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Study of curing process of glass fiber and epoxy resin composite by FT-NIR, photoacoustic spectroscopy and luminescence spectroscopy

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Abstract This article investigates the application of the luminescence spectroscopy technique in steady-state conditions to study the glass fiber–epoxy F155 *prepreg*. The study was conducted by comparing the results obtained from the intrinsic fluorescence with the data obtained by application of Fourier Transform Near Infrared spectroscopy (FT-NIR) and photoacoustic spectroscopy in the medium infrared spectroscopy (PAS) to the same material. Extrinsic fluorescence of 9-anthroic acid (9-AA) was also used. Infrared spectroscopy with Fourier transform the medium region (FT-IR) was also used to characterize the epoxy resin. *Prepregs* containing 9-AA or not were heat treated at 121 °C (F-155) for 360 min at a 2 °C/min heating rate. The results obtained by both methods indicated that the cross-linking reaction can be monitored by analyzing the spectrometric changes of the emission bands of the *prepreg* and 9-AA. The intrinsic emission at 368 nm was used to calculate the conversion degree. The photophysical behavior of 9-AA probe indicated a reduction of free volume of the polymeric matrix with curing process.

Introduction

The spatial and aeronautic industries were the first industries using advanced composites; since they are lighter than alloys and have excellent mechanical properties. In order to achieve high performance in applications such as primary structures in aircrafts, the degree of cure is crucial, especially at elevated temperature [1].

Composites materials are not well understood yet. Within each class of matrix many different resin formulations and material systems are available. This great variation, with the capability of tailoring the material to specific applications, prevents generalizations related to material properties and processing. Because of this limitation, it is necessary to characterize each individual material [47]. In the last two decades, some researchers have applied luminescence spectroscopy technique in moisture aging effects and the composites and resins curing process. Luminescence spectroscopy is suitable nondestructive technique for monitoring the curing of resins. Network formation due to crosslinking in polymers is a complex process, and it is specific interest in both basic and applied research. During the thermal curing of epoxies, the sample changes from a low-molecular-weight liquid mixture to a highly crosslinked network. The molecular mobility in the system decreases as the cure reaction proceeds [45, 60].

The technique sensitivity allows studying the resin when an adequate fluorophore is added to the polymeric matrix [4, 56]. It is possible with this technique obtain information about polymers miscibility in blends, chain mobility,

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microviscosity, and molecular mobility in different environments. When such a probe is incorporated in a polymerizing medium, its fluorescence changes with the conversion of monomers into a polymer [21, 38, 50, 51].

The fluorescence technique is more versatile than the other techniques as dielectric spectroscopy and infrared absorption with Fourier Transform, since the first requires the adaptation of a micro-sensor remote dieletrometric and the second requires the use of an attenuated total reflectance accessory [8, 30], once the laminated composite materials, made with carbon or glass fibers, are opaque materials. Several authors [35, 36, 41] are using the fluorescence technique to study the curing process in epoxy systems.

Then, the purpose of this study is to characterize and study the heat treatment effect of glass/epoxy *prepreg* F-155 through the application of the luminescence technique in steady state using intrinsic and extrinsic fluorescence methods, comparing the results with the data obtained by Fourier Transform Near Infrared spectroscopy (FT-NIR) and photoacoustic spectroscopy in the medium infrared spectroscopy (PAS).

Materials and methods

Preparation of the samples

A unidirectional glass fiber/epoxy resin *prepreg*, F-155 (Hexcel Composites Ltd), with a nominal size (30 × 20 mm) was used. 9-anthroic acid (9-AA) (Aldrich Chemical Company, Inc) was dissolved in *prepreg* samples through the addition of 0.025 mL of a solution 0.1 mol/L of the molecular probe in *n*-butanol (Aldrich Chemical Company, Inc). Two *prepreg* samples, with and without 9-AA, were analyzed before the heat treatment and were considered the first point of the analytical curves. The *prepreg* samples, with and without 9-AA, were heat treated to 121 °C at a 2 °C/min heating rate, using an oven EDG3000-EDGCON3P. In the beginning of heat treatment, each sample was removed from the oven at every 17 min until reaching 121 °C, after that each sample was removed from the oven at every 1 h until 6 h. All samples were cooled down to room temperature for 20 min before to be analyzed. The same sample was used to obtain the fluorescence and FT-IR spectra.

The molecular probe 9-AA was chosen since it presents a photophysical behavior strongly dependent on the concentration and the medium. Previous studies have shown that the carboxylic ion of the 9-AA ionized form remains in the perpendicular plane in relation to the anthracene ring in the excited electronic state and so, the net result is an anthracene-like emission [54]. Therefore, it can conclude that structured emission band can be assigned to the ionized form of 9-AA. As the concentration increases, it appears a broad band at, that can be assigned to the protonated form of 9-AA. It was discussed that the protonated form presents a rotation of the carboxyl group in the excited state into a position approaching co-planarity with the anthracene ring. There can be significant resonance interaction between the carboxyl groups changing the nature of the excited state and resulting in the broad emission band.

