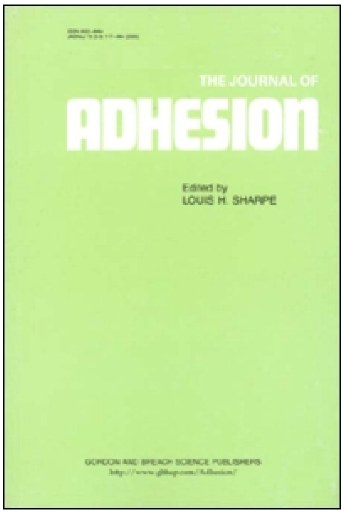

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Influence of processing conditions on adhesion between carbon fibers and electron-beam-cured cationic matrices

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INFLUENCE OF PROCESSING CONDITIONS ON ADHESION BETWEEN CARBON FIBERS AND ELECTRON-BEAM-CURED CATIONIC MATRICES

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Adhesion between an electron-beam-cured Diglycidyl Ether of Bisphenol A (DGEBA) epoxy matrix and AS4 carbon fibers has been evaluated with the microindentation test method and compared with similar thermally cured materials. The results indicate that the absence of amine compounds and of high temperature treatment associated with thermally cured epoxy matrices are detrimental to fiber–matrix adhesion in electron-beam-cured epoxy matrices when measured by the microindentation test. Electron beam processing was not found responsible for any adsorption and/or deactivation of the irradiated carbon fiber surface as determined by surface analysis with X-ray Photoelectron Spectroscopy (XPS). Moreover, the relationship between electron-beam processing conditions (namely, dose and dose increment) with the resulting matrix properties and the adhesion to carbon fiber have revealed a strong dependency of fiber–matrix adhesion on the bulk matrix properties independent of the electron beam processing history. Undercured electron-beam-processed matrices exhibit higher adhesion to carbon fibers that can be explained by a higher matrix shear modulus.

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Keywords: Fiber–matrix adhesion; Carbon fiber; Electron beam curing; Epoxy resin; Composite materials; Radiation processing

INTRODUCTION

Electron-beam-initiated cross-linking polymerization is a highly attractive technique compared with conventional time-consuming thermal curing. Many benefits have been identified when electrons are used rather than thermal energy for curing composite materials, including low energy consumption, high polymerization speed, reduced residual stresses that result from curing, improved material handling, and possible process automation [1–3]. Carbon-fiber-reinforced polymer composite materials based on epoxy monomers for high performance composite applications can be efficiently cured when exposed to electron beam radiation with the use of initiators of diaryl iodonium or triarylsulfonium salts. Strong protonic acids generated during the reaction initiate the cationic ring-opening polymerization of epoxy resins [4, 5]. Such electron-beam-cured matrices can reach properties that are equivalent to thermally cured thermosets; however, adhesion between fibers and matrices is generally lower than measured for equivalent thermally cured epoxies [6]. In the present work, we investigated the causes of the limited adhesion between carbon fiber and the epoxy matrix. The adsorption of each constituent of the matrix on the carbon fiber surface and the resulting deactivation of the carbon surface was evaluated and compared with thermally processed compounds. Attention was also directed to studying the influence of electron beam processing conditions, particularly total absorbed dose and dose increments, on the fiber-matrix interfacial properties and adhesion. The objective of this research is to gain a better understanding of the causes of the poor adhesion of epoxy matrices to carbon fibers in electron-beam-cured composites so that an approach might be developed to eliminate this problem.

EXPERIMENTAL MATERIALS AND METHODS

Reinforcing Fