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Influence of thermal history on the mechanical properties of carbon fiber–acrylate composites cured by electron beam and thermal processes

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ABSTRACT

The mechanical properties of an acrylate resin and its carbon fiber composite, as well as the adhesion strength between them, were characterized in the case of thermal and electron beam curing (with and without thermal post-cure). It was shown that the properties of the matrix were similar but that the thermal history during the curing had a direct influence on the type of interactions that were generated at the interface, leading to different level of adhesion strength and level of performance for the associated composites. In the case of a thermal cure, the thermal profile allowed the generation of covalent bonding at the interface by thermal degradation of carboxylic acid functionalities and simultaneous production of radicals at the surface of the fiber. A high level of adhesion strength was obtained, which was not the case for electron beam curing without a thermal post-cure at the appropriate temperature.

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1. Introduction

The composite industry keeps growing, so energy efficiency and environmental concerns are more and more required. The electron beam curing of composite materials represents a promising alternative technology to conventional thermal curing. The development of high energy electron accelerators (10 MeV) and adapted initiators and monomers enabled the scale-up of electron beam curing at the industrial level. The manufacture of high performance composite parts was demonstrated first in France at Aerospatiale in the late 1970s [1], and then in Canada [2,3] and USA [4–6]. Electron beam curing has undeniable advantages compared to autoclave processing. Indeed, its energy efficiency can be around 10 times higher [7], it produces much less volatile organic compounds and it eliminates the use of toxic hardeners in the case of epoxy composites and radical initiators in the case of unsaturated resins based composites. The curing is complete after a few minutes only, and the remaining thermal stress is less important than in the case of thermal curing because the temperature created inside the material during the cure is lower [8]. Moreover, the size of the composite parts tends to increase, so the use of bigger autoclave devices that would consume more energy seems to be compromised [9].

The main factor still preventing the use of that process comes from the mechanical properties of composites cured by electron beam that cannot currently compete with the mechanical properties of the best composites cured by a thermal treatment. Indeed, the values associated to the resilience, the InterLaminar Shear Strength (ILSS) and the transverse mechanical properties of composites cured by electron beam are usually lower. In order to improve the toughness of composites cured by electron beam, some research was done to improve the fracture resistance of the matrix, in the case of epoxy [10,11] and acrylate [12–14] resins. A major accomplishment was obtained through an increase of the fracture toughness (K_{IC}) from 1 MPa m$^{0.5}$ to 2.2 MPa m$^{0.5}$ of some acrylate resin [15], thus competing with the toughness of thermally cured resins. The physico-chemical and mechanical properties of a composite material also depend on the properties of the interface/interphase [16,17], which depend on the conditions used during the manufacturing [18]. Factors influencing adhesion strength are mechanical interlocking [19,20] , physical [21–25] and chemical interactions [26,27] , the presence of defects [28,29] and remaining stress due to the thermal history of the material [30] or the shrinkage of the matrix [31]. Therefore, the mechanical properties in the interphase region have to be investigated in the case of electron beam curing and efficient carbon fiber surface treatments have to be developed.

The development of carbon fiber surface treatments adapted to electron beam curing is relatively modest in comparison with what has been achieved for the conventional thermal curing process. Most of the developed surface treatments consisted in a coating which chemistry was compatible with cationic polymerization (epoxy resins). Some of them resulted in a significant improvement

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of the InterFacial Shear Strength (IFSS) [32–35]. It was also noticed that a coating of epoxy enriched with photoinitiator led to a significant improvement of the mechanical properties of the interphase and of the composite [36]. Mäder [37] investigated a plasma surface treatment. Zhang et al. [38] studied an electrolytic oxidation in acid and basic media. A limited improvement of adhesion strength was obtained and only the use of an adapted coupling agent resulted in a significant increase. Most of the surface treatments that were suggested still presented technological issues, especially for the development of a continuous surface treatment [39]. The influence of the electron beam curing process and post processing have also been studied for epoxy resins [40,41], but generally little attention was focused to the effect of a thermal post-cure. In France, some surface treatments were developed for acryate based systems. They were based on coupling agents containing silanes, isocyanates or allyl functionalities [42,43]. All in all, no specific surface treatment that was able to induce comparable transverse mechanical properties with the ones obtained via a conventional thermal curing process was published, with the exception of the coating of the carbon surface with a high density of specific functionalities (vinyl groups, thiols) by the use of plasma polymerization [44].

More fundamental research is necessary in order to understand why the mechanical properties of the interphase and the adhesion strength are low in composites cured by electron beam. It is necessary to determine which parameters are the most influent on the level of adhesion strength. It was shown that different commercial oxidation surface treatments, generating different roughnesses and different chemistries at the surface of carbon fibers, were leading to the same level of adhesion strength with an acrylate resin [45]. It was also reported that different oxidative surface treatments did not really change the adhesion strength in comparison with the equivalent untreated fibers [46,47] and in comparison to the improvements that are usually obtained with a thermal cure. Evidently, a factor to be identified was responsible for the fact that some interactions between the fiber surface and the matrix were generated with a conventional thermal curing and were not created with electron beam curing. In this study, the mechanical properties of the matrix, the interphase and the composite, corresponding to electron beam curing and thermal curing, were compared. Data obtained with a thermal post-cure of the parts cured by electron beam were also investigated. The influence of the thermal history of the composite during the cure on the interactions that were generated at the interface was highlighted.

2. Materials and methods

2.1. Acrylate resin

The resin used in this study was Ebecryl 600® obtained from Cytec Industries Inc. It is a diacrylate resin with a polyether structure derived from Di-Glycidyl Ether of Bisphenol A (DGEBA) epoxy resin and it can be cured by ultraviolet (UV) light and electron beam. The chemical structure of the monomer is presented in Fig. 1. It was degassed before use under vacuum. A temperature of 90 °C had to be set during the degassing in order to reduce its high viscosity (80 Pa s at 30 °C).

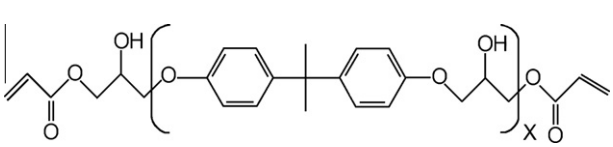

Fig. 1. Structure of the monomer of Ebecryl 600®. A Steric Exclusion Chromatography analysis gave $x = 1–2$ and low polydispersity.

2.2. Carbon fibers

Intermediate Modulus PAN-based Tenax® IMS 5001 and Intermediate Modulus PAN-based Hextow IM7® carbon fibers used in this study were produced by Toho Tenax Europe GmbH and by Hexcel respectively. Both fibers are surface treated (oxidation treatment) but non-sized. They were used as received from the manufacturer. The main mechanical properties of IMS 5001 fibers and IM7 fibers are presented in Table 1. It has to be noticed that the values of the average fiber diameter are equal and the mechanical properties are almost identical, which means that any difference in the mechanical properties of a unidirectional composite laminate made with the same matrix and cured in the same conditions is potentially due to a difference in the surface properties (surface chemistry and roughness). The cross-section of both fibers is circular. In this study, the characterization of the surface properties of those fibers is limited to the surface chemistry by the use of X-ray Photoelectron Spectroscopy (XPS) but more data related to the topography at a micrometric and nanometric scale and measurement of specific surface area by gas adsorption can be found elsewhere [45].

2.3. Manufacturing of pure resin panels

Some panels were manufactured from pure resin and samples with specific required size were cut from these panels for flexural test, fracture toughness test (K_{IC}) and density measurement. As explained hereafter, Ebecryl 600® is subjected to an important shrinkage during the cure. So the use of silicon molds in which the shape of the sample is carved is not recommended. The samples obtained with this method are often twisted and present uncontrolled thicknesses. Instead, two steel plates were hold vertically and sealed with silicon rubber cord and paperclips. In this case, perfectly flat panel with controlled thickness depending on the diameter of the silicon rubber cord were obtained. A very small amount of PolyTetraFluoroEthylene (PTFE)-based MS-136W release agent from Miller Stephenson was spread with a paper towel on the surface of the plates. All the sample cut from those panels were polished successively with a VP-50 Vari/Pol LECO polisher, using LECO silicon carbide coated disks Grit 400 and Grit 600. Samples were continuously rinsed with tap water, to remove of a layer of resin that was in contact with the steel plate and which polymerization may have been affected in comparison to the bulk.