Fourier transformed infrared spectroscopy

The uncured *prepreg* samples were analyzed using Fourier transform infrared spectrometer PerkinElmer Spectrum 2000 using KBr pellets between 4000 and 400 cm^{-1}, resolution 4 cm^{-1}, gain 1 and 40 scans.

During the heat treatment, the analyses of each sample were performed using a PerkinElmer spectrometer Spectrum 2000 with photoacoustic detection in the medium infrared region. The samples were analyzed in the near region by SPECTRUM ONE PerkinElmer spectrometer using a universal attenuated total reflectance (UATR) accessory with acquisition parameters as 8000–4000 cm^{-1}, 4 cm^{-1} resolution, 1 gain and 40 accumulations.

Equation 1 was used to calculate the epoxy conversion:

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

where $A_{E,0}$ and $A_{R,0}$ are the initial areas of the NIR absorption peaks at 4530 and 4623 cm^{-1}, attributed to the epoxy and phenyl groups (internal reference), respectively, and their corresponding values at a given time t, $A_{E,t}$ and $A_{R,t}$ [26, 33, 35].

Emission and excitation spectra

Fluorescence spectra were measured using a steady-state luminescence spectrometer (FS920-Edinburgh Analytical Instruments) in the photo-counting mode, equipped with a xenon arc lamp 450 W (Osram Co) and double holographic grating monochromator 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, since the epoxy resin presented many emission bands in the 290–380 nm range [43].

The conversion degree through the intrinsic luminescence technique was calculated using Eq. 2.

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

where I_t, I_0, and I_∞ are the relative intensities of the 360 nm emission band at time $t = t$, $t = 0$, and $t = \infty$, respectively, during the curing process [35, 36].

Results and discussion

Prepreg F-155 characterization by FT-IR

Infrared spectroscopy with Fourier transform in the medium region (FT-IR) of *prepreg* F-155 (Fig. 1) was used to characterize the components of the polymeric matrix and the effect of curing process. In comparison with the literature, the spectrum of the *prepreg* F-155 shows a similarity in the band shape and peak positions with the diglycidyl ether of bisphenol-A (DGEBA) [39] indicating that this type of epoxy resin was used as *prepreg* matrix. It is also possible the identification of the curing agent dicyandiamide (DDA) and the accelerator DIURON® analyzing the FT-IR spectrum of *prepreg* [58]. Table 1 shows a detailed assignment of normal modes of vibration of the FT-IR spectrum.

DGEBA epoxy resin shows some characteristic bands, whose assignments are discussed in the literature. The wavenumber at 1608, 1456, and 1511 cm^{-1} are attributed to the aromatic ring stretching of C=C [9, 13, 28], and the band setting at 1246 cm^{-1} is related with the stretching of C–O groups bonded to the aromatic rings, although some authors [29, 55, 62] attribute the same band to the epoxy group vibration C–O–C. Bondzic et al. [5] have attributed the band at 1184 cm^{-1} to the stretching mode of Ar–C–Ar, where Ar represents the aromatic ring. The band at 1037 cm^{-1} was attributed to the stretching between carbon atom of aromatic ring and oxygen atom [28]. The aromatic ring breathing is verified at 1011 cm^{-1}, observed by Tait et al. [55]. Finally, DGEBA shows a characteristically epoxy band at 914 and at 830 cm^{-1}, attributed to the C–H deformation at the *para* position in the aromatic rings [28].

The bands in the region between 3200 and 3100 cm^{-1} are attributed to the normal stretching mode vibration of the C–H bond of CH_2 and CH_3 groups. The band at 3057 cm^{-1} is attributed to the asymmetric stretching of C–H bond of CH_2 terminal epoxy groups [6, 28, 55]. Bondzic et al. [5] have assigned the band at 2965 cm^{-1} to the aromatic ring stretching of C–H bond. The bands at 2926 and 2872 cm^{-1} are attributed to the symmetric stretching of C–H bonds of CH_2 [19, 55] and CH_3 [55] groups, respectively. Gong et al. [19] have attributed the last band to the CH methyl groups bond stretching. In relation to the methyl groups, there are bands related with symmetric and asymmetric angular deformation of C–H bond at 1362 and 1450 cm^{-1}, respectively [48].

Finally, three intense bands are observed in the region between 3450 and 3350 cm^{-1}, a doublet at 2206 and 2163 cm^{-1} and bands in the 670–470 cm^{-1} region. Comparing theses bands with the cyanoguanidine or DDA curing agent spectrum, there is a significant similarity in relation to the bands position and shape [46]. The bands at 3430, 3382, and 3345 cm^{-1} can be attributed to the symmetric and asymmetric stretching of N–H bonds in primary and secondary amino groups [5, 20, 34].

