

Understanding the water uptake in F-161 glass-epoxy composites using the techniques of luminescence spectroscopy and FT-NIR

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Abstract

This paper investigates the application of the luminescence spectroscopy technique in steady-state to study the moisture influence in glass fiber/epoxy prepreg and their laminates. The studies were monitored by intrinsic luminescence comparing the results with gravimetric analysis and near infrared with Fourier transform. Samples are cured and submitted to humidity controlled at 60 and 80 °C until 90 days. It is verified that the decrease in the maximum emission of the samples is directly related to the material moisture content. However, for very short periods, there is an increase in the relative intensity and blue shift of the emission band for all samples treated at 60 °C, which is related to an increase of the rigidity of the polymeric matrix. The results in this paper have a great significance because it brings a wide discussion on the interaction of water in epoxy composites materials.

Keywords: *F-161 laminates, FT-NIR, luminescence spectroscopy, water uptake.*

1. Introduction

The composite materials present in the aircraft structures are exposed to environmental conditions with elevated levels of moisture. The composite materials can absorb water molecules and this chemical interaction can result in a delamination process^[1]. The delamination process consists on separating the layers resulted from interlaminar tensions.

The study of the water interaction with the polymer matrix at the molecular level is very important since the water uptake will determine the mechanical strength of the material at the macroscopic level. These materials are used in primary structural parts of aircraft under great mechanical stress. The knowledge of the mechanisms which drive moisture sorption, as well as of the influence of sample dimensions, temperature and relative humidity, becomes crucial when the long-term properties of the material are needed^[2].

Many researches have been done to understand the behavior of water in epoxy resin and composites, since this cured polymeric matrix contains strongly polar groups, such as hydroxyl groups and amine groups^[3-6]. Adamson^[6] has done experiments of thermal expansion of two graphite/epoxy composite systems and concluded that water is initially absorbed and diffuses into the resin; then it begins to occupy polymer free volume, causing no swelling, while some of the water disrupts intermolecular hydrogen bonds, causing swelling by hydrogen bonding with the resin. In the final stage of water absorption, the swelling efficiency drops far below that observed in the initial stage. Apicella et al.^[2] have analyzed epoxy resin cured with amine compounds using DSC. These authors proposed three sorption mechanisms: (1) bulk dissolution of the water in the polymer network; (2) adsorption on hydrophilic sites and (3) adsorption on the surfaces of free volume elements.

Li et al.^[7] used time-resolved attenuated total reflection Fourier transform infrared spectroscopy (ATR-IR), near-infrared (NIR) spectroscopy and positron annihilation lifetime spectroscopy (PALS) to investigate water diffusion processes and the state of water molecules in six different epoxy resins. These authors concluded that water diffusion is controlled by local chain reorientation and bond dissociation of water molecules from epoxy networks. Four types of water molecules were detected: nonbonded, single bonded and two types of double hydrogen bonded.

Cotugno et al.^[8] e Roy et al.^[9] showed that water molecules can affect the epoxy matrices by (a) plasticization, (b) changes in physical properties and (c) hygrothermal degradation. The plasticization effects have been previously discussed. The changes in physical properties induce a decrease of yield strength and change of yield/deformation mechanisms. The hygrothermal degradation is characterized by micro-cracking, aging, breakdown of the polymer chain and the degradation of the fiber-matrix interface in polymer composites.

Usually, water absorption by the epoxy resin decreases the glass transition temperature (T_g) due to the plasticization of the polymer network. This effect can lead to a decrease of the mechanical performance of the composite material. Those properties related to the compressive strength and intralaminar/interlaminar shear is significantly affected by the moisture absorbed, especially at high temperatures^[10-12]. According to Asp^[13], the water absorption can cause interlaminar delamination or damage in carbon-epoxy composites.

One of the most important hygrothermal aging processes of the epoxy composites involves molecular interactions between water and epoxy resin, such as the plasticization

phenomenon of the molecular network. This process may be reversible, but can lead to irreversible loss of mechanical properties^[14]. According to Majerus et al.^[15], this phenomenon is related to the presence of water molecules in the matrix microcavities, by the interaction between water molecules with specific segments of the polymeric matrix. Epoxy resins can absorb water through three different ways: (a) bulk dissolution of water in polymer network, (b) adsorption on the hydrophilic sites and (c) adsorption in the voids. The transport of moisture below the T_g consists of a three-step process. First, the water occupies the voids of the polymer matrix. Next, the water molecules bind to the polymer network by hydrogen bonds, causing swelling. Finally, water diffuses into the densely crosslinked resin. Polarity and topology of the structure of crosslinked epoxy resin influence the adsorption of water^[16].

The effects of water absorption on the epoxy resin have been widely investigated by several techniques. However, none of them is sensitive and non-destructive for monitoring the moisture aging effects on composite materials like luminescence spectroscopy^[17-21]. Sung and Sung^[17,21] used luminescence spectroscopy, intrinsic and extrinsic methods, to characterize the water uptake and the curing extension in composite materials. The intrinsic method involved the study of the emission of the resin matrix itself, while the extrinsic one consisted in adding a luminescent probe in the resin. These researchers noticed that there was some spectral shift in the wavenumber and/or some decrease in intensity of the emission spectra when water molecules were uptaken.

In this work, it was used glass fiber/epoxy prepreg F161 (Hexcel®), a composite system that is widely used in aeronautics industry in the manufacture of structural parts. The moisture effect on glass fiber/epoxy prepreg and glass fiber/epoxy laminates was studied by luminescence spectroscopy in steady-state condition using the intrinsic fluorescence method. The results were compared to Fourier Transform Near Infrared Spectroscopy (FT-NIR) and the sample weighting was performed according to ASTM D 5229/D 5229M-12^[22]. The changes in the maximum emission of the samples is directly related to the moisture content of the material. Other authors had not previously observed this photophysical behavior.

