approaching coplanarity with the anthracene ring. There was significant resonance interaction between the carboxyl groups, which, hence, changed the nature of the excited state and resulted in the broad emission band. We presumed that the increase in the 9-AA concentration caused a displacement of the acid-base equilibrium (Fig. 7) to the protonated form. However, a supplementary increase in the 9-AA concentration led to the formation of dimeric species because a redshift of the broad band was observed. This redshift of the emission maximum was observed in the emission spectra of 9-AA highly concentrated solutions in ethanol.[11]

It was established that the increase in the crosslinking density led to a decrease in the specific volume of the polymeric matrix and, as a consequence, a decrease in the free volume. This effect was directly related to the increase in the material cure degree.[45,46] The decrease in the free volume available to dissolve the probe led to an increase in the local concentration of 9-AA and the consequent dimer formation. These effects were confirmed by the samples' excitation spectra. The excitation spectra of 9-AA at the beginning of the heat treatment showed

TABLE II
Attribution of the Main Bands of FTIR, FT-NIR, and Intrinsic Fluorescence Spectra Used in the F161 Prepreg Characterization

	λ_{em} (nm)	Attribution	FTIR (cm^{-1})	Attribution	FT-NIR (cm^{-1})	Attribution
Epoxy resin[a]	320 $\lambda_{exc} = 290$ nm	Fluorophore containing the epoxy group	3492	νOH	6064 4524	Epoxy group
			1610 1585 1510	νC=C phenyl group	4625	Phenyl group
			1237 972 913	ν COC epoxy		
			1158 1110	ν C—O		
Curing agent[b]	420 450 470 $\lambda_{exc} = 360$ nm	Primary, secondary, and tertiary amines	3228	ν_s N—H		
			1078 756 1596[c] 1485[c] 1358[c]	δ_aC—N δCCN δN—H		

[a] Poly(glycidyl ether) of phenol formaldehyde novolac.
[b] Curing agent containing amine groups.
[c] Controlled pyrolyzed sample.

a structured band peak at 352, 369, and 388 nm with the same excitation spectra profile of 1×10^{-4} mol/L 9-AA in DGEBA solution.[11] Nevertheless, the spectra of the heat-treated samples showed a decrease in the relative intensity of the peaks at 352 and 369 nm until the complete disappearance of the same peaks at the end of the curing process. This photophysical behavior confirmed the formation of the 9-AA dimeric form.
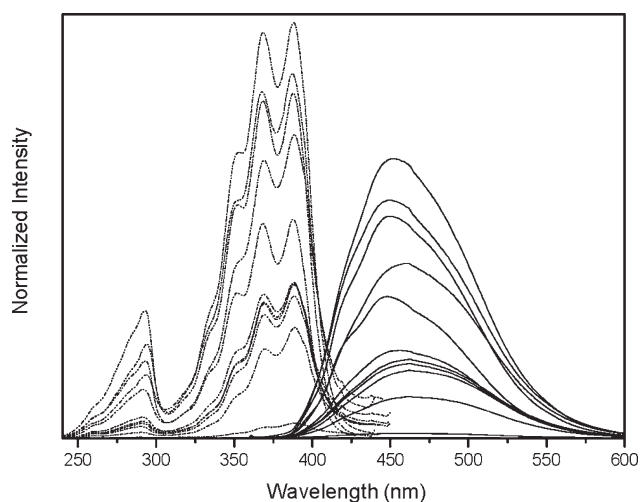

Figure 6 Electronic excitation ($\lambda_{em} = 450$ nm) and emission spectra ($\lambda_{exc} = 350$ nm) of the F161 prepreg samples with 9-AA.

Comparison between the FT-NIR and luminescence spectroscopy

Figure 8 shows the conversion curves of the F161 prepreg obtained through the FT-NIR and intrinsic luminescence techniques. The FT-NIR curve [Fig. 8(a)] showed two different segments; the first one, from the beginning of the cure reaction to approximately 60 min, presented a very fast rate, and the second one showed a slow rate, which is usually attributed to a reduction in the curing rate when the reaction becomes diffusion controlled.[17]

The intrinsic luminescence curve [Fig. 8(b)] shows four distinct segments: (1) a decrease in the epoxy conversion at approximately 20 min, (2) a significant increase in the time range of 20–60 min, (3) a slow increase in the time range 60–300 min, and finally, (4) the practical stabilization of the curing degree at 0.95 from 300 to 1000 min.