2.4. Measurement of the cure volume shrinkage of pure matrix

As mentioned in the introduction, the cure volume shrinkage of the matrix can have a negative influence on adhesion strength between the fibers and the matrix. The cure volume shrinkage of the matrix was calculated according to

$$\text{Cure volume shrinkage}(\%) = \left(1 - \frac{d_{\text{uncured resin}}}{d_{\text{cured resin}}}\right) * 100 \qquad (1)$$

where d is the density of the resin. The density of the uncured resin was given by the manufacturer and is 1.189 g cm^3 at 20 °C. The density of the cured resin was measured by the displacement method (ASTM D792) using water. Twenty samples were tested.

2.5. Measurement of the fraction conversion of the matrix by Fourier Transform Infra Red spectroscopy (FTIR)

A Bruker Vertex 70 Infra-Red spectrometer was used with a Harrick Scientific MVP ATR accessory including a diamond internal reflection element and was controlled by Opus 6.5 software. Data were collected between 400 cm^{-1} and 4400 cm^{-1}. The resolution

Table 1
Properties of IMS 5001 and IM7 carbon fibers.

	Number of filaments	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)	Diameter (μm) [44]
IMS 5001	12,000	5600	290	1.9	5.4 ± 0.3
IM7	12,000	5670	276	1.9	5.4 ± 0.2

was 4 cm^{-1}. Each spectrum was an average of 60 scans. The fraction conversion of the resin π was calculated according to Eq. (2) by following the decrease of the intensity of the peak located at 806 cm^{-1} corresponding to the out of plan deformation of C = C bonds, reduced by the contribution of the peak located at 827 cm^{-1} corresponding to an out of plane C—H deformation:

$$\pi = 1 - \frac{I_c^{806} - 0.16 * I_c^{827}}{I_0^{806} - 0.16 * I_0^{827}} \quad (2)$$

In Eq. (2), I_c^{806} and I_c^{827} are the intensities of the two peaks corresponding to the cured samples and I_0^{806} and I_0^{827} are the intensities of the two peaks corresponding to the uncured samples.

2.6. K_{IC} and flexural test on pure resin

K_{IC} test was carried out following ASTM D 5045, using the single-edge-notch bending method and 10 samples were tested. The dimensions of the specimens were 56.0 mm × 10.0 mm × 5.0 mm. The initial length of the crack was kept between 4.5 and 5.5 mm, considering the width of the specimen, and was obtained by machining and tapping with a fresh razor blade. The samples were cut in the pure resin panels described before and were polished with the same protocol as the one reported in Section 2.3.

The flexural test was performed on 10 samples according to ASTM 790. The samples were also cut in the pure resin panels and polished by following the same protocol. The dimensions of the specimens were 127 mm × 12.7 mm × 3.2 mm and the span-to-depth ratio was 16.

2.7. Characterization of the surface chemistry of the fibers by X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) analysis of the carbon fiber surface was carried out with a Thermo Scientific K-Alpha X-ray photoelectron spectrometer. It was equipped with a conventional electron energy analyzer operated in the fixed transmission mode at constant pass energy of 200 eV for the survey spectra and 50 eV for the core level spectra. Incident radiation was generated by a monochromatic Al Kα source (1486.6 eV) operated at 420 W (14 kV; 30 mA). Photo-emitted electrons were collected at a take-off angle of 90° from the sample. The pressure was about 10^{-7} Pa. The spectrometer energy scale was calibrated with respect to Ag 3d5/2, Au 4f7/2 and Cu 2p3/2 core level peaks, set with binding energies of 368.3, 84.0 and 932.7 eV, respectively. All binding energies are referenced to the adventitious C(1s) peak located at 284.6 eV. Instrumental sensitivity factors were taken as C(1s):O(1s):N(1s) equals 0.919:2.449:1.882, respectively. C(1s), O(1s) and N(1s) core level spectra were fitted to GL function (product of a Lorentzian by a Gaussian) using Avantage 4.44 software. The background was a Tougaard type. The fitting of C(1s), O(1s) and N(1s) peaks was done using the component peaks presented in Table 2. The O(1s) peak was fitted according to components suggested by Zielke et al. [48] and Biniak et al. [49]. The N(1s) peak was fitted according to components suggested by Pels et al. [50] and Biniak et al. [49]. The C(1s) peak fitting was done so that the total area of all the oxy-carbonated components could not be higher than the total area of the O(1s) peak and that the total area of all the nitro-carbonated components could not be higher than the total area of the N(1s) peak.

2.8. Washing procedure of carbon fibers exposed to Ebecryl® 600

Some samples of fibers previously dipped into the resin were exposed to specific thermal programs (see Section 3.3). Afterwards, to remove the resin from the fiber surface, a washing procedure was carrying out as follows. The fibers were dipped in a sealed beaker full of acetone and the mixture was stirred with a magnetic stirrer for 3 days, the contaminated acetone being purged each day and the excess of resin covering the surface of the fibers being removed by washing the fibers with fresh acetone. The fibers were then extracted in acetone with a Soxhlet extractor during 8 h. The process was repeated twice. The extracted fibers were then dried at 50 °C in a regular oven for 30 min.

2.9. Manufacturing of composite samples

2.9.1. Pull-out test samples

The adhesion strength between the carbon fibers and the resin was measured by a micromechanical test derived from the single fiber pull-out test. A resin drop was deposited at the junction of two single filaments (Fig. 2). After curing, a tensile force was applied on the filaments thanks to an MTS Alliance RT/5 twin screw load frame equipped with a 5 N load cell and controlled by the software Testworks 4. The displacement speed was 1 mm min^{-1}. The shortest embedded length led to the pull-out phenomenon. The shear strength at a given embedded length was then calculated according to Eq. (3), considering that the maximum force F_{max} measured during the test was the force applied when the debonding of the interface occurred:

$$\tau = \frac{F_{max}}{2\pi r \ell_e} \quad (3)$$

where r is the fiber radius and ℓ_e the shortest embedded length leading to the pull-out phenomenon.

Data reduction was performed according to Greszczuk's model, leading to the estimation of the InterFacial Shear Strength (IFSS) by an extrapolation at an embedded length equal to zero [51]. The interfacial shear is related to the shortest embedded length leading to the pull-out phenomenon according to

$$\tau_{max} = \frac{\tau \alpha \ell_e}{\tan h(\alpha \ell_e)} \quad (4)$$

with α and the value of the interfacial shear strength τ_{max} being two constants that are characteristics of the considered fiber–matrix interface. α is related to the Young modulus of the fiber E_f, the shear modulus of the matrix G_i and the thickness of the interphase that transfers the stress from the matrix to the fiber b_i according to

$$\alpha^2 = \frac{2G_i}{b_i r E_f} \quad (5)$$

Lawrence [52], Chua and Piggott [53], Zhandarov et al. [54,55] and Hsueh [56] published more advanced models. Nevertheless, Désarmot and Favre [57] used several models to fit experimental data and showed that the Greszczuk's model was the one that fitted their data the best. For each curing process, the IFSS was determined with

Table 2
Component peaks used in the fitting of C(1s), O(1s) and N(1s) peaks.