Cyanguanidine presents a tautomeric equilibrium (Fig. 2) between two forms: cyanoamine and cyanoimine [46]. Aliá et al. [3] have attributed the absorption bands at 2186 and 2147 cm^{-1} to the amine and imine, respectively. Hong et al. [23] have verified two absorption bands at 2210 and 2165 cm^{-1}, which were attributed to the nitrile groups and N=C=N, respectively. In this study, a doublet at 2206 and 2163 cm^{-1} can be attributed to the same groups first considering the cyanoguanidine′s characteristic. Finally, the bands from 670–470 cm^{-1} show a significant similarity with cyanoguanidine spectrum that can be related to stretching mode vibration of N–H bonds [25, 48]. Therefore, it can be supposed that cyanoguanidine was used as curing agent in *prepreg* F-155.

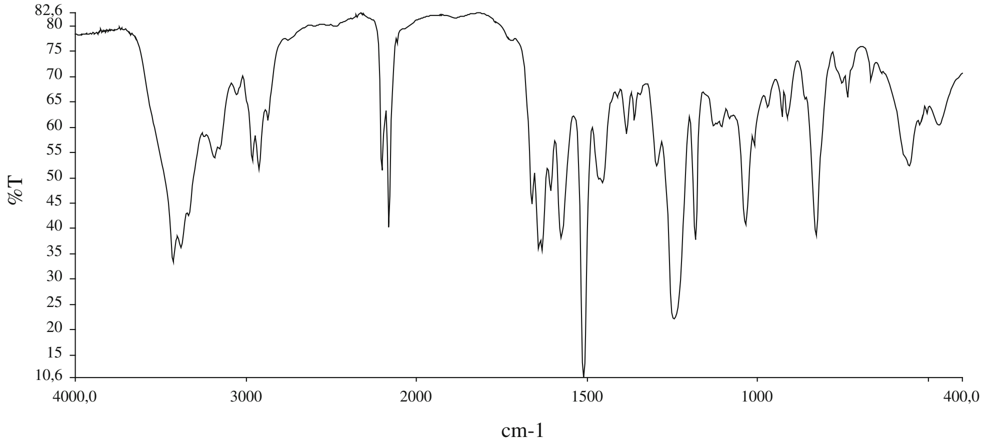

Fig. 1 FT-IR spectrum of uncured *prepreg* F-155 sample

Table 1 Band assignments of the *prepreg* F-155 FT-IR absorption spectrum [6, 7, 9, 12–14, 22–24, 27, 28, 32, 34, 48, 55, 61]

Wavenumber (cm^{-1})	Band assignments
3430	ν OH free
3382	ν_s N–H
3188	Combination bands ν COC epoxy and ν_s CH$_3$
3057	ν CH aromatic ring
2965	ν_a CH$_2$, ν CH
2926	ν_s CH$_3$
2872	ν CH
2206	ν C=N
2163	ν N–C=N
1736	ν O=C–N oxazolidone ring
1663	ν N–H absorption peak of imino group from DICY-epoxy product of bound amine-2-oxazoline
1644	
1633	ν N–H primary amine
1608	ν C=C aromatic ring
1577	ν N–C=N
1511	ν C=C aromatic ring
1456	δ CH$_2$ aromatic ring
1413	ν_s CH$_3$N
1385	ν_a C–N
1362	ν O=C–
1297	δ CH$_2$ of the ether group
1246	ν COC epoxy or ν Ar–O
1184	ν Ar–H
1107	ν C–O
1037	ν C–O ou ν ArO–C
1011	ν C–O
972	ν COC epoxy
930	ν COC epoxy
914	ν COC epoxy
830	δ phenyl –H *para* substitution
754	ν COC trisubstituted epoxy
738	ρ CH$_2$/δ phenyl-H
669	δ_a NH

* ν stretching; ν_a asymmetric stretching; ν_s symmetric stretching; δ deformation, δ_a axial deformation

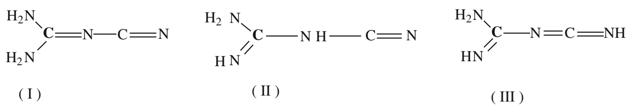

Fig. 2 Tautomeric equilibrium from cyanoimine (I), cyanoamine (II), and dyciandiamide transition state (III) [16]

Besides the bands discussed previously, F-155 spectrum shows common bands to the cyanoguanidine spectrum at 1663, 1644, and 1633 cm^{-1}, that can be attributed, respectively, to the stretching vibration mode of C=N bonds, N–H from amine groups, and N–H bond deformation from amine [12, 15, 34].

The FT-IR spectrum of the F-155 sample (Fig. 1) shows an absorption band at 3430 cm^{-1}, due to hydroxyl group. Delor-Jestin et al. [12] attributed the band at 3382 and 1644 cm^{-1} to the NH$_2$ amine group stretching vibration mode. The absorption band at 2206 and 2163 cm^{-1} are attributed to the consumption of cyano groups from dyciandiamide (DDA) (Fig. 2), and the band at 915 cm^{-1} is attributed to the epoxy group from epoxy resin [23, 46].