The first segment (1) that presented a decrease in the epoxy conversion indicated the gel formation of the polymeric matrix. We established that the gelation process consisted of the formation of a
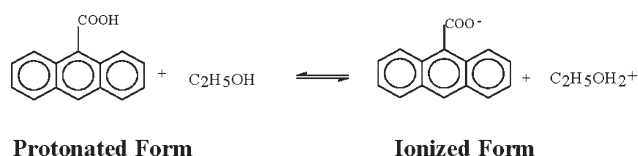

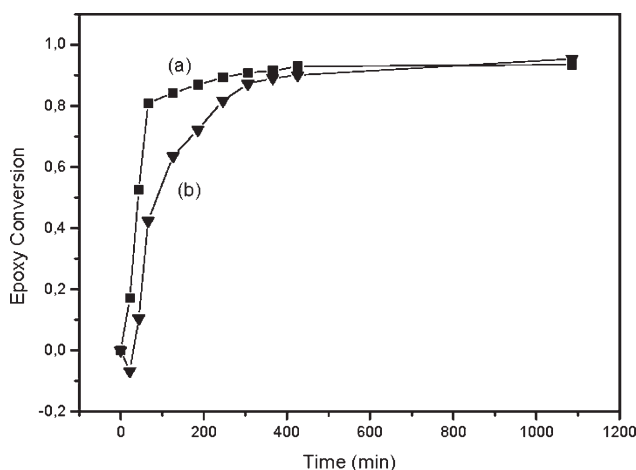**Figure 7** Acid-base equilibrium of 9-AA in ethanol.

Figure 8 Epoxy group conversion as a function of curing time (min) measured at 177°C with (a, ■) FT-NIR and (b, ▼) intrinsic luminescence methods.

crosslinked network, which lost its ability to flow and was no longer able to be processed above the gel point. This suggested that a decrease in the mobility of the polymeric matrix occurred, which led to an increase in the rate constants of the radiative processes and a consequent increase in the relative intensity of the band at 320 nm that was used to calculate the epoxy conversion. Therefore, the technique could not be used to obtain the curing degree in the first stage of the curing process. Rigail-Cedeno and Suñg[15] studied the curing process of the DGEBA-amine system and verified the same behavior.

The second segment (2) showed the same tendency observed in the FT-NIR curve and indicated a very fast crosslinking reaction; the third one (3) also showed a diffusion-controlled reaction, but it presented a better resolution at approximately 200 min in relation to the FT-NIR curve. The last segment (4) shows a stabilization of the epoxy conversion that varied from approximately 0.90 at 400 min to about 0.95 at 1100 min. It is important to emphasize that the curing degree at the end of both curves was very close.

Comparing both techniques, we concluded that with the FT-NIR technique (Fig. 8), a chemical reaction was followed, so higher changes in conversion were observed from the beginning until the gel conversion was reached. At this point, the viscosity of the system increased very rapidly to effectively infinity, and minor changes in the chemical reaction took place until the vitrification was reached, when the reaction stopped. On the other hand, with the fluorescence technique, it was possible to detect physical changes in the system associated with chemical reaction at the gel point that were compatible with the time of 7 min provided by the prepreg's

supplier (Hexcel, http://www.hexcel.com).[17] After the gel point, it was possible to detect the chemical reaction of epoxy ring opening as it was sensed through FT-NIR.

CONCLUSIONS

The epoxy resin used in the F161 prepreg was the poly(glycidyl ether) of phenol formaldehyde novolac that was identified through the FTIR technique. Although the curing agent was not clearly identified, the FTIR bands at 3228, 1078, and 756 cm^{-1} were attributed to the vibrational modes symmetric stretching of N—H group (v_s N—H), asymmetric deformation of C—N group (δ_aC—N), and deformation of CNN group (δCCN), respectively; this indicated that it contained amine groups. The FTIR spectrum of the sample's oxidation products confirmed the presence of the amine groups of the curing agent.

The intrinsic fluorescence method was very useful in the quantitative analysis of the cure characterization of the composite through the emission band at 320 nm, attributed to the fluorophore containing the epoxy ring, because it was opened during the curing process. However, it was not possible to calculate the curing degree in the first stage of the polymeric matrix crosslinking. On the other hand, the gel point could be detected through the technique because it was sensitive to both the physical and chemical changes of the polymeric matrix. It is important to emphasize that the curing degree at the end of both FT-NIR and luminescence curves was very close.

The photophysical behavior of the molecular probe 9-AA used in the extrinsic luminescence method showed that there was a reduction of the specific free volume, as was indicated by the formation of the dimeric species, which presented a broad and redshifted band.

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