C(1s)		O(1s)		N(1s)	
Binding energy (eV)	Component peak	Binding energy (eV)	Component peak	Binding energy (eV)	Component peak
284.4 ≪ 284.6	Csp^2	531.2 ≪ 531.4	Ph=O (quinone), Ph—C=O,amides	398.4 ≪ 399.0	Pyridine
284.9 ≪ 285.1	Csp^3	532.0 ≪ 532.2	C=O (ester, anhydride, amide), carboxylic acids	399.4 ≪ 399.8	Amines, amides, nitriles
284.8 ≪ 285.0	C—COOR	532.7 ≪ 532.9	R—OH, C—O—C	400.1 ≪ 400.7	Pyrrolidine, pyridone
285.4 ≪ 285.6	C—N	533.5 ≪ 533.7	Ph—OH, C—O (ester, anhydride)	401.1 ≪ 401.7	Pyridinium, protonated N
286.1 ≪ 286.4	C—O—R, C≡N	534.8 ≪ 535.2	Chemisorbed H_2O	403.7 ≪ 404.3	Shake up
287.4 ≪ 287.6	C=O	536.2 ≪ 536.6	Physisorbed H_2O	405.5 ≪ 405.7	NO_x
288.3 ≪ 288.9	COOR	538.2 ≪ 538.6	Shake up		
290.1 ≪ 290.5	Physisorbed H_2O				
291.3 ≪ 291.7	Shake up				

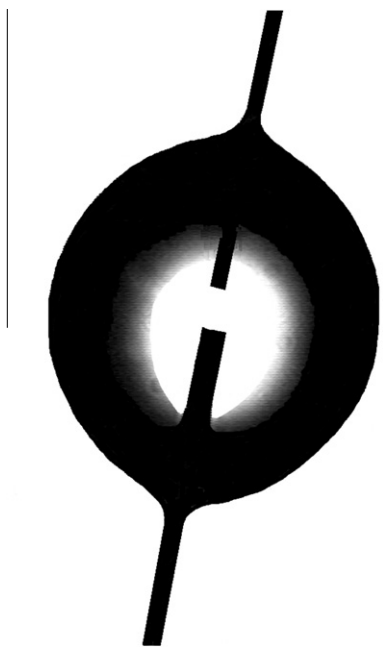

Fig. 2. The pull-out test system.

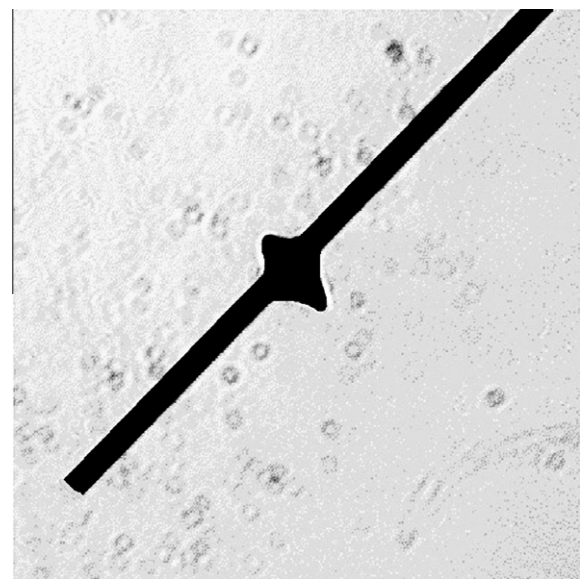

Fig. 3. Image of the fiber that has been pulled-out from the resin (magnification = 200×).

at least twenty eight pull-out validated experiments. The values of α and τ_{max} were obtained by fitting the data with the Greszczuk's model and the least square method, using the software Origin™. The embedded length l_e was measured after pull-out using an optical microscope and the image analysis software ScnImage™, thanks to a residual piece of resin corresponding to the point of entrance of the single fiber in the matrix droplet (Fig. 3).

2.9.2. Unidirectional panels

A detailed description of the manufacture of the panels cured by electron beam, based on a pre-impregnation and lay-up, and of the electron beam processing can be found elsewhere [45]. The dose received by the samples was 4 × 25 kGy. For the panels cured by a thermal treatment, Ebecryl 600® was first heated at 90 °C to reduce its viscosity and then thoroughly mixed with 1.5 wt.% of tert-butylperoxybenzoate (initiator) by the use of a DAMON/IEC CRU-5000 centrifuge (rotation speed: 3000 rpm, time: 4 min), which also enabled a degassing of the mix, the radical polymerization of acrylate resins being inhibited by oxygen. Unidirectional composite panels were obtained by winding the carbon fibers around a steel frame that kept them under tension and placing them in a two-piece steel mold preheated at 90 °C. The fibers were impregnated with an excess of resin by lay-up with the use of a roller made out of Teflon®. When closing the mold with pressure, the excess of resin was expelled. The dimensions of free space in the mold controlled the dimensions of the composite samples, which was constant. The mold was then placed in a digitally controlled furnace. The thermal program for the cure was 2 h at 150 °C followed by 1 h at 160 °C. The volume fraction of fibers of all panels was 60%.

2.9.3. Record of the thermal history of the sample during the cure

The thermal history of the resin during the cure was recorded using a thermocouple inserted in the composite and connected to an Omega Interface controlled by the software ChartView. Temperature measurements were collected in 30 s intervals.

2.10. Mechanical testing

Short beam shear and flexural tests were done according to ASTM D2344 and ASTM 790 respectively. In the case of the flexural test, 10 samples were tested. Their dimensions were 127 mm × 12.7 mm × 3.2 mm and the span-to-depth ratio was 16. In the case of the short beam shear test, 20 samples were tested. Their dimensions were 19.2 mm × 6.4 mm × 3.2 mm and the span-to-depth ratio was 4. A MTS Alliance RT/5 twin screw load frame equipped with a 5 kN load cell was used. The testing device was controlled by the software Testworks 4. All coupons broke according to an interlaminar shear failure mode.

2.11. Dynamic Mechanical Analysis (DMA)

The viscoelastic properties of the fully cured resin were determined using a TA Instruments RSA 3 Dynamic Mechanical Analyser controlled by the software TA Orchestra. The three point bending testing mode was used. The strain was set to 0.02%, at a frequency of 10 Hz. The ramp of temperature was 5 °C min^{-1} from room temperature to 230 °C. The glass transition temperature was considered to be the temperature corresponding to the highest value of $\tan\delta$.

2.12. Differential Scanning Calorimetry (DSC)

A Q2000 DSC apparatus from TA Instruments was used. The samples were hold in liquid cells and under nitrogen atmosphere. A ramp from 25 °C to 250 °C with a rate of 5 °C min^{-1} was applied during the analysis.

3. Discussion and results

3.1. Comparison of the properties of Ebecryl 600® cured by thermal treatment or by electron beam

The FTIR spectra of pure Ebercryl 600® before and after the thermal cure are given in Fig. 4, with a focus on the peaks located at 806 and 827 cm^{-1}. The disappearance of C=C bonds during the cure is clearly seen by the decrease of the intensity of the peak located at 806 cm^{-1}. The calculated fraction conversion value from FTIR spectra was 0.82 for thermal cure, which was slightly higher than the value obtained with the electron beam cure (0.80). Values of the fraction conversion below 0.80 (with a maximum at around 0.78) were reported by Coqueret et al. [58,59] in the case of 1.5 mm thick films, both for UV and electron beam curing. The final fraction conversion is indeed very sensitive to the thermal history of the sample and its thickness (a thicker sample generating more internal heat during the polymerization, which results in more mobility of the reactive species and delays the glass transition according to Glauser et al. [60]). A value of 0.83 was mentioned by Gang et al. [61] for the cure of Ebecryl 600® by UV, which is similar to our findings. Typically, Ebecryl 600® has a high viscosity as compared to most common thermosets because of the presence of hydroxyl groups in the monomer (Fig. 1). Hence, this resin quickly reaches a glassy state when considering the evolution of the viscosity in function of the fraction conversion. A value of 0.80 for the fraction conversion is then typical when considering the curing of Ebecryl 600®. Using reactive diluents seems to be the only way to reach higher values [62]. Both of the glass transition temperature and the cure volume shrinkage were higher for thermal cure, showing a significantly more advanced cross-linking compared to electron beam curing, which is in accordance with the values of the fraction conversion measured by FTIR (see Table 3). When it comes to the fracture toughness, the values of K_{IC} were measured as 1.0 ± 0.2 and 0.9 ± 0.2 [64] for thermally cured and electron beam cured samples, respectively. The flexural properties reflected the slight difference in fraction conversion and reticulation density, as the strength was slightly lower with a thermal treatment, with a similar value of the modulus. A slight difference in the fraction conversion of the resin is reflected in the mechanical properties. Nevertheless, other work [65] showed that the mechanical properties of blends of similar acrylate resins did not change significantly after reaching a fraction conversion of 0.65, as the flexural strength and flexural modulus reached a plateau. The cure volume shrinkage of the matrix should have a significant negative effect on the mechanical properties of the interface in the case of the thermal cured composite. Indeed, it was shown [31] that the adhesion strength in carbon fiber–vinyl ester composites is affected when its value is higher than 4–5%. As mentioned earlier, the properties of a composite material are not only dependent on the properties of the fibers and the matrix but also on the interfacial properties. So, the adhesion strength between the matrix and the carbon fiber was also investigated.