Figure 3 shows the absorption spectra FT-IR/PAS of *prepreg* F-155 samples heat treated at 121 °C to the following time periods: 0, 1, 2, 3, 4, 5 to 6 h. It can be observed the appearing of new absorption bands setting at 1736, 1663, 1644, and 1633 cm^{-1} (Fig. 3) during the thermal treatment. The last absorption band is related to the deformation mode of primary amine that decreases during the cure process. All these spectral modifications of *prepreg* F-155 bands during the cure process can be better observed using the PAS technique (Fig. 3). This is a non-destructive superficial analysis technique that allows to monitor the opaque samples curing process. The absorption bands changes are carbonyl groups characteristic formed by structural rearrangement of imine esters into 2-oxazolidones and guanyl ureas and the formation of imine groups by hydroxyl group intermolecular addition of hydroxyl at the imine functionality (DDA) and/or by intramolecular nucleophilic substitution of hydroxyl at the imide functionality (Fig. 4) [16, 23, 24, 61].

There are additional bands in the PAS spectrum not related with epoxy resin. Low intensity bands can be observed at 1577 and 1362 cm^{-1} that can be attributed to the triazine rings formed by the crosslinking process. It can be supposed that the triazine rings react transforming oxazolidone in oxazoline and increasing the bands intensity at 1736 and 1663 cm^{-1} [24, 28].

The absorption bands at 1608, 1511 and 1456, 1184 cm^{-1} are attributed to the aromatic rings. The disappearing or modification of these bands is associated to the strong increase of the relative intensity of bands that are attributed to the vibrational normal modes of hydroxyl and carbonyl groups [12]. The bands at 1246, 1107, 1037, and 1011 cm^{-1} are associated to the vibrational normal modes of the ether groups [6, 10, 13, 22].

The bands at 1413 and 1385 cm^{-1} are related to the symmetrical and asymmetrical stretching of C–N groups in amines, respectively [48]. The band at 1297 cm^{-1} is related to the CH$_2$ absorption of ether group, appearing in the cure process beginning. This band can be used to monitor the curing process, allowing verification of ether group proportion present in the resin. However, this band is influenced by hydroxyl group, and then the quantitative analysis is not possible, even though it is established that

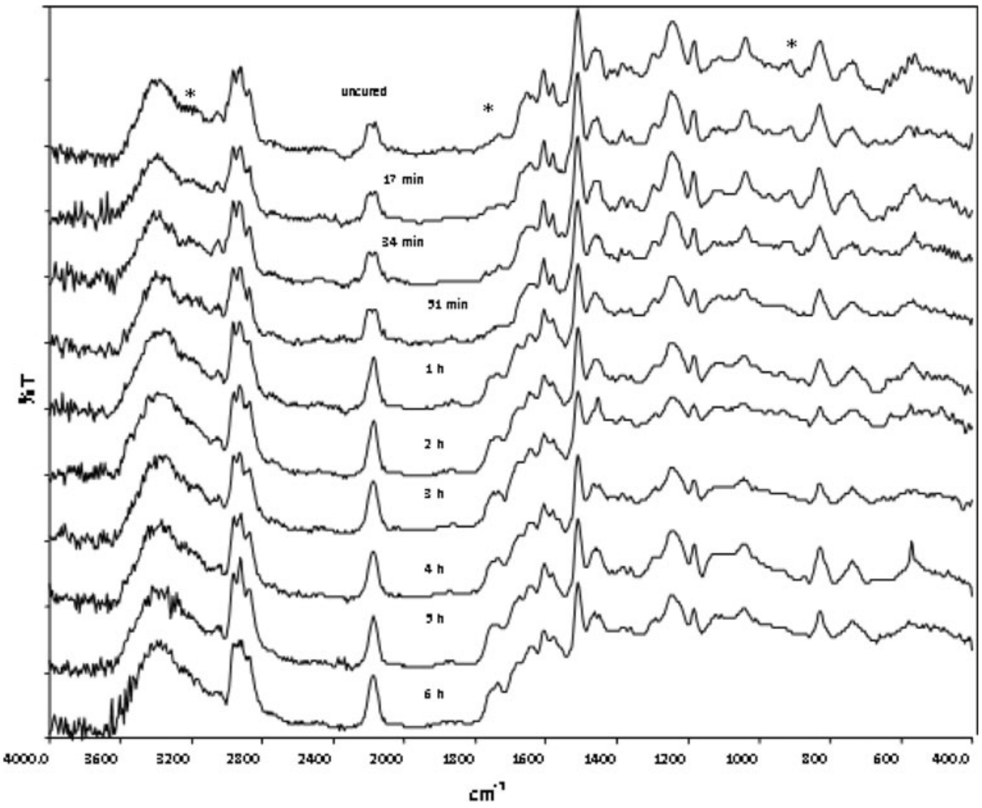

Fig. 3 FT-IR/PAS spectra of *prepreg* F-155 heat-treating samples at 121 °C

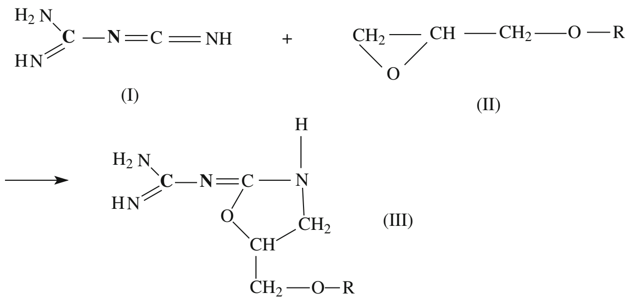

Fig. 4 Reaction between DDA (I) and DGEBA (II) producing an intramolecular cycle, the imino group (III) [16]

the ether bond formation is the most important secondary reaction in the epoxy resin curing using amines as curing agents [6].