2. Materials and Methods

2.1 Sample preparation

These experiments used a plain wave glass fiber/epoxy resin prepreg, F161 (Hexcel Composites Ltd., Livermor, CA), with size of 30 mm × 20 mm. Some prepreg samples were analyzed as received to understand their photophysical behavior and they were named as btt-pre (btt= before thermal treatment and “pre”= prepreg). The curing process was made according to the manufacturer’s instructions. The prepreg samples were heated from room temperature to 177 °C at a heating rate of 2 °C/min, and then, they were maintained in this temperature for 120 min. After this time, the samples were removed from the oven and maintained at room temperature for 20 min. Samples submitted to this thermal treatment were named as tt-pre (tt=thermal treatment).

A set of desiccators was maintained at 60 and at 80 °C. Beckers with saturated aqueous solution of NaBr, NaCl and KCl (Merck) were added to these desiccators to simulate a relative humidity of 58, 75 and 84%, respectively. Pieces of samples already thermally treated were put onto glass plates next to the salt solution inside of each desiccator. The samples were maintained for 1, 7, 15, 30, 60 and 90 days in each desiccator. The samples obtained after exposure to different environmental conditions were named pre-relative humidity-T-t, where “pre”, relative humidity, T and t are, respectively, prepreg, relative humidity value, temperature and time, for example, pre-75-60-30 stands for a cured F-161 prepreg sample exposed to a relative humidity of 75% at 60 °C for 30 days.

To manufacturing the laminate samples, the prepreg layers were laid down in a plain mold forming a rectangular panel (160 mm × 160 mm) with 14 layers. The curing process was running using a hydraulic press (SOLAB) at a pressure of 50 kgf/cm² and 177 °C using a heating rate of 2 °C/min and then maintained at this temperature for 120 min. After that, samples were cut in pieces of 25mm × 15mm and added to desiccators for 1, 7, 15 and 30 days. The laminated samples were exposed to the same environmental conditions as the prepreg samples into desiccators. The samples obtained after the exposure to different environmental conditions were named lam-relative humidity-T-t, where lam stands for a cured laminate sample constituted of 14 prepregs. The remaining labels are similar to pre- relative humidity -T-t that was previously described.

2.2 Water absorption analysis

The water absorption (% H₂O_{abs}) was determined using Equation 1, according to ASTM D 5229/D 5229M-12^[22]:

$$\%H_2O = \frac{(M_f - M_i)}{M_i} \times 100 \quad (1)$$

where M_f and M_i are, respectively, the mass of the samples after and before being added into the desiccators.

2.3 Water diffusion

The diffusion coefficients are easily calculated from the moisture-uptake profiles with Fickian diffusion^[23] (Equation 2):

$$\frac{M_t}{M_\infty} = 4 \left(\frac{Dt}{h^2} \right)^{1/2} \left[\frac{1}{\pi^{1/2} + 2} \sum_{n=1}^{\infty} (-1)^n \operatorname{ierfc} \frac{nh}{2(Dt)^{1/2}} \right] \quad (2)$$

where M_t is the moisture uptake at time t , M_∞ is the equilibrium moisture uptake, h is the sample thickness, D is the diffusion coefficient, ierfc is the integral error function of each element and n is the concentration starting at 0 at the surface and spreading infinitely deep in the material. This solution of Fick’s second law holds true for the conditions of an infinite sheet with constant penetrant activity on both sides of the sheet and a concentration independent of D . At very short times, where M_t/M_∞ is less than 0.5, Equation 2 can be defined approximated by the following (Equation 3):

$$\frac{M_t}{M_\infty} = \frac{4}{h} \sqrt{\frac{Dt}{\pi}} \quad (3)$$

Equation 3 is easily rearranged to reveal that the initial slope in a plot of Mt/M versus \sqrt{t}/h is related to the diffusion coefficient D through the following (Equation 4):

$$D = \frac{\pi}{16} \left(\frac{M_t / M_\infty}{\sqrt{t}/h} \right)^2 \quad (4)$$

2.4 Infrared spectroscopy in the near region

The infrared spectroscopy was also used to analyze the water content in the samples. The samples were analyzed in the near region using a Spectrum One Perkin Elmer spectrometer with a universal attenuated total reflectance (UATR) accessory; the acquisition parameters were: 8000-4000 cm^{-1} , 4 cm^{-1} resolution, 1 gain and 40 accumulations. The relation between the epoxy group intensity band (4523 cm^{-1}) and reference band (4623 cm^{-1}). The reference band selected is the combination of the two stretching modes, C-H and C=C, of the phenyl group of the epoxy group. They were analyzed in order to determine the water absorption by the samples. The water content (w_t) was calculated by Equation 5:

$$w_t = 0,096 + 0,587 \frac{A_{w,t} - A_{w,0}}{A_{ref}} \quad (5)$$

where $A_{w,0}$ is the integrated absorbance related to the non-exposed sample to moisture, $A_{w,t}$ is the integrated absorbance of sample exposed to moisture for time equals to t and A_{REF} is the integrated absorbance of the reference band. Gonzales-Benito and co-workers described this procedure in details as well the meaning of the constants of the Equation 5^[24].

2.5 Emission and excitation spectra

Fluorescence spectra were measured with a steady-state luminescence spectrometer (FS920-Edinburgh Analytical Instruments) 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 range of wavelength of excitation (290-380 nm) was chosen taking into account that the curing agent groups shows emission band after this region. The first moment of luminescence ($\langle \nu \rangle$), defined by the weighted average wavenumber (Equation 6)^[25], was used in order to analyze the water absorption into F-161 prepregs and laminates:

$$\langle \nu \rangle = \frac{\sum_i \nu_i I(\nu_i)}{\sum_i I(\nu_i)} \quad (6)$$

where $I(\nu_i)$ is the relative emission intensity at wavenumber ν_i .

3. Results and Discussions

3.1 F-161 prepreg samples under different humidities at 60 and 80 °C

Figure 1A shows the spectra of electronic emission of the samples pre-84-80-t. These samples presented two superimposed emission bands: one centered at range 451-455 nm and another centered at 488 nm. The emission bands in the region from 400-600 nm of pre-relative humidity-60-t samples can be attributed to the curing agent, which probably contains amine groups^[26]. The band profile is very similar to the emission band of the cured prepreg sample. Sales et al.^[26] have discussed that the spectra of the

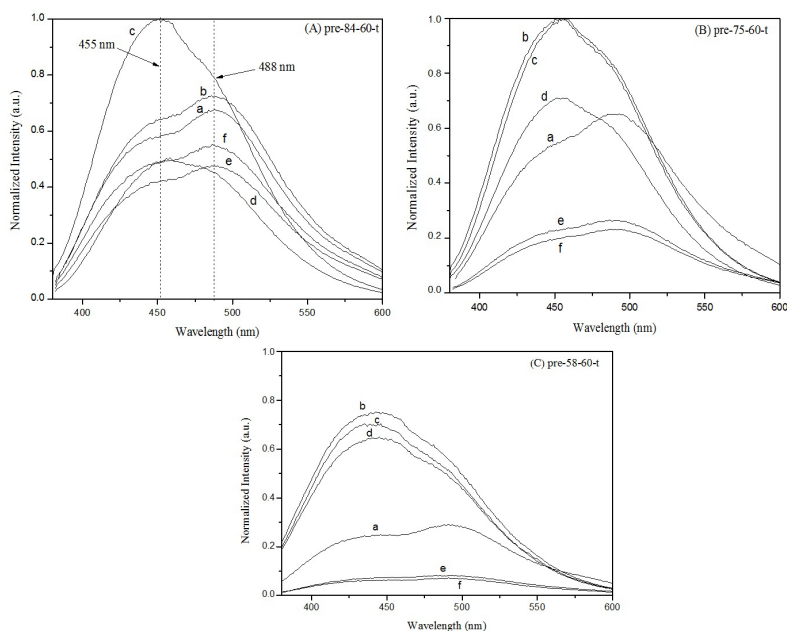


Figure 1. Electronic emission spectra of the samples ($\lambda_{exc} = 370$ nm): (A) pre-84-60-t, (B) pre-75-60-t and (C) pre-58-60-t in the following periods of time (t in days): (a) 1, (b) 7, (c) 15, (d) 30, (e) 60 and (f) 90.

samples non-totally cured showed a red shift of maximum emission due to the conversion of primary amines into secondary and tertiary amines. As might be expected, the sample pre-84-80-1 (Figure 1A.a) showed no significant influence of water absorption in the polymeric matrix. The band centered at 488 nm is the most intense one for samples with $t=1, 7, 60$ and 90 days, while the band centered in the range 451-455 nm is the most intense for samples with $t=15$ and 30 days. Another remarkable observation is that the displacements were dependent on the exposure time. Therefore, one can observe a displacement towards to the blue region for exposure time from 7 to 15 days and another displacement towards to the red region for periods of time of 30 to 60 days.

The emission spectrum of pre-84-60-7 (Figure 1A.b) does not present a significant change when compared to the pre-84-60-1. However, the spectrum of the sample pre-84-60-15 (Figure 1A.c) when compared to that sample pre-84-60-7 shows a considerable increase in the relative intensity of the maximum emission and a blue shift to 455 nm. The relative intensity of the emission band of sample pre-84-60-30 (Figure 1A.d) is lower than samples pre-84-60-15 and its maximum is centered at 455 nm. Sample pre-84-60-60 and pre-84-60-90 show emission bands whose profiles are very similar to the band of the pre-84-60-1, but there is a decreasing of the relative intensities. Emission spectra of samples pre-75-60-t (Figure 1B) and pre-58-60-t (Figure 1C) are very similar with spectra of the pre-84-60-t samples; the only difference is related to exposure time where the blue shift is observed. The emission spectrum of sample pre-84-60-t shows a shift towards the blue region with 15 and 30 days, while those related to samples pre-75-60-t and pre-58-60-t show the same shift after a period of time of 7, 15 and 30 days.

These two effects on the photophysical behavior of samples subjected to moisture at intermediate times can be related. The relative emission intensity increases when there is an increase in the radiative rate constant of the fluorophores, which can be attributed to the stiffness of the polymeric matrix. On the other hand, the blue shift can be related to an important change of the polarity of the medium, which could influence the fluorophore photophysical behavior. According to Lakowicz^[27], a decrease in the medium polarity can lead to a blue shift of maximum emission. On other hand, the interaction with a more polar solvent could lead to the stabilization of the excited electronic state, shifting the emission maximum to the red region. Since the emission band was attributed to secondary and tertiary amine compounds, one can assume that water molecules diffuse through the polymeric matrix and form hydrogen bonds with the amine and hydroxyl groups. The effect of water diffusion through the polymeric matrix in the photophysical behavior of the fluorophores is the increase in energy of its excited electronic state and consequent shift of the maximum emission to the blue region. The shift to the blue region could indicate that the formation of hydrogen bonds of water with polar groups reduces its polarity. In this case, water would act as a pseudo curing agent and would contribute to an increase in the stiffness of the polymeric matrix, which is related to an increase in the rate constants of radiative processes and

consequent increase in emission intensity, as observed in the spectra of samples.

Novolac epoxy matrix of F-161 prepreg type is a very polar material, since it contains a considerable number of hydroxyl^[25]. These groups result from the opening of the epoxy rings by crosslinking reaction. The water molecule could act as a pseudo-curing agent by its interaction with hydroxyl groups of the different polymer chains. This interaction increases the polymer matrix stiffness and increases the radiative decay rate constant. Consequently, an increase in the relative intensity of the luminescence emission is observed for very short times of exposure to moisture. According to Soles et al.^[28], resin polarity is of primary importance in determining the equilibrium moisture uptake. Less polar resins, such as the non-amine series, absorb very little water compared to the amine-containing materials. Accompanying polarity, topology has a secondary effect on uptake. A greater intrinsic hole volume fraction (V_0) leads to an increase in the equilibrium moisture content. V_0 is isothermally elevated by increasing crosslink density, the consequence of which is enhancement of the effective polarity. Steric hindrances at the crosslink junctions introduce unoccupied volume elements coincident with the polar hydroxyls and amines. V_0 is localized to regions immediately adjacent to crosslink junctions. Calculations indicate there will be approximately 7×10^{20} nanopores per cm^3 for epoxy matrix and 2×10^{21} polar groups per cm^3 . If a typical equilibrium uptake (for the bifunctional resins) of 3 wt% is assumed, approximately 1×10^{21} water molecules per cm^3 of resin will be absorbed^[28,29].