3.2. Comparison of the adhesion strength between Ebecryl 600®, cured by thermal treatment or by electron beam, and IMS 5001 fibers

The pull-out test data and their curve fitting are presented in Fig. 5. The adhesion strength between fiber and matrix was notably low for the electron beam cured samples (35 MPa) as compared to the value obtained from thermally cured samples (82 MPa) (Table 4). Krzeminski et al. [59,66] studied the mechanisms

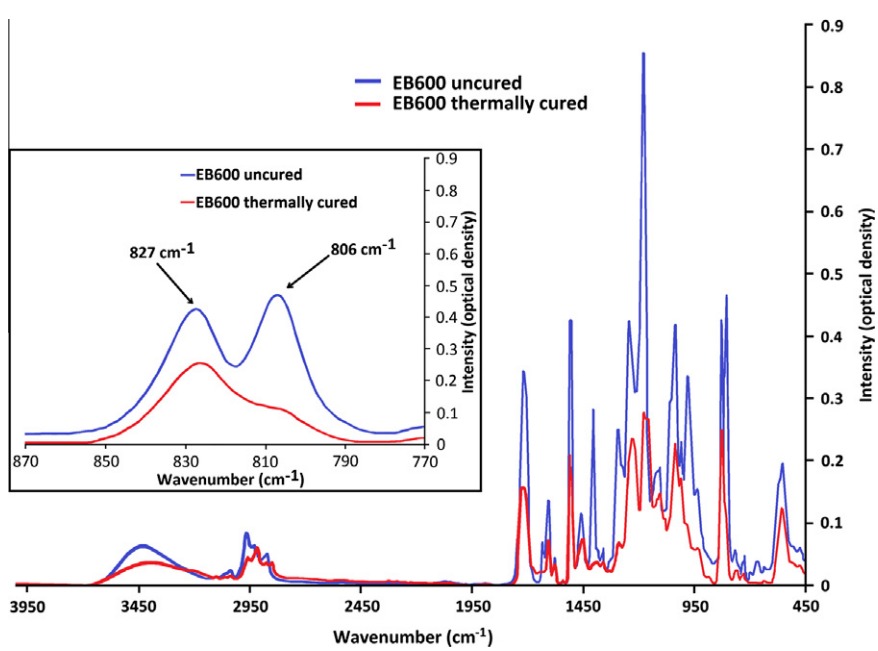

Fig. 4. FTIR analysis of Ebecryl 600® cured by electron beam and thermal treatment. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 3
Physical and mechanical properties of Ebecryl 600® cured by thermal treatment and electron beam.

	Density before cure (g cm^3)	Density after cure (g cm^3)	Cure volume shrinkage (%)	*Tg* (°C)	Fraction conversion (FTIR)	Flexural modulus (GPa)	Flexural strength (MPa)	K_{IC} (MPa m$^{0.5}$)
Electron beam (4 × 25 kGy)	1.24	–	4.7 [63]	137 [63]	0.80 [63]	4.0 ± 0.2 [63]	144 ± 8 [63]	0.9 + 0.2 [64]
Thermal cure 2 h 150 °C + 1 h 160 °C		1.17	5.6	144	0.82	4.2 ± 0.1	128 ± 8	1.0 ± 0.2

influencing the generation of the structure of Ebecryl 600® polymer network. They concluded that the structure of Ebecryl 600® polymer network does not depend on the initiation mechanism, curing temperature and polymerization time scale for a same value of fraction conversion. With similar fraction conversions and similar interactions at the interface, the adhesion strength is expected to be lower in the case of the thermal cure because of the cure volume shrinkage of the matrix. However, this has not been observed. So, the value of the fraction conversion of the matrix of the pull-out samples was measured with the same method as for pure resin. The fraction conversion of the pull-out samples cured by electron beam was found to be 0.75, which is a typical value for thin films. The fraction conversion of the pull-out samples cured by thermal treatment was 0.80. The value obtained for the electron beam cured samples is indeed different from the values obtained with thick films due to the shape of the pull-out samples that was potentially responsible for a high transfer of thermal energy to the surrounding atmosphere and the carbon fiber. Especially in the case of electron beam curing, there is a higher gradient between the temperature created inside the resin drop by the exothermicity of the polymerization and the surrounding atmosphere (room temperature). In the case of a thermal cure, the gradient of temperature was much lower, because the surrounding atmosphere and the carbon fiber were already at 150 °C before the start of the cure.

A thermal post-cure of 1 h at 160 °C was applied to the samples cured by electron beam. Raising the temperature of the sample above its glass transition temperature allowed some mobility of the unreacted species that were trapped in the glass state and completed the cure. The fraction conversion increased to 0.79. The corresponding adhesion strength was 86 MPa, that is to say an equivalent adhesion strength to the one of samples cured by a thermal treatment (Table 4). Apart the consideration about the value of the fraction conversion, it is also expected that the fraction conversion is more homogeneous in the whole sample with thermal curing. By reaching a value of fraction conversion of the matrix that is slightly higher, the transfer of an external load on the reinforcement material is more efficient, so it is expected to increase the adhesion strength. Nevertheless, there was some concern about the fact that such a slight variation of the fraction conversion would lead to such a significant variation of the adhesion strength between the matrix and the carbon fiber. Indeed, the fracture profile of a unidirectional composite IMS 5001-Ebecryl 600® cured by electron beam showed a pure interfacial rupture mode [45], in accordance with the very low value of interfacial shear strength measured by the pull-out test. On the contrary, a SEM picture of the fiber (Fig. 6) that was pulled out, in the case of a thermal treatment, clearly showed a mixed interfacial-cohesive rupture mode, which was in accordance with the high value of interfacial shear strength obtained with a thermal cure. Two mechanisms can be possible to explain the difference in adhesion strength depending on the curing process. The first hypothesis is the creation of an under-crosslinked interphase in the case of electron beam curing, similar to a weak boundary layer, that would lead to poor adhesion strength. The relative volume of this interphase being small, the variation of the fraction conversion would barely be seen by FTIR analysis. It is not known at this point if such an interphase would lead to a pure interfacial failure. The second hypothesis would be a difference in the nature of the interactions that are generated at the interface, strong in the case of a thermal cure and weak in the case of electron beam curing. That is why it was necessary to characterize any eventual change in the interactions that were created at the interface with both curing processes. It was then decided to study the influence of the thermal history of the matrix on the nature of the interactions that were generated at the interface.

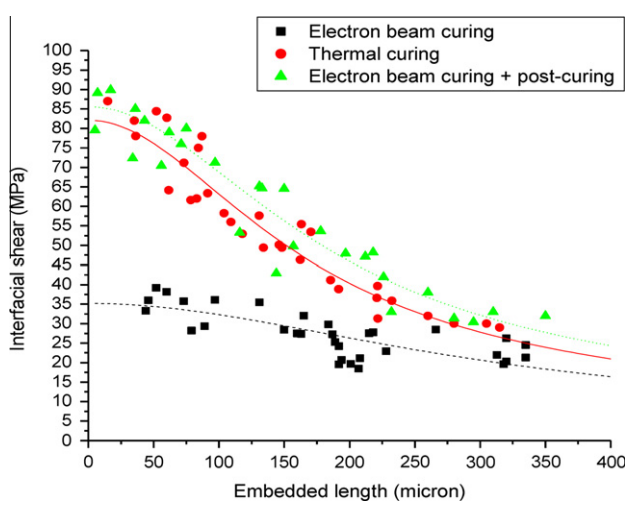

Fig. 5. Calculation of the InterFacial Shear Strength (IFSS) according to Greszczuk's approach. Comparison of interfaces IMS 5 001-Ebecryl 600® cured by thermal treatment, by electron beam, and electron beam with a thermal post-cure. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.3. Influence of the thermal history of the sample on the nature of the interactions generated at the interface

In order to check if a reaction at the fiber/matrix interface could be induced only by a heat treatment, pure Ebecryl 600® and a composite IMS 5001 fibers-Ebecryl 600® (∼ 40% of fibers by volume) were subjected to a DSC analysis with a thermal program described in Section 2.12. As displayed in Fig. 7, the DSC analysis of pure Ebecryl 600® highlighted a homopolymerization with a maximum reaction rate at 220 °C, showing that this resin is relatively stable at high temperature. The same analysis, in the case of the composite, showed an exothermic reaction starting at around 150 °C, with a maximum reaction rate at 173 °C. It is clear that the presence of the carbon fiber initiated a partial polymerization of the matrix, which was complete after an exposure above 250 °C, just as for pure resin. Since the resin is stable at that temperature (150 °C), it is reasonable to consider that the polymerization was due to a thermal degradation of some of the fiber surface functional groups.