The epoxy absorption bands are observed at 972, 930, and 913 cm^{-1}, indicating the epoxy ring substitution [8, 14]. The phenyl-H deformation is attributed at 830 and 738 cm^{-1} [12, 32]. According to Poisson et al. [39], the bands at 902, 754, 574, and 526 cm^{-1} are attributed to the *N*,*N*′-dimethyl-*N*′-(3,4-dichloro)phenylurea (DIURON®) accelerator, but these bands can overlap with the epoxy absorption bands (930 and 574 cm^{-1}) and the curing agent bands DDA (928, 669, 554, and 471 cm^{-1}).

Characterization of F155 *prepreg* through FT-IR technique was successful, since its composition was completely unknown. The results shown that epoxy resin, curing agent, and accelerator used in the F155 *prepreg* were, respectively, DGEBA, dyciandiamide, and *N*,*N*′-dimethyl-*N*′-(3,4-dichloro)phenylurea, respectively.

Prepreg sample analysis by FT-NIR

The NIR region absorption spectra of uncured *prepreg* F-155 sample and samples submitted to the thermal treatment in the following periods of time: 0, 17, 34, 51 min, 1, 3, and 6 h at 121 °C are shown in Fig. 5.

FT-NIR spectra (Fig. 5) present spectral changes attributed to epoxy resin, accelerator (DIURON®), curing agent (DDA), and the OH group at 4529, 4394, 5047, and 5246 cm^{-1}, respectively. In the uncured *prepreg*, the epoxy resin is partially polymerized in a stage called “B” [2], where the gel formation occurs, but not the complete crosslinking network, and then there is significant quantity of hydroxyl bands from the opening of epoxy ring in this stage [57]. The relative intensity of bands related to these groups is decreased after the curing process, which disappears completely after post-curing process (Fig. 5). The main absorption bands, including epoxy, methylene, primary amines, and phenyl groups, are listed in Table 2. The band assignments generally agree with those reported in the literature [8, 14, 34, 49, 50, 61].

The epoxy concentration was obtained from the epoxy combination band at 4534 cm^{-1}. This peak is a

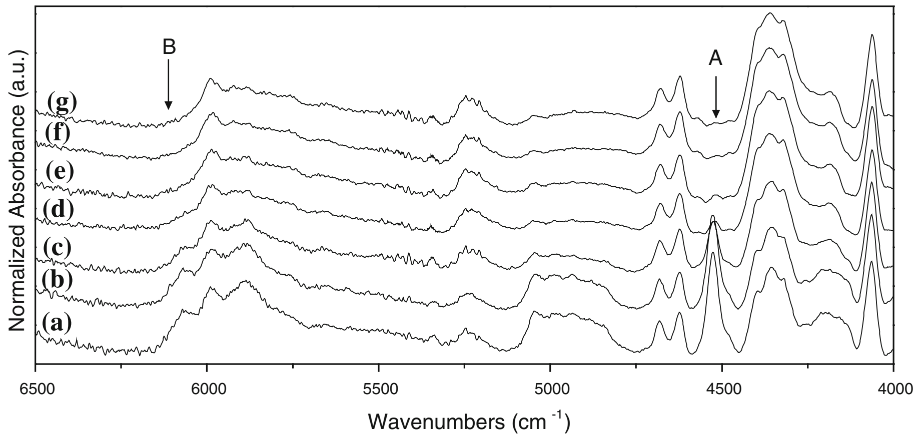

Fig. 5 FT-NIR spectra of *prepreg* F-155 uncured and samples submitted to the thermal treatment at 121 °C, in the following periods of time: **a** 0 min, **b** 17 min, **c** 34 min, **d** 51 min, **e** 1 h, **f** 3 h, and **g** 6 h

Table 2 Band assignments of normal vibration modes of the FT-NIR absorption spectra of *prepreg* F-155 [8, 14, 17, 34, 48, 50, 61]

Wavenumber (cm^{-1})	Band assignments
6071	Overtone CH Stretching vibration of terminal epoxy group
5970	Phenyl CH stretching overtone band and C–Cl combination band from
5989	DIURON®
5885	Aromatic CH combination band
5246	CH_2, CH combination band/–OH combination band
5048	NH_2 combination band primary amine of DDA
4681	Combination of the aromatic conjugated C=C stretch (1625 cm^{-1}) with the aromatic CH fundamental stretch (3050 cm^{-1})
4626	Combination of the aromatic conjugated C=C stretch
	Combination of the aromatic conjugated C=C stretch (1625 cm^{-1}) with the aromatic CH fundamental stretch (3050 cm^{-1})
4527	Combination band of the second overtone of the CO fundamental stretch (~900 cm^{-1}) with the fundamental CH stretch (~2715 cm^{-1})
4394	Aromatic –CH combination band/
	C–Cl combination band from DIURON®
4358	–CH_2 combination band
4318	Aromatic CH combination band
4210	CH_2, CH combination band
4159	Aromatic –CH combination band
4066	Aromatic combination band