The decrease in the relative intensity of samples treated for longer periods of time (30 and 60 days) denotes an increasing of the rate constant of non-radiative decay that can be related to the plasticization effects of the polymer matrix due to water uptake. This process is associated to the amount of unbound water that occupies the free volume of the polymeric matrix. On the other hand, higher water content in the bulk increases the medium polarity, resulting in the red shift of the emission band. Sung and Sung et al.^[19] verified that water absorption induces changes in the medium polarity and a decrease in the relative intensity of the emission band luminescence. According to Zhou and Lucas^[30], there are two ways that water molecules can bind to the epoxy matrix. In the first one, the absorbed water can diffuse into the polymer chain breaking the van der Waals bonds, resulting in an increase of the chain segment mobility and swelling. Water molecule interacts strongly with hydrophilic functional groups such as hydroxyl or amine in epoxy resin. The second one occurs when the absorbed water molecule connects to the polymer chain forming pseudo or secondary crosslinking. This process turns the secondary amine groups into tertiary amines, increasing the conversion degree.

The results of this work strongly suggest that water first acts as a pseudo curing agent, since it was observed an increasing of the emission intensity. Then occurs plasticization of the polymeric matrix related to decreasing of the emission intensity. It must be clear that this photophysical behavior was observed for all samples submitted to different relative humidities treated at 60 °C.

Prepreg samples submitted to relative humidities of 84 (Figure 2A), 75 (Figure 2B) and 58% (Figure 2C) at 80 °C showed emission bands with the same profiles and a wavelength maximum at 488 nm, a band overlapped around 450 nm and there are no shift of the maximum emission bands. Comparing these spectra with those obtained for samples submitted to the same relative humidity at 60 °C, it is observed that the bands have the same emission band profile than those submitted for longer times, in which the water content is higher.

First moment of fluorescence (Equation 6) allows the comparison of the emission spectra of the samples exposed to three conditions of relative humidity for different periods. This equation has been used for many authors not only to study the influence of water in polymeric matrix^[24], but also to study polymerization reaction^[21,31] and investigate the structure of elastomeric network^[32]. Figure 3A shows the first moment ($\langle v \rangle$) versus exposure time for samples pre-84-60-t, pre-75-60-t and pre-58-60-t. For a better evaluation of water effects in epoxy matrix, all scales are in the same range. The sample pre-58-60-t showed the highest value for the luminescence band first moment ($\langle v \rangle$) and the lowest one for water content. The variation of first moment of samples pre-58-60-1 and pre-58-60-7 has a significant difference of 857 cm^{-1} , indicating that the absorbed water has an influence in polymeric matrix.

On the other hand, the values of water content and luminescence band first moment ($\langle v \rangle$) for the samples pre-84-60-t and pre-75-60-t are very close (Figure 3A). The effect of increased emission intensity is much more pronounced in samples pre-58-60-7, pre-58-60-15 and

pre-58-60-30 compared with the other samples (Figure 3A). However, the results of gravimetric analysis showed water contents between 0.1 and 0.3% m/m, which are half the water content of the samples exposed to relative humidity of 84% for the same periods of time (Figure 3B). The photophysical behavior of the samples pre-58-60-t can indicate that the influence of bound water is significant only for lower water contents. For higher water contents, one can conclude that the $\langle v \rangle$ variation is inversely proportional to the water content.

Figures 3A and 3B show the first moment of luminescence ($\langle v \rangle$) and water content of the samples pre-58-80-t, pre-75-80-t and pre-84-80-t, respectively. It can be observed that $\langle v \rangle$ does not change significantly for samples submitted at 80 °C, in relation to the same parameter for samples treated at 60 °C. According to Sales^[33], the increase in the relative luminescence emission intensities and in the rate constant of radiative decay is due to the increased rigidity of the polymer matrix. Probably, the water forms hydrogen bonds with polar groups of the polymer matrix, acting as pseudo-curing agent by exposure time periods for each specific humidity, but as the rate of diffusion of water in the polymer matrix should be greater than 80 °C (Table 1), it is assumed that the matrix plasticization occurs in a shorter time period (between 7 to 30 days) when the samples are submitted to the higher relative humidity and temperature.

Table 1 summarizes the wavelengths of the emission bands, water contents, first moments of luminescence and diffusion coefficients of prepreg F161 samples at 60 and 80 °C. Sample pre-58-60 treated for 15 days presented the higher first moment of luminescence – 21986 cm^{-1} . The emission maximum of this sample was shifted to the blue region at