Table 4
IFSS values corresponding to interfaces IMS 5001-Ebecryl 600® cured by thermal treatment, by electron beam, and electron beam with a thermal post-cure.

	Electron beam (4 × 25 kGy)	Electron beam (4 × 25 kGy) + post-cure 1 h at 160 °C	Thermal cure 2 h 150 °C + 1 h 160 °C
IFSS (MPa)	35 ± 2	86 ± 2	82 ± 3

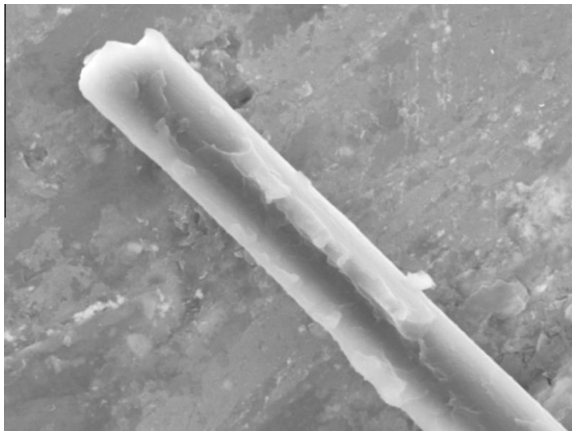

Fig. 6. SEM picture of a pulled-out fiber in the case of a thermal cure.

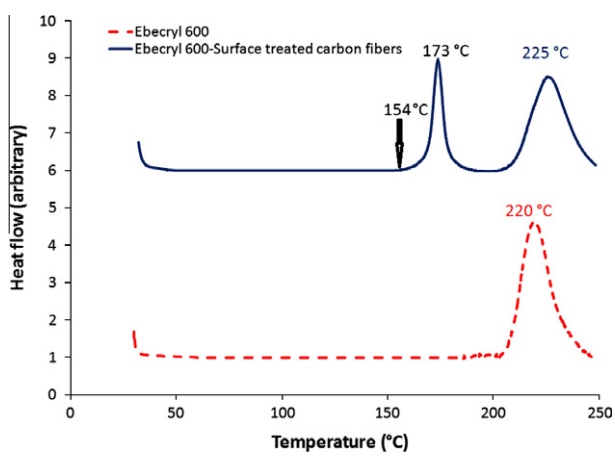

Fig. 7. DSC curves corresponding to the reaction of Ebecryl 600® with the CF surface under temperature and to the homopolymerization of Ebecryl 600®. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

It is known that in this range of temperature the only mechanism that can generate radicals that would initiate the polymerization is the thermal degradation of carboxylic acids (Fig. 8). Such a reaction at the surface of the fiber would generate covalent bonding and increase interfacial strength. This mechanism has already been described in the literature related to thermal programmed desorption of carbon materials [67,68]. Similar effects have been reported by Hüttinger et al. [69] to explain the generation of covalent bonding between carbon fiber surfaces and thermoplastics (like polycarbonate or polyethersulfone) and by Zielke et al. [70] in the case of a polyetherimide matrix. A DSC analysis highlighted a reaction in the interphase region that was induced by the fiber surface. It was necessary to check if the resin was strongly bonded to the surface if the thermal history of the composite allowed the reaction to happen.

A thermocouple was placed into the mold to record the thermal history of the matrix during the cure of the composite for both processes. That thermal history is presented in Fig. 9 by the plain curves. In the case of the thermal curing, the dashed curve represents the thermal program that was applied to the sample with the help of a programmable oven. There was a little delay between the applied thermal program and the response given by the thermocouple because of the steel mold. In the case of the electron beam cure, the dashed curve corresponds to the thermal program that was chosen in order to mimic the thermal history of the matrix with an oven.

Two samples of IMS 5001 fibers dipped in Ebecryl 600® without initiator were exposed to the thermal programs represented by the dashed curves of Fig. 9, in order to probe if it was possible to generate some covalent interactions with each of the thermal histories. The resin was then removed from the surface of the fibers by washing them with acetone, according to the protocol described in Section 2.8. The measurement of the fraction conversion of the resin by FTIR, in the case of the thermal program that corresponded to the thermal cure revealed that the resin was stable and did not homopolymerized at all. It was not expected to have some non-soluble polymer at the surface of the fiber. An XPS analysis of the fiber surface was carried out before and after exposure to the resin and the thermal program. An increase of the content of oxygen was noticed with the fibers exposed to the thermal treatment corresponding to a thermal cure (Table 5). No increase was noticed with the thermal treatment corresponding to the electron beam cure. The fitting of the peaks highlighted an increase of ester functionalities, as explained later, as well as a clear conversion of all the nitrogen-containing functionalities into amine–amide like functionalities for both type of samples (Table 6), but the increase was sharper with the thermal treatment corresponding to a thermal cure. It was clear that some of the matrix was covalently bonded to the fiber surface in the case of a thermal treatment corresponding to a thermal cure and that effect was barely seen with a thermal treatment corresponding to electron beam curing. The mechanism based on the thermal degradation of carboxylic acids seemed valid. Other mechanisms were also observed. It is known that primary and secondary amines (like aniline and pyrrolidine) can react with an acrylate functionality through an aza-Michael addition reaction and give secondary and tertiary amines [71] that would participate in the component of the N(1s) peak located between 399.4 eV and 399.8 eV. That reaction was demonstrated for diacrylate ester type monomers such as Ebecryl 600® [72]. Tertiary amines (like pyridine) can also potentially react with the ester functionality of the Ebecryl 600® monomer to give a differently substituted ester [73,74]. It seems obvious that the yield of the suggested reactions between diacrylate monomers and amine functionalities existing at the surface of the fiber will depend on the temperature generated in the sample (in order to reach the energy of activation of the reaction) and the time given to the sample to stay at that temperature (kinetics limitation). The creation of covalent bonding between the fiber surface and the matrix with this mechanism will be surely more favored with a thermal cure. It is confirmed by the fitting of the N(1s) peak, as the relative area of the component peak located between 399.4 eV and 399.8 eV is increasing after the exposure of the fiber to the resin, that phenomenon being more important with the thermal program corresponding to the thermal cure, while the relative area of the other components is inversely decreasing. Moreover, the diacrylate monomer has the ability to create hydrogen bonding and some extra covalent bonding with

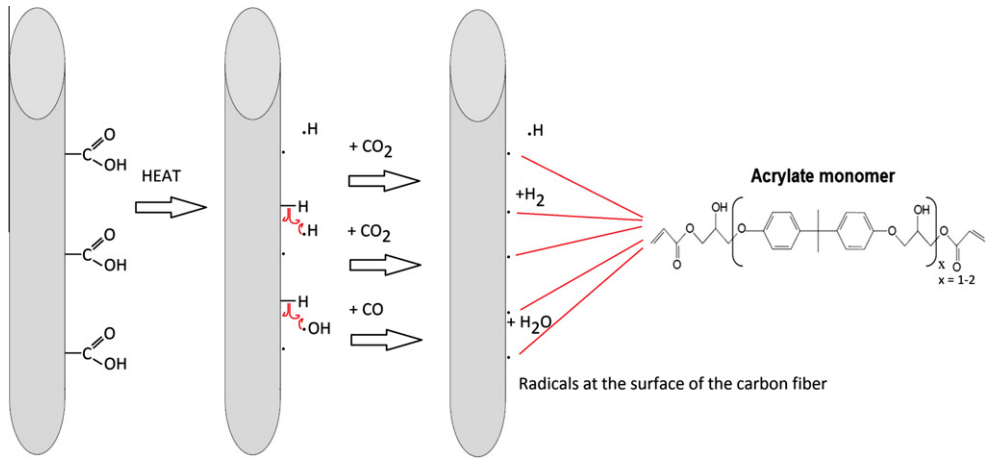

Fig. 8. Initiation of a local polymerization of the matrix by thermal degradation of the carboxylic acids located at the surface of the carbon fibers. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