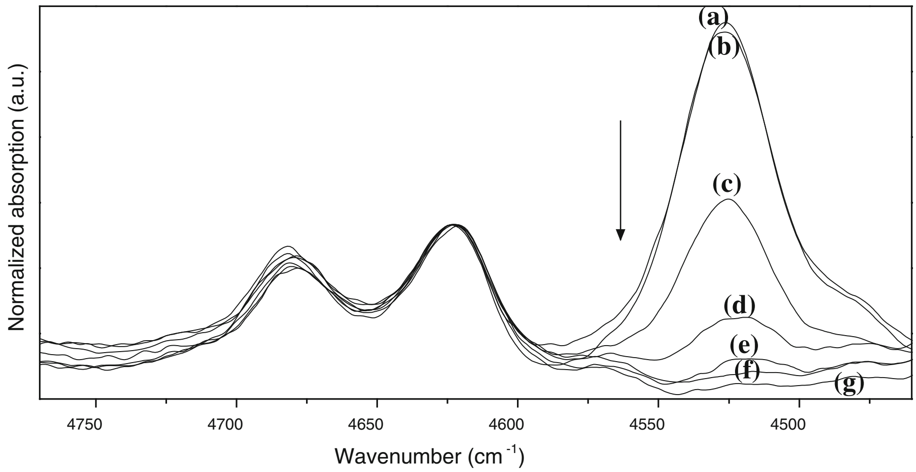

Fig. 6 Changes of the NIR spectra of *prepreg* F-155 during the curing reaction in the region 4750–4480 cm^{-1} in the following periods of time: **a** 0 min, **b** 17 min, **c** 34 min, **d** 51 min, **e** 1 h, **f** 3 h, and **g** 6 h

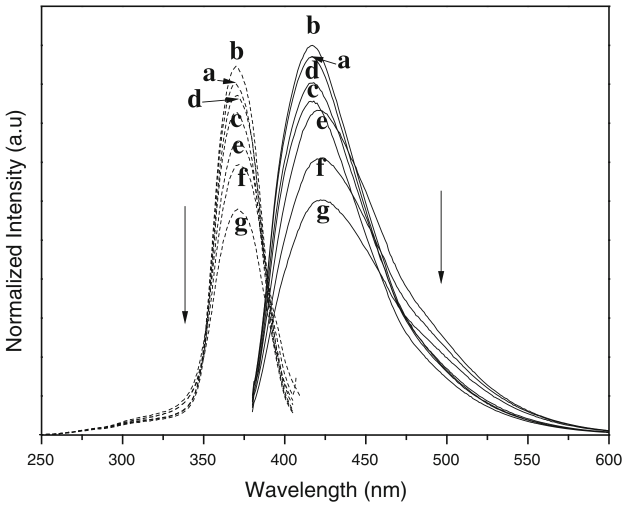

Fig. 7 Fluorescence spectra of *prepreg* F-155 during the heating treatment at 121 °C: (*straight line*) emission ($\lambda_{em} = 368$ nm) and (*dotted line*) excitation ($\lambda_{exc} = 417$ nm), following the periods of time: **a** 0 min, **b** 17 min, **c** 34 min, **d** 51 min, **e** 1 h, **f** 3 h, and **g** 6 h

combination of stretching fundamental (3050 cm^{-1}) with the CH_2 deformation fundamental (1460 cm^{-1}) of the epoxy ring [27, 42, 59]. The decreasing of the relative intensity of this band with the reaction time can be seen in Fig. 6.

Intrinsic fluorescence

The emission spectrum of the F-155 *prepreg* sample in the beginning of the curing process (Fig. 7) shows a band with maximum wavelength at 417 nm. At the first 30 min, a variation of the relative intensity in the fluorescence is observed. These spectral changes in the beginning of process can be attributed to the formation of different compounds when the DDA reacts with the epoxy resin. The DDA presents two configurations depending on the chemical environmental and the temperature (Fig. 2) [16]. Many authors [24, 49, 59] have suggested that the reaction could be explained by two competitive reaction pathways: the main one consists of the formation of a 1-(2-hydroxyalkyl)-3-cyanoguanidine by reaction of amino groups with epoxy groups, and the second one the formation of a small quantities of polyether chain by a base-catalyzed ring-opening polymerization of epoxy groups.

After 1 h of heat treatment, the band emission maximum of F-155 (Fig. 7) is 4 nm red shifted, and the intensity of fluorescence starts to decrease. The spectral red shift is related to the epoxy-amine curing reactions [11, 37, 52, 61]. This behavior is usually attributed to an increase of viscosity and rigidity of the medium [18].