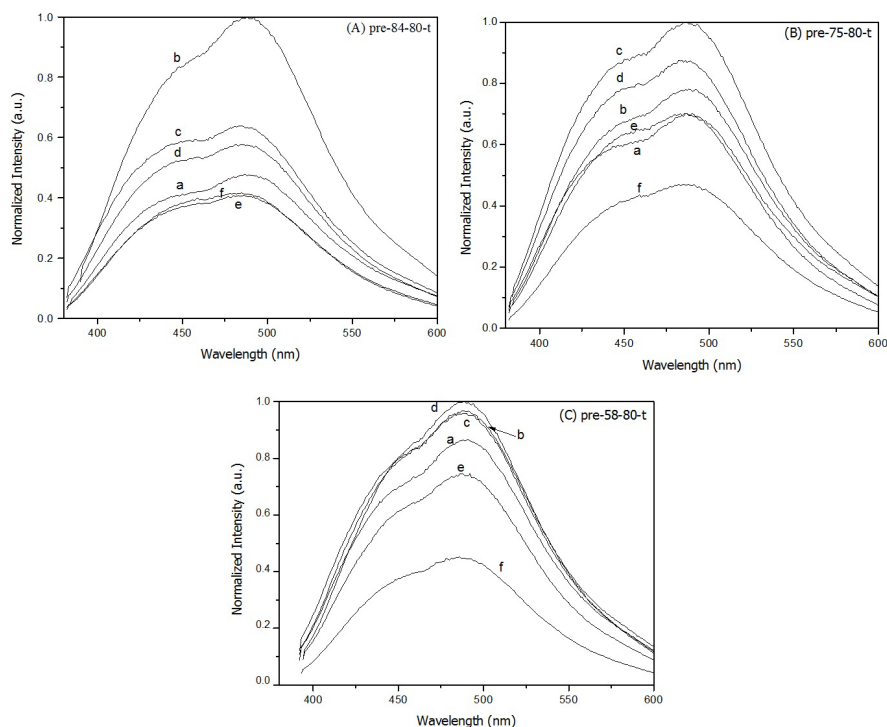


Figure 2. Electronic emission spectra of the samples ($\lambda_{exc} = 370 \text{ nm}$): (A) pre-84-80-t, (B) pre-75-80-t and (C) pre-58-80-t in the following periods of time (t in days): (a) 1, (b) 7, (c) 15, (d) 30, (e) 60 and (f) 90.

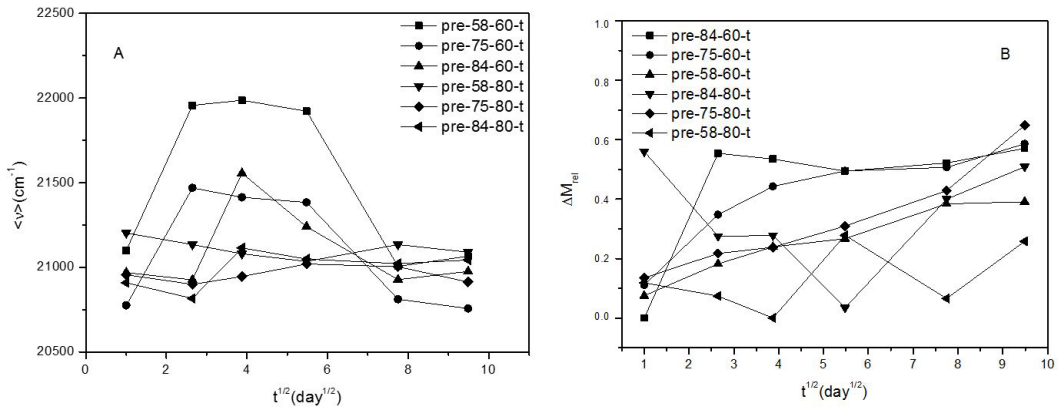


Figure 3. F-161 prepreg samples at 60 and 80 °C: (A) First moment of luminescence $\langle v \rangle$ versus exposure time and (B) Dependence of the water content with exposure time.

Table 1. Summary of wavelengths of the emission bands, water content, first moment of luminescence and diffusion coefficients of prepreg F161 samples at 60 and 80 °C.

Samples	λ_{max} (nm)	Water content (ΔM_{rel} %)	First moment of fluorescence (cm^{-1})	Diffusion coefficient (cm^2/min)
pre-84-60-t ^a	452			1.22475x10 ⁻⁷
	488	0.00	20969	
		0.55	20926	
	15 ^b	0.54	21556	
	30	0.49	21240	
		0.52	20927	
pre-75-60-t		0.08	20775	2.01633x10 ⁻⁸
	7 ^b	0.35	21469	
	15	0.44	21413	
	30	0.49	21383	
		0.50	20811	
		0.59	20757	
pre-58-60-t		0.08	21100	2.0742x10 ⁻⁸
	7 ^b	0.18	21957	
	15	0.24	21986	
	30	0.27	21922	
		0.38	21005	
		0.39	21066	
pre-84-80-t ^a		0.56	20909	5.1126x10 ⁻⁸
	7 ^b	0.28	20816	
	15	0.28	21115	
	30	0.03	21049	
	60	0.40	21023	
	90	0.51	21043	
pre-75-80-t		0.14	20957	1.61816x10 ⁻⁹
	7	0.22	20900	
	15 ^b	0.24	20946	
	30	0.31	21020	
	60	0.43	21003	
	90	0.65	20913	
pre-58-80-t		0.12	21203	1.8963x10 ⁻⁸
	7	0.07	21134	
	15	0	21081	
	30 ^b	0.28	21035	
	60	0.07	21134	
	90	0.26	21089	

^at = exposure time; ^bmost intense band.

452 nm and was the more intense one. The water content and diffusion coefficient were 0.24% and $2.0742 \times 10^{-8} \text{ cm}^2/\text{min}$, respectively. Samples treated at 75 and 84% of relative moisture at 60 °C for 15 days presented maximum first moments of luminescence of 21413 and 21556 cm^{-1} both lower than that of the sample pre-58-60-15. The water contents for samples pre-75-60-15 and pre-84-60-15 were of 0.44 and 0.54%. The water content increases as the increase of the relative humidity, as it was expected, but decreases the effect of water uptake in the first moment of luminescence. Samples pre-58-60-t and pre-75-60-t presented diffusion coefficients very close, but the first sample had the effect of increasing the emission intensity more pronounced. Results indicate that the sample contains a significant amount of bound water, since there is an increased relative intensity of the emission band related to the increased rigidity of the polymer matrix and shift of the emission band to the blue region, due to hydrogen bonding of water with amine and hydroxyl groups.

All the samples treated at 80 °C present emission maxima at 488 nm and values of first moment of luminescence very close. Emission spectra of the samples pre-84-80-7 and pre-84-80-15 show an increase of the relative intensity of the band that could indicate an increase of the stiffness of

the polymeric matrix, but there is no noticeable change in the polarity of the medium, since it was not a blue shift. Values of diffusion coefficient were to close too. It should be emphasized that the gravimetric measurement of the sample pre-58-80-15 is unreliable since there is no mass change. It must be assumed that the samples treated at 80 °C do not contain detectable amounts of bound water. Soles et al.^[29] have discussed that this behavior is partially understood in terms of the interactions between water and a polar group. Increasing the temperature increases the external heat and shifts the above reaction toward the formation of free water. The analysis of the luminescence spectra of the samples treated at 80 °C confirms the conclusions of those authors. There is a great amount of free water in the samples that maintains a higher polarity of polymeric matrix.