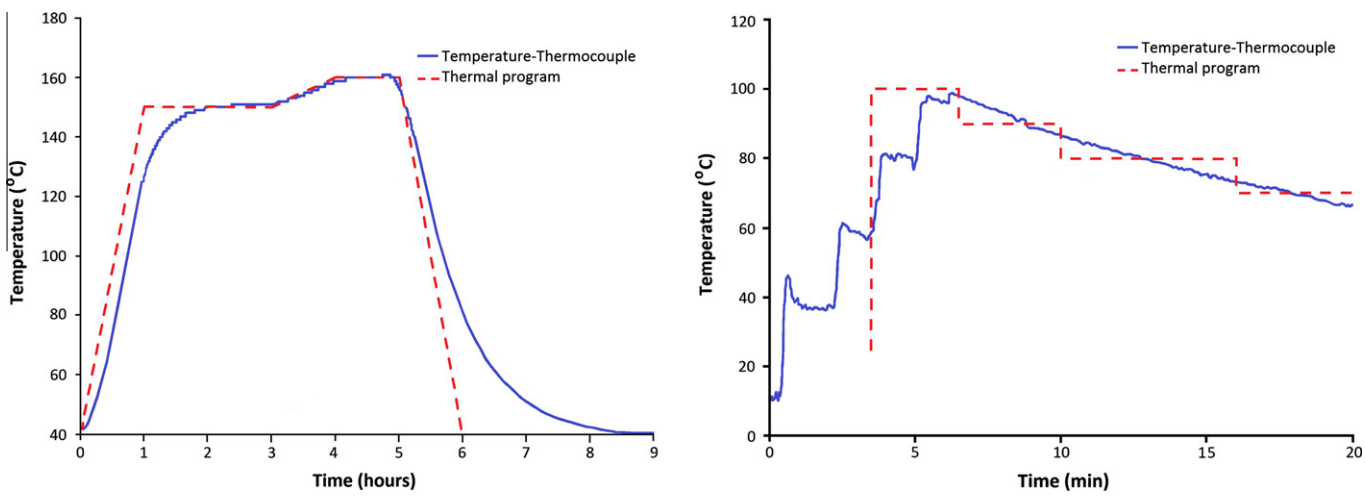

Fig. 9. Thermal program and thermal history of the matrix corresponding to each curing process. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 5
Atomic composition of the surface of IMS 5001 fibers before and after exposure to Ebecryl 600®.

	%C	%O	%N
IMS 5001	87	11	2
Thermal cure-maximal temperature = 160 °C	85	13	2
Electron beam cure-maximal temperature = 100 °C	87	11	2

the oxy-carbonated functionalities. Such interactions have been reported in the case of vinyl-ester monomers [75]. It is more difficult to confirm the existence of those mechanisms by considering the evolution of the relative areas of the components of the O(1s) peak, as the functionalities that may be consumed (hydroxyl groups and carboxylic acid functionalities) and the functionalities that may be created (ester and ether) are included in the same components of the O(1s) and C(1s) peaks. The only parameter that can support that concept is the decrease of the relative area of the component corresponding to hydroxyl groups and ether functionalities and the relative increase of the components corresponding to ester functionalities. Again, that evolution is sharper with a thermal program corresponding to a thermal cure. The establishment of hydrogen bonding and ester and ether functionalities will be favored if the monomers have the sufficient energy and time to adopt the

Table 6
Relative area of each component in the fitting of C(1s), O(1s) and N(1s) XPS peaks, in percentage of the total area of each peak. IMS 5001 fibers before and after exposure to Ebecryl 600®.

	C(1s)							O(1s)						N(1s)		
	Csp^2	Csp^3	C—O—R	C=O	COOR	C—COOR	C—N	Ph—OH, C—O	R—OH, C—O—C	C=O	Ph=O, Ph—C=O	H_2O	Amides, amines, C—N	Pyridine	Pyrrolidine, pyridone	Pyridinium, protonated N
IMS 5001	81	4	5	2	3	3	2	15	35	11	36	3	10	17	35	38
Thermal cure	53	23	12	1	3	6	2	28	20	32	18	2	71	1	21	7
Electron beam cure	62	16	10	3	3	4	2	17	17	39	26	1	25	11	47	17

Table 7
Mechanical properties of the unidirectional composites cured by electron beam and/or thermal treatment.

		Electron beam (4 × 25 kGy) [45]	Electron beam (4 × 25 kGy) + post-cure 1 h at 160 °C [45]	Thermal cure 2 h 50 °C + 1 h 160 °C
ILSS (MPa)	IM7-Ebecryl 600®	63 ± 3	74 ± 3	79 ± 4
	IMS 5001-Ebecryl 600®	71 ± 3	80 ± 3	83 ± 5
90° Flexural strength (MPa)	IM7-Ebecryl 600®	24 ± 5	45 ± 3	53 ± 5
	IMS 5001-Ebecryl 600®	26 ± 3	58 ± 3	59 ± 5

The 90° flexural modulus was 7.0 ± 0.2 GPa for all systems.

optimized configuration. All in all, it is possible to reach high conversion of the matrix by both processes and therefore obtain similar thermo-mechanical properties for the matrix, but the difference in the thermal history of the sample creates a significant difference in the density of interactions generated at the interface, which explains the difference in adhesion strength. Moreover, it was shown that amine and phenol functionalities could inhibit locally the polymerization of the matrix, as they behave as radical scavengers [63]. The thermal program corresponding to a thermal cure allowed the sample to be exposed up to 150 °C with a relatively slow ramp. The amines could have been converted into more substituted amines by the aza-Michael reaction before the start of the polymerization, which could have affected their inhibition potential, as in the case of pyrrolidine or aniline based structures which are known to be efficient radical scavengers. Such a phenomenon could not be possible with electron beam curing since the raise of temperature in the matrix was linked to the polymerization, which was instantaneous. A post-cure at 160 °C of electron beam cured composites enabled a slight increase of the fraction conversion of the matrix, as well as the reaction of the polymer network and the non-reacted acrylate functionalities with the radicals generated by the thermal degradation of carboxylic acids and with amines functionalities, inducing a sharp improvement of the adhesion strength, to a level similar to the one obtained with a thermal cure. The influence of the thermal history of the sample during the cure seemed to be the reason of the low transverse mechanical properties of composites cured by electron beam.

3.4. Comparison of the thermo-mechanical properties of a unidirectional carbon fiber-Ebecryl 600® composite cured by thermal treatment or electron beam

The mechanical properties of composites constituted by IMS 5001 and IM7 fibers and Ebecryl® 600, cured in each case by electron beam and thermal treatment are displayed in Table 7. The 90° flexural strength is the property that is the most sensitive to interfacial adhesion in unidirectional composites according to Drzal and Madhukar [76]. Its value was low with electron beam curing (around 25 MPa) and was half of the value obtained with a thermal cure, with both types of fibers (52 and 59 MPa). Low interfacial mechanical properties of composites cured by electron beam were confirmed. A post-cure led to similar values to the ones obtained with a thermal cure, which is consistent with the study about the evaluation of the adhesion strength with the pull-out test. It seemed that after a post cure, the value of the 90° strength was slightly lower with IM7 fibers, which may have been the results of a higher concentration of surface amines functionalities in comparison with IMS 5001 fibers, as reported previously [45]. The value of the InterLaminar Shear Strength was between 12 and 16 MPa lower with electron beam curing in comparison to a thermal cure, depending on the fibers. It was significantly lower with IM7 fibers, certainly due to a higher concentration of inhibiting surface functionalities. After a post-cure, similar values to the ones obtained with a thermal treatment were obtained and no significant difference was found between the types of fiber. The value of the InterLaminar Shear Strength depends on the adhesion strength, on the toughness of the matrix and the void concentration. As the void concentration and the properties of the matrix are almost similar for each curing process, the changes in the value of the InterLaminar Shear Strength were attributed to the change in adhesion strength. The thermal history of the sample, through its influence on the interfacial mechanical properties, was shown to be responsible for the low transverse mechanical properties of the carbon fiber composites cured by electron beam. In order to improve those properties, two ways are suggested. The first way would be to optimize the processing conditions so that the exothermicity of the polymerization leads to the generation of higher temperatures in the sample, with a longer time at high temperatures. It could be done by using higher doses or a pre-heat of the sample, which would also imply that the reactions at the interface are generated before the cure of the matrix. The second way would be to transform the surface chemistry of the carbon fiber surface so that it is compatible with a radical polymerization of unsaturated resins, that is to say generate functionalities that will be able to create covalent bonding with the diacrylate monomer within the thermal history specific to an electron beam curing.