The excitation spectra of F-155 *prepreg* before the curing process (Fig. 7) show a broad band at 367 nm. After the F-155 *prepreg* was cured, the relative intensity of the band at 365 nm (Fig. 7) decreases due to a conversion of primary amines into secondary and tertiary amines [11, 37, 52, 61], following the same process as the emission spectra.

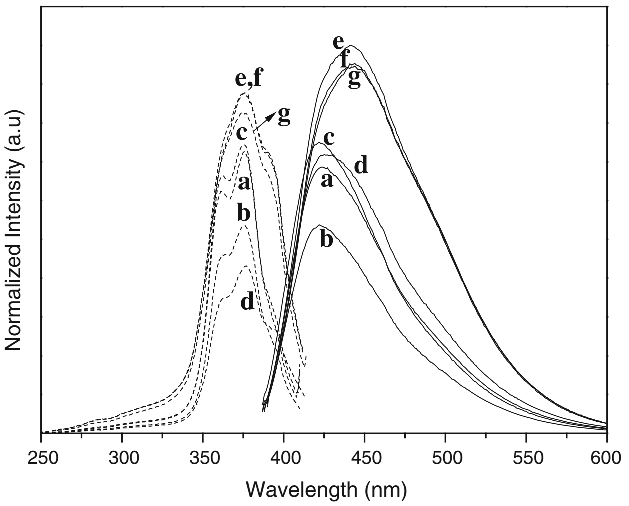

Fig. 8 Fluorescence spectra of *prepreg* F-155 with 9-AA during the heating treatment at 121 °C: (*dotted line*) excitation ($\lambda_{exc} = 424$ nm) and (*straight line*) emission ($\lambda_{em} = 376$ nm), following the periods of time: **a** 0 min, **b** 17 min, **c** 34 min, **d** 51 min, **e** 1 h, **f** 3 h, and **g** 6 h

Extrinsic fluorescence

The emission spectrum of *prepreg* F-155 containing the molecular probe 9-AA before cure (Fig. 8) shows two superimposed bands with emission maxima at 450 and 490 nm. According to Sales [44], the first band is related to the protonated form of 9-AA, and the second band can be attributed to the equilibrium of the dimer and monomeric protonated forms of 9-AA. The emission spectrum of the

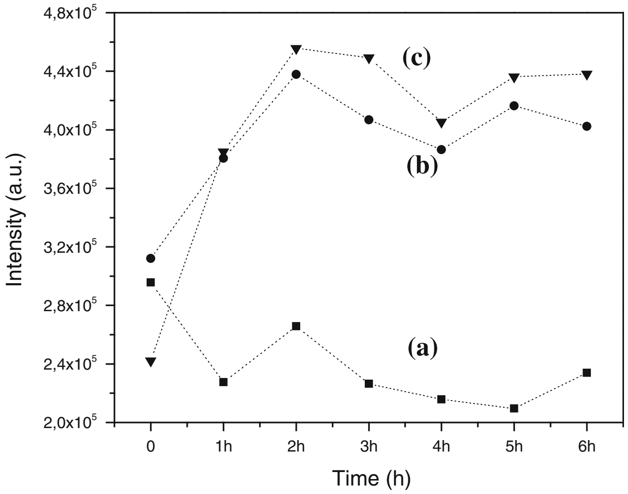

Fig. 9 Relative intensity of the emission band maxima at the following wavelengths (nm) **a** 420, **b** 450, and **c** 480 versus curing time of F-155 prepreg containing 9-AA

Table 3 Attribution of the main bands of intrinsic fluorescence, FT-IR, FT-IR/PAS, FT-NIR spectra used in the F155 *prepreg* characterization

	λ_{em}(nm)	Attribution	FTIR (cm^{-1})	Attribution	PAS (cm^{-1})	Attribution	FT-NIR (cm^{-1})	Attribution
DGEBA epoxy resin			3430	ν OH free	1736	ν carbonyl groups formed during heat treatment	4534	Epoxy group
					1663			
					1644			
			1608	ν C=C phenyl group	1608	ν C=C phenyl group	5970	Phenyl group
			1511		1511			
			1456		1456			
			1184		1184			
			1107	ν C–O				
			1037					
			1011					
			972	ν COC epoxy				
			930					
			913					
DDA curing agent	417 λ_{exc} = 360 nm	*pr*[a], *sec*[b], *ter*[c]	3382	ν_s N–H			5048	amine group
			2206	ν C=N				
			2163	ν N–C=N				
			1577					
			1736	ν O=C–N oxazolidone ring				
			1663	ν N–H of bound amine-2-oxazoline				
			1644					
			1633	ν N–H of *pr*	1633	ν N–H of *pr*		
			1413	ν_s CH_3N	1577	Triazine groups		
			1385	ν_a C–N	1362			
			670–470	ν N–H				
DIURON® accelerator							5970	C–Cl group
							5989	
							4394	

[a] Primary amine, [b] Second amine, [c] Tertiary amine

9-AA in DGEBA in concentration 1×10^{-4} mol/L has shown a band at 462 nm that was attributed to the formation of the hydrogen-bonded dimer of the 9-AA protonated form [31, 53].