3.2 F-161 laminated samples under different humidities at 60 °C e 80 °C

Figure 4A shows the intrinsic luminescence spectra of samples lam-84-60-t. The spectra related to samples lam-75-60-t (Figure 4C) and lam-58-60-t (Figure 4E) are quite similar to those of pre-84-60-t (Figure 1A). All spectra

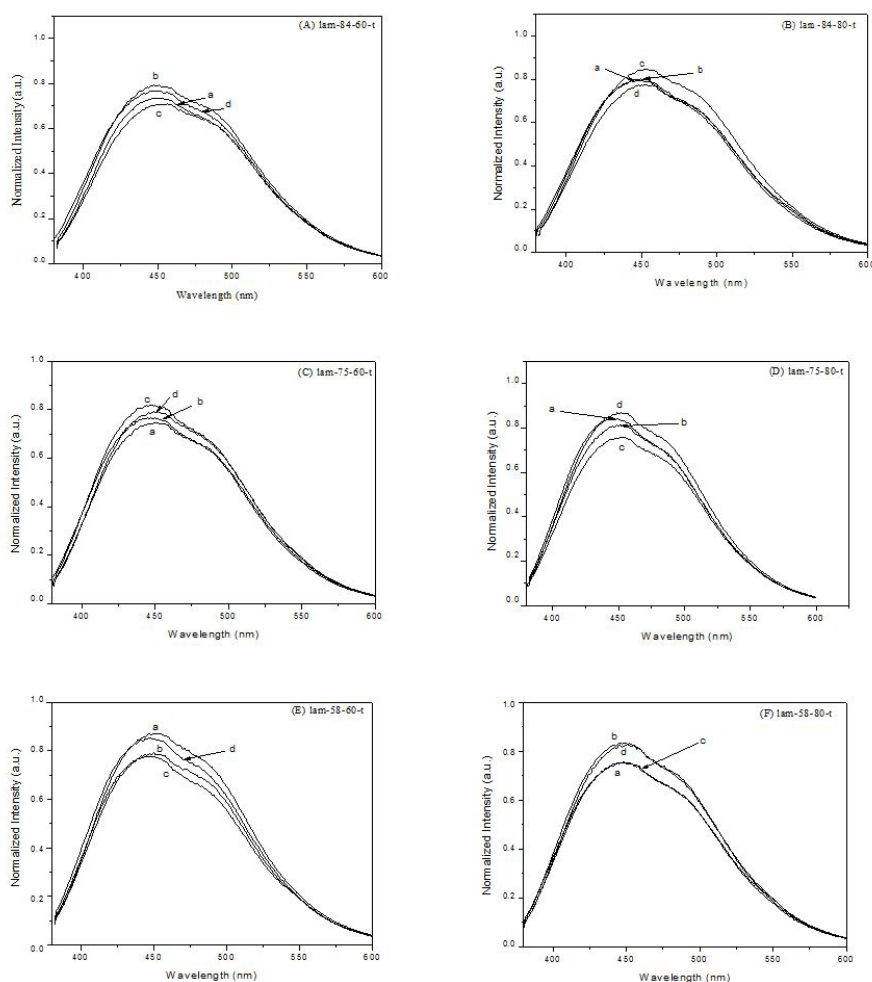


Figure 4. Electronic emission spectra of the samples (A) lam-84-60-t, (B) lam-84-80-t, (C) lam-75-60-t, (D) lam-75-80-t, (E) lam-58-60-t and (F) lam-58-80-t in the following periods of time (in days): (a) 1, (b) 7, (c) 15 and (d) 30.

show the emission bands with the same profile and the wavelength of the maximum emission around 450 nm, as well as the samples pre-84-60-t treated for 1, 7, 60 and 90 days. These bands are attributed to the emission of secondary and tertiary amine groups of the curing agent, which are covalently bound to the epoxy matrix. The emission band at 450 nm can indicate a reducing of the medium polarity related to hydrogen bonding of water with polar groups. All intrinsic luminescence spectra related to samples lam-84-80-t, lam-75-80-t and lam-58-80-t are quite similar and show emission bands with the same profile and the maximum emission of the sample lam-84-60-t do not showing significant changes.

Figures 5A and 5B show the luminescence first moment and the water content variations with the exposure time of the samples lam-84-60-t, lam-75-60-t, lam-58-60-t, lam-58-80-t, lam-75-80-t and lam-84-80-t, respectively. The dependence of the values of first moment luminescence ($\langle \nu \rangle$) of the three samples on the root square of the exposure time is very small. The biggest difference between the higher value and the lower one was equal to 142 cm^{-1} , while the curve related to the prepreg samples showed the major difference equal to 982 cm^{-1} . This behavior was expected, since the amount of the free volume decreased during the curing and lamination process. This increase in the laminate bulk density decreases the capacity of water absorption. However, the matrix polarity does not change during the experiments, but the emission maximum is located at 448 nm and is attributed to bound water. This same photophysical behavior was observed mainly for the samples pre-58-60-7, pre-58-60-15, pre-58-60-30 and pre-75-60-7 and indicated the presence of bound water.

Table 2 summarizes wavelengths of the emission bands, water content, first moment of luminescence and diffusion coefficients of laminated F161 samples at 60 and 80 °C. All spectra showed a maximum emission at 448 nm that indicate a less polar medium due to hydrogen bonding of water to amine and hydroxyl groups. However, samples of laminates not showed a significant increase in the relative emission intensity as observed for samples of prepreg. It can be inferred that the amount of bound water in the laminate is not enough to increase the rigidity of the polymer matrix. Water contents confirm this conclusion since they were much

smaller compared with the samples of prepreg, as it was expected since laminated samples have a lower free volume. The values of the first moment of fluorescence showed no significant variations too. The values of the diffusion coefficients ranged from 2.021×10^{-5} to $4.28 \times 10^{-5} \text{ cm}^2/\text{min}$ for samples lam-84-60, lam-75-60 and lam-58-60. Samples treated at 80 °C had diffusion coefficients varying from 4.9537×10^{-7} to $1.233 \times 10^{-5} \text{ cm}^2/\text{min}$.