4. Conclusions

The mechanical properties of a diacrylate resin and its carbon fiber composite, as well as the adhesion strength, were characterized for an electron beam curing, with and without a thermal post-cure, and for a thermal curing. It was possible to achieve similar properties of the pure resin with both curing processes. The thermal history of the sample, linked to the exothermicity of the polymerization and the applied external thermal energy, was directly responsible for a major difference in adhesion strength, the values of the interfacial shear strength being very low in the case of electron beam curing. It was demonstrated that the reactions happening at the interface with a thermal cure were almost not taking place with an electron beam curing, thus limiting the density of interfacial interactions. This was especially the case for the generation of radicals at the surface of the fiber by thermal degradation of the carboxylic acid functionalities and for the aza-Michael reaction between amine functionalities and the acrylate functionalities of the matrix. A post-cure enabled an increase of the adhesion strength to a level that was similar to the one resulting from a thermal cure. The transverse mechanical properties of unidirectional composites, as well as the InterLaminar Shear Strength followed the same trend as the one given by the adhesion strength. That led to the conclusion that the thermal history of the sample was directly responsible for the difference observed in the mechanical properties of acrylate–carbon fibers composites.

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References

[1] Parrot P. Electron beam curing at Aerospatiale. In: Proceedings of 44th international SAMPE symposium conference, May 23–27, 1999. p. 1354–8.
[2] Saunders CB, Dickson LW, Singh A, Charmichael AA, Lopata VJ. Radiation-curable carbon fiber prepeg composites. Polym Compos 1988;9:389–94.
[3] Saunders CB, Charmichael AA, Kremers W, Lopata VJ, Singh A. Radiation-curable prepeg composites. Polym Compos 1991;12:91–5.
[4] Crivello JV, Walton TC, Malik R. Fabrication of epoxy matrix composites by electron beam induced cationic polymerization. Chem Mater 1997;9:1273–84.
[5] Crivello JV. Advanced curing technologies using photo- and electron beam induced cationic polymerization. Radiat Phys Chem 2002;63:21–7.
[6] Crivello JV. UV and electron beam-induced cationic polymerization. Nucl Instrum Meth Phys Res Sect B 1999;151:8–21.
[7] Singh A, Saunders C. Radiation processing of carbon fiber–acrylated epoxy composites. In: Singh A, Silverman J, editors. Radiation processing of polymers. New York: Hanser Publishers; 1992.
[8] Raghavan J. Evolution of cure, mechanical properties, and residual stress during electron beam curing of a polymer composite. Compos Part A 2009;40:300–8.
[9] Sands JM, Fink BK, Mcknight SH, Newton CH, Gillepsie Jr JW, Palmese GR. Environmental issues for polymer matrix composites and structural adhesives. Clean Prod Process 2001;2:228–35.
[10] Janke CJ, Dorsey GH, Havens SJ, Lopata VJ. Toughened epoxy resins cured by electron beam radiation. In: Proceedings of 28th international SAMPE technical conference, November 4–7, 1996. p. 877–89.
[11] Berejka AJ, Eberle C. Electron beam curing of composites in North America. Radiat Phys Chem 2002;63:551–6.
[12] Glauser T, Hult A, Johansson M, Kornmann X, Berglund L. Toughening of electron beam cured acrylate resins. Macromol Mater Eng 2000;280(281):20–5.
[13] Defoort B, Chauray E, Vautard F, Ponsaud P, Nardin M, Schultz J, et al. Improvement of mechanical properties of acrylate based EB cured composite materials. In: Proceedings of international SAMPE conference, Long Beach, California, USA; May 2005.
[14] Krzeminski M, Defoort B, Coqueret X. Nanoscale toughening for advanced composite matrices cured by electron beam activation. In: Proceedings of 2nd international carbon composites conference, Arcachon, France, October 27–29, 2009.
[15] Kreminski M, Defoort B, Coqueret X. Nanoscale toughened matrices cured under electron beam activation for high performance composite applications. In: Proceedings of international SAMPE conference, Seattle, USA; May 2010.
[16] Schultz J, Nardin M. Interfacial adhesion, interphase formation and mechanical properties of single fiber polymer based composites. In: Ishida H, editor. Controlled interphases in composites materials. New York: Elsevier; 1990. p. 561–7.
[17] Schultz J, Nardin M. Some physico-chemicals aspects of the fibre–matrix interphase in composite materials. J Adhes 1994;45:59–71.
[18] Nardin M, Asloun EM, Schultz J. Physico-chemical interactions between carbon fibers and PEEK. In: Ishida H, editor. Controlled interphases in composite materials. New York: Elsevier; 1990. p. 285–93.
[19] Jennings CW. Surface roughness and bond strength of adhesives. J Adhes 1972;4:25–38.
[20] Drzal LT, Sugiura N, Hook D. The role of chemical bonding and surface topography in adhesion between carbon fibers and epoxy matrices. Compos Interface 1997;5:337–54.
[21] Raghavendran VK, Drzal LT, Askeland P. Effect of surface oxygen content and roughness on interfacial adhesion in carbon fiber–polycarbonate composites. J Adhes 2002;16:1283–306.
[22] Owens DK, Went RC. Estimation of the surface free energy of polymers. J Appl Polym Sci 1969;13:1741–7.
[23] Fowkes FM. Role of acid-base interfacial bonding in adhesion. J Adhes Sci Technol 1987;1:7–27.
[24] Fowkes FM. Acid-base contribution to polymer–filler interactions. Rubber Chem Technol 1984;57:328.
[25] Schultz J, Lavielle L, Martin C. The role of the interface in carbon–fiber epoxy composites. J Adhes 1987;23:45–60.
[26] Hook KJ, Agrawal RK, Drzal LT. Effects of microvawe processing on fiber–matrix adhesion. 2. Enhanced chemical bonding epoxy to carbon-fibers. J Adhes 1990;32:157–70.
[27] Pisanova E, Mäder E. Acid–base interaction and covalent bonding at a fiber–matrix interface: contribution to the work of adhesion and measured adhesion strength. J Adhes Sci Technol 2000;14:415–36.
[28] Bikerman JJ. The science of adhesive joints. New York: Academic Press; 1961.
[29] Pastor-Blas MM, Sanchez-Adsuar MS, Martin-Martinez JM. Weak boundary layers in styrene–butadiene rubber. J Adhes 1995;50:191–210.
[30] Paiva MC, Nardin M, Bernardo CA, Schultz J. Influence of thermal history on the results of fragmentation tests on high-modulus carbon–fiber/polycarbonate model composites. Compos Sci Technol 1997;57:839–43.
[31] Vautard F, Xu L, Drzal LT. Carbon fiber–vinyl ester interfacial adhesion improvement by the use of an epoxy coating. In: Daniel IM et al., editors. Major accomplishment in composite materials and sandwiches structures: an anthology of ONR sponsored research. Springer; 2009. p. 27–50.
[32] Eberle CC, Janke CJ, Sands JA, Wilenski MS. Interfacial properties of electron cured composites. In: Cooperative research and development agreement final report for cooperative research and development agreement Number ORNL99-0544; January 2005.
[33] Defoort B, Drzal LT. Adhesion between carbon fibers and cationic matrices in electron-beam processed composites. In: Proceedings of SAMPE ACCE midwest advanced materials and process conference, Dearborn, Michigan; September, 12–14, 2000.
[34] Defoort B, Drzal LT. Interfacial phenomena and fiber matrix adhesion in electron beam processed composites. In: Proceedings of 33rd international SAMPE technical conference, Seattle, Washington, USA; 2001.
[35] Defoort B, Drzal LT. Adhesion between carbon fibers and cationic matrices in electron-beam curing processed composites. In: Proceedings of 46th international SAMPE symposium, Long Beach, California, USA; May 6–10, 2001. p. 2063–75.
[36] Janke CJ, Yarborough KD, Drzal LT. Fiber–matrix interface studies on electron beam cured composites. In: Proceedings of 44th international SAMPE symposium conference, May 23–27, 1999.
[37] Mäder E. Nanostructured surfaces and interphases for improved performances of radiation cured composites. In: First Euraycure workshop, radiation curing of composites, Baden Baden, October 8–9, 2003.
[38] Zhang Z, Liu Y, Huang Y, Liu L, Bao J. The effect of carbon–fiber surface properties on the electron-beam curing of epoxy-resin composites. Compos Sci Technol 2002;62:331–7.
[39] Lopata VJ, Chung M, McDougall TE, Weinberg V. Electron-curable adhesives for high performance structures. In: Proceedings of 39th SAMPE conference, Anaheim, California; 1994.
[40] Defoort B, Drzal LT. Influence of processing conditions on the electron beam curing kinetic of an epoxy resin for composites. In: Proceedings of the 2000 international chemical congress of Pacific Basin Society, Honolulu, Hawaii, USA, December 14–19, 2000.
[41] Defoort B, Drzal LT. Influence of thermal postcuring on electron beam cured composites. In: Proceedings of 46th international SAMPE symposium, Long Beach, California, USA, May 6–10. p. 2550–62.
[42] Thomas Y, Parisi JP, Boutevin B, Beziers D, Chataignier E. Synthesis of (6-isocyanaton-hexyl)carbamoyloxyethyl-methacrylate and its uses as sizing-agent for carbon fiber composite materials cured by electron beam. Polym Bull 1992;29:259–64.
[43] Thomas Y, Parisi JP, Boutevin B, Beziers D, Chataigner E, Désarmot G. Improvement of fiber/matrix bonding in carbon–fiber/acrylic composites by electron irradiation: concept of difunctional chemical coupling agent. Compos Sci Technol 1994;52:299–307.
[44] Vautard F, Schultz J, Nardin M, Roucoules V, Defoort B. Process for improving the adhesion of carbon fibers with regards to an organic matrix. US patent 2010/0092695 A1.
[45] Vautard F, Fioux P, Vidal L, Schultz J, Nardin M, Defoort B. Influence of the carbon fiber surface properties on interfacial adhesion in carbon fiber–acrylate composites cured by electron beam. Compos Part A 2011;42:859–67.
[46] Vautard F, Fioux P, Vidal L, Schultz J, Nardin M, Defoort B. Influence of an oxidation of the carbon fiber surface on the adhesion strength in carbon fiber–acrylate composites cured by electron beam. Int J Adhes Adhes 2012:93–106.
[47] Vautard F, Fioux P, Vidal L, Dentzer J, Schultz J, Nardin M et al. Influence of an oxidation of the carbon fiber surface by boiling nitric acid on the adhesion strength in carbon fiber–acrylate composites cured by electron beam. Surf Int Anal; in press. http://dx.doi.org/10.1002/sia.5147.
[48] Zielke U, Hüttinger KJ, Hoffman WP. Hoffman, surface oxidized carbon fibers: I. Surface structure and chemistry. Carbon 1996;34:983–98.
[49] Biniak S, Szymański G, Siedlewski J, Światkowski A. The characterization of activated carbons with oxygen and nitrogen surface groups. Carbon 1997;35:1799–810.
[50] Pels JR, Kapteijn F, Mouljin JA, Zhu Q, Thomas KM. Evolution of nitrogen functionalities in carbonaceous materials during pyrolysis. Carbon 1995;33:1641–53.
[51] Greszczuk LB. Theoretical studies of the mechanics of the fiber–matrix interface in composites. In: Interfaces in composites ASTM STP 452; 1969. p. 42–58.
[52] Lawrence P. Some theoretical considerations of fiber pull-out from elastic matrix. J Mater Sci 1972;7:1–6.
[53] Chua PS, Piggott MR. The glass–polymer interface. I. Theoretical consideration for single pull-out tests. Compos Sci Technol 1985;22:33–42.
[54] Zhandarov SF, Mäder E, Yurkevich OR. Indirect estimation of fiber/polymer bond strength and interfacial friction from maximum load values recorded in the microbond and pull-out tests. Part I: local bond strength. J Adhes Sci Technol 2002;16:1171–200.
[55] Zhandarov SF, Pisanova EV. The local bond strength and its determination by the fragmentation and pull-out tests. Compos Sci Technol 1997;57:957–64.