The excitation spectra of the 9-AA molecular probe dissolved in F-155 *prepreg* before heat treatment (Fig. 8) show a maximum band at 374 nm and two shoulders at 366 and 390 nm that indicate protonated form of 9-AA. When the sample was submitted to heat treatment at 121 °C after 1 h (Fig. 8), the shoulder at 366 nm disappeared, the intensity of shoulder at 391 nm increased and the red shifted band at 376 nm, indicating an equilibrium between aggregate and protonated forms of 9-AA.

Deconvolution of the emission bands at 375 nm of *prepreg* F-155 with 9-AA sample was performed to analyze modifications of the photophysical behavior of 9-AA during the curing process (Fig. 9). The following deconvolution bands are obtained at 420, 450, and 480 nm.

The band intensity at 420 nm decreases when the band intensities at 450 and 480 nm increase, during the curing process. Therefore, these changes in relative intensity can be associated to the increase of environment rigidity and decrease of free volume in the epoxy matrix. The free volume decreasing can cause an increase of 9-AA local concentration and consequent dimeric formation [43].

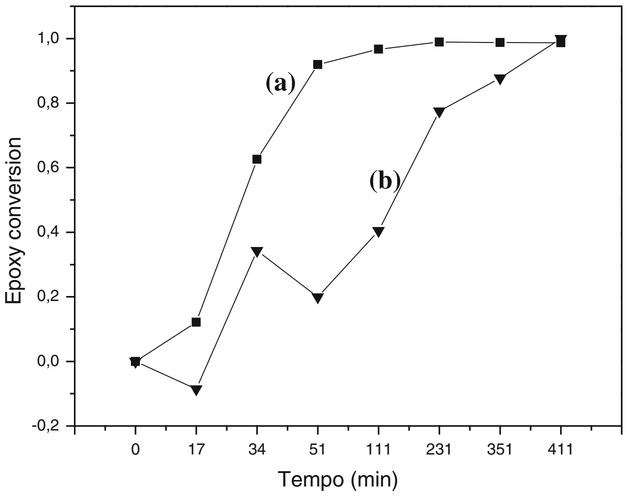

Fig. 10 Epoxy group conversion as a function of curing time at 121 °C using FT-NIR (*filled square*) and luminescence (*filled inverted triangle*) techniques

Table 3 summarizes the most important bands for the characterization of the F-155 prepreg through the intrinsic luminescence, FT-IR, FT-IR/PAS, and FT-NIR techniques.

Comparison between FT-NIR and luminescence spectroscopy

Comparing both techniques, it can be concluded that with FT-NIR (Fig. 10) a chemical reaction is followed, so higher changes in conversion are observed from the beginning until the gel conversion is reached. At this point, the viscosity of the system increases very rapidly to effectively infinite, and little changes in the chemical reaction can take place until the vitrification is reached where at this point the reactions stops. On the other hand, the fluorescence allows monitoring all the physical changes of the system associated with chemical reaction. The fluorescence during cure seems to give more information about changes in the viscosity of the system than real chemical changes due to its higher sensitivity. Therefore, lower changes in the fluorescence conversion are observed at the beginning of the cure process since the increase of the viscosity is lower. The gel point is observed when an abrupt increase of the viscosity and consequent decreasing of the system mobility that is related to the fluorescence intensity increasing due to rate constant increasing of the radiative process [36, 40]. Olmos et al. [35, 36] observed the same behavior in some epoxy/curing agent systems.

Conclusion

The infrared techniques, such as FT-IR, FT-NIR, and PAS, were used to indentify the components present in the polymeric matrix of composite material, to study the curing process and the chemical changes that happened during this process. It was possible to identify the epoxy resin DGEBA in which the *prepreg* F-155 was made. The curing agent DDA was also identified mainly through the bands at 3382, 2206, 2163, and 1736 cm^{-1} attributed to stretching vibrations of the following groups: C=N, N–C=N, and O=C–N, respectively. The DIURON® accelerator was identified through the bands at 5970, 5989, and 4394 cm^{-1} related to combination bands of C–Cl group of the FT-NIR spectra. PAS technique allowed not only to monitor the curing process through the decreasing of epoxy band (915 cm^{-1}), but also the chemical transformations that occurred between the curing agent and epoxy resin during the curing process.

Fluorescence spectroscopy is a powerful tool to monitoring physical changes of the system associated with chemical reactions. In this research, it was possible to monitor the epoxy conversion and observed the gel time using the intrinsic luminescence. In extrinsic luminescence, the shifting in emission spectrum shows an equilibrium between the protonated and dimeric form of 9-AA due to the decreasing of the free volume in the polymeric matrix during the curing process.

These results suggest that FT-NIR and fluorescence actually can be considered as complementary techniques to study epoxy-curing process. However, both of them allow the obtaining of kinetic parameters that could help in designing conditions for preparing epoxy materials.

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