3.3 FT-NIR spectroscopy

Figure 6 shows FT-NIR spectrum of samples btt-pre, pre-84-60-90 and pre-84-80-90. Table 3 shows the main absorption bands, including epoxy, methylene, and phenyl groups. These assignments agreed with those from literature^[34] related to epoxy resin. Peaks at 6064 cm^{-1} and at 4524 cm^{-1} are related to the epoxy ring^[35] and they can be attributed to^[35,36]: i) the first overtone of the terminal CH_2 stretching mode; ii) 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} . Table 3 shows the attribution of the vibrational modes of the FT-NIR bands of the prepreg F-161. The band at 4524 cm^{-1} can be attributed to a combination of the stretching fundamental (3050 cm^{-1}) with the CH_2 deformation fundamental (1460 cm^{-1}) of the epoxy ring^[37-39].

The band at 5238 cm^{-1} is related to water absorption process by epoxy resin^[40] and can also be attributed to a combination band of groups $-\text{CH}$ and $-\text{CH}_2$ ^[41]. The intensity of the band at 5238 cm^{-1} of the sample exposed to moisture at 60 and 80 °C (Figure 6B) did not show an increase of intensity when compared with the btt-pre band; this band did not make the water absorption analysis possible. The Novolac epoxy resin structure shows an oxirane group attached to each benzene ring, consequently the density of OH group of this resin is higher than other epoxy resins. Therefore, the band at 4524 cm^{-1} is the best for monitoring the water uptake in the polymeric matrix, since it is related to the epoxy ring. According Gonzalez-Benito et al.^[24], when water molecule enters into the epoxy resin, some molecules may interact with the functional groups of resin, since the resin may not be fully cured^[24]. Water molecule is considered a curing agent of the "Lewis base" type^[42]. The anion generated by the reaction between the amine and

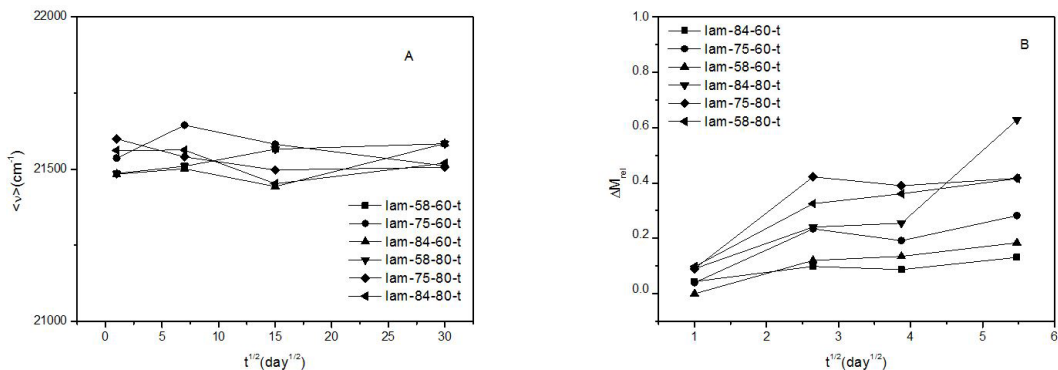
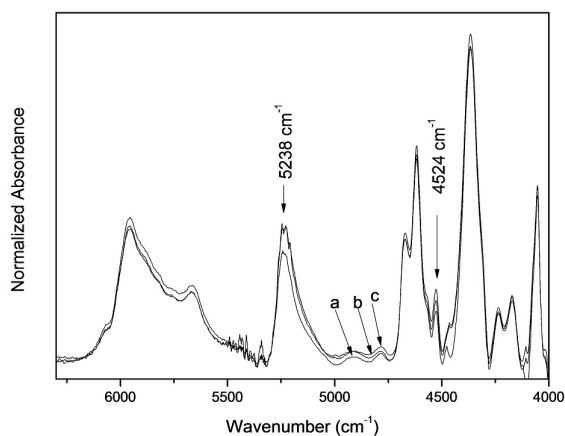


Figure 5. F-161 laminated samples at 60 and 80 °C: (A) First moment of luminescence $\langle \nu \rangle$ versus exposure time and (B) Dependence on the water content with exposure time.

Table 2. Summary of wavelengths of the emission bands, water content, first moment of luminescence and diffusion coefficients of laminated F161 samples at 60 and 80 °C.

Samples	λ_{\max} (nm)	Water content (ΔM_{rel} %)	First moment of fluorescence (cm^{-1})	Diffusion coefficient (cm^2/min)
	448	478		
lam-84-60-t ^a	1	0.044	21483	3.3803.10 ⁻⁵
	7 ^b	0.098	21502	
	15	0.087	21443	
	30	0.131	21584	
lam-75-60-t	1	0.040	21536	2.0220.10 ⁻⁵
	7	0.234	21644	
	15 ^b	0.192	21582	
	30	0.282	21510	
lam-58-60-t	1 ^b	0.000	21486	4.2864.10 ⁻⁵
	7	0.120	21510	
	15	0.135	21566	
	30	0.184	21584	
lam-84-80-t ^a	1	0.091	21562	4.9537.10 ⁻⁷
	7	0.241	21563	
	15 ^b	0.255	21452	
	30	0.628	21520	
lam-75-80-t	1	0.091	21599	1.2333.10 ⁻⁵
	7	0.422	21540	
	15	0.390	21498	
	30 ^b	0.417	21506	
lam-58-80-t	1	0.098	21486	5.8829.10 ⁻⁶
	7 ^b	0.325	21510	
	15	0.361	21566	
	30	0.416	21584	

^at = exposure time; ^bmost intense band.


Figure 6. FT-NIR spectra of samples: (a) btt-pre (b) pre-84-60-90 and (c) pre-84-80-90.

the epoxy ring can react with an active hydrogen present in water, alcohol, phenol or carboxyl to form a new anion. This anion is able to open a second epoxy ring continuing the curing reaction^[10,42-46].

Figure 7A shows the absorbed water content by the samples of F-161 prepreg samples submitted to moisture of 84, 75 and 58% at 60 °C. There is a significant increase in the water content during periods of time^{1/2} of 2.6, 3.9 and 5.5. In the following periods of time^{1/2} there is an abrupt decrease in intensity, because of the stabilization of the quantity of

absorbed water by samples. This behavior suggests that in the early periods, the water binds to epoxide groups increasing the intensity of the band at 4524 cm^{-1} and, in the subsequent period of time, water molecule acts as a curing agent, promoting the opening of the epoxide ring supporting the curing process. Comparing the results obtained by the weight measurements and water content measured by FT-NIR, one can observe the same behavior: an increase in the earlier periods of time due to water absorption and, in the subsequent periods a stabilization of water content due to the crosslink process promoted by water.

Table 3. Attribution of the normal mode vibrations of the NIR absorption spectra of prepreg samples.

Wavenumber (cm ⁻¹)	Band assignments
6071	First overtone of terminal (methylene)-CH fundamental stretching vibration (epoxy ring).
5961	Overtone of the CH axial deformation of the phenyl group.
5886	First overtones of the fundamental -CH ₂ and -CH stretching vibration.
5661	-OH combination band.
5247	-CH, -CH ₂ combination band.
4672	Combination band of the aromatic conjugated C=C stretching (=1625 cm ⁻¹) with the aromatic -CH fundamental stretching (=3050 cm ⁻¹).
4625	Combination band of the aromatic conjugated C=C stretching (=1625 cm ⁻¹) with the aromatic -CH fundamental stretching (=3050 cm ⁻¹).
4524	Conjugated epoxy CH ₂ deformation band (=1460 cm ⁻¹) with the aromatic -CH fundamental stretch (=3050 cm ⁻¹), -NH ₂ absorption band.
4480	-CH, -CH ₂ combination band.
4362	-CH ₂ combination band.
4216	-CH, -CH ₂ combination band.
4155	Aromatic -CH combination band.
4058	Aromatic combination band.

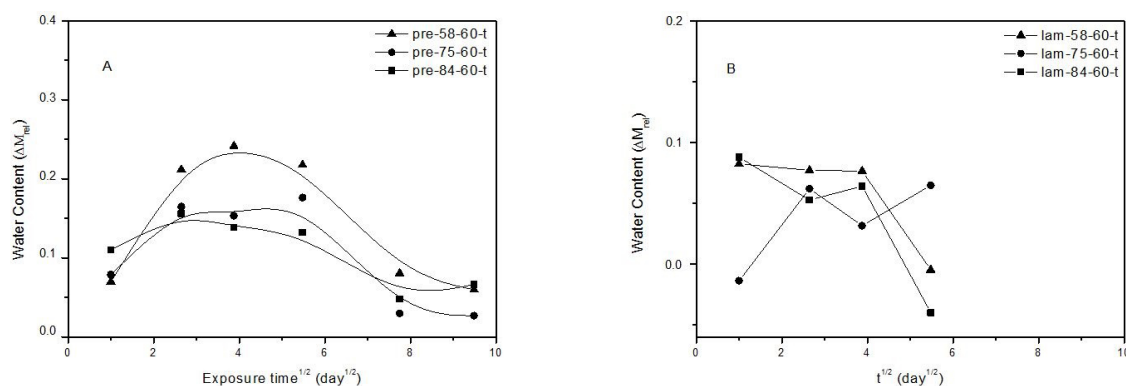
**Figure 7.** Water content versus time measured by FT-NIR: (A) F-161 prepreg samples at 60 °C for the following periods of time (in days^{1/2}): 1.0, 2.6, 3.9, 5.5, 7.7 and 9.5 and (B) F-161 laminates samples at 60 °C, for the following periods of time (in days^{1/2}): 1.0, 2.6, 3.9 and 5.5.

Figure 7B shows the amount of water absorbed by F-161 laminates samples submitted to relative humidity of 84, 75 and 58% at 60 °C measured by FT-NIR, respectively. It can be claimed that no significant changes in the water content of the laminates (Figure 5). This behavior was expected because laminate samples were already cured and this process decreases free volume of polymeric matrix. Therefore, there is a greater compression of the polymer chains and less capacity to absorb water.

4. Conclusions

All samples of prepreg F-161, independent on relative humidity and exposure time, showed very similar photophysical behavior: (a) a blue shift of the maximum emission and (b) an increase in relative intensity of luminescence. This photophysical behavior can be attributed to a change of the medium polarity.

The decrease in the relative intensity of luminescence in the spectra of samples treated for longer times (30, 60 and 90 days) may be related to the plasticization process of the polymer matrix performed by water molecules. The results of this

work strongly suggest that water first acts as an pseudo curing agent, since it was observed an increasing of the emission intensity and then occurs plasticization of the polymeric matrix related to decreasing of the emission intensity. It must be clear that this photophysical behavior was observed for all samples submitted to different relative humidities. This photophysical behavior had not been previously observed by other authors

The first moment of luminescence (ν) variation is inversely proportional to the quantity of water absorbed by the polymer matrix. Prepreg samples results indicated that the polarity of prepreg samples change during the experiments, characterized by the red shift of the emission spectra. On the other hand, it is not observed either a red shift emission or an increasing of water content in laminated samples, due to the curing process conditions of temperature and pressure.

The results provided by FT-NIR of samples treated for short periods of time showed an increase in the intensity of the band 4524 cm⁻¹. This increase is related to hydrogen bonding between the absorbed water molecules and epoxy groups and confirms the presence of bound water observed through luminescence spectroscopy.

5. Acknowledgements

The authors thank Instituto de Aeronáutica e Espaço (IAE), Fundação de Apoio à Pesquisa do Estado de São Paulo (FAPESP) and Coordenação de Aperfeiçoamento de Nível Superior (CAPES) (Brazil).

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Received: May 23, 2016

Revised: Aug. 19, 2016

Accepted: Dec. 20, 2016