[56] Hsueh CH. Interfacial debonding and fiber pull-out stresses of fiber-reinforced composites. Mater Sci Eng A Struct 1990;123:1–11.
[57] Désarmot G, Favre JP. Advances in pull-out testing and data analysis. Compos Sci Technol 1991;42:151–87.
[58] Coqueret X, Krzeminski M, Ponsaud P, Defoort B. Recent advances in electron-beam curing of carbon fiber-reinforced composites. Radiat Phys Chem 2009;78:557–61.
[59] Krzeminski M, Molinari M, Troyon M, Coqueret X. Calorimetric characterization of the heterogeneities produced by the radiation-induced cross-linking polymerization of aromatic diacrylates. Macromolecules 2010;43:3757–63.
[60] Glauser T, Johansson T, Hult A. Electron beam curing of thick thermoset composite matrices. Polymer 1999;40:5297–302.
[61] Gang X, Yongbin Z, Wenfang S. Properties and morphologies of UV-cured epoxy acrylate blend films containing hyperbranched polyurethane acrylate/hyperbranched polyester. J Polym Sci Pol Phys 2005;43:3159–70.
[62] Decker C, Decker D. Photoinitiated polymerization of vinyl ether and acrylate monomer mixtures. J Macromol Sci A 1997;A34:605–25.
[63] Ponsaud P. Amélioration des propriétés mécaniques transverses de matériaux composites polymérisés sous rayonnement ionisant: étude des facteurs influents. PhD Thesis. France: Université des Sciences et Technologies de Lille; 2005.
[64] Chauray E, Defoort B, Boursereau F, Soum A. High toughness vinylester and/or epoxy resin-based material, its process of manufacture, composite material comprising it and uses thereof. US Patent 7556,853 B2.
[65] Calheiros FC, Daronch M, Rueggeberg FA, Braga RR. Degree of conversion and mechanical properties of a BisGMA:TEGDMA composite as a function of the applied radiant exposure. J Biomed Mater Res B 2008;84B:503–9.
[66] Krzeminski M, Molinari M, Troyon M, et al. Characterization by atomic force microscopy of the nanoheterogeneities by the radiation-induced cross-linking polymerization of aromatic diacrylates. Macromolecules 2010;43:8121–7.
[67] Figueiredo JL, Pereira MFR, Freitas MMA, Órfão JJM. Modification of the surface chemistry of activated carbons. Carbon 1999;37:1379–89.
[68] Li N, Ma X, Zha Q, Kim K, Chen Y, Song C. Maximizing the number of oxygen-containing functional groups on activated carbon by using ammonium persulfate and improving the temperature-programmed desorption characterization of carbon surface chemistry. Carbon 2011;49:5002–13.
[69] Hüttinger KJ, Krekel G, Zielke U. Evidence for chemical bond formation between surface treated carbon fibers and high temperature thermoplastics. J Appl Polym Sci 1994;51:737–42.
[70] Zielke U, Hüttinger KJ, Hoffman WP. Hoffman, surface-oxidized carbon fibers: IV. Interaction with high-temperature thermoplastics. Carbon 1996;34:1015–26.
[71] Mather BD, Viswanathan K, Miller KM, Long TE. Michael addition reactions in macromolecular design for emerging technologies. Prog Polym Sci 2006;31:487–531.
[72] Robson JH, Marcus E. Amine acrylate addition reaction products. US patent 3963,771.
[73] Eliel EL, Anderson RP. Reactions of esters with tertiary amines. I. Benzyl esters from methyl esters and benzyldimethylamine. J Am Chem Soc 1952;74:547–9.
[74] Eliel EL, Ferdinand Sr TN, Herrmann MC. Reactions of esters with tertiary amines. II. The reaction of substituted benzyldimethylamines and other amines. J Org Chem 1954;19:1693–8.
[75] Vautard F, Ozcan S, Meyer H. Properties of thermo-chemically surface treated carbon fibers and of their epoxy and vinyl ester composites. Compos Part A Appl S 2012;43:1120–33.
[76] Drzal LT, Madhukar M. Fiber matrix adhesion and its relationship to composite mechanical properties. J Mater Sci 1993;28:569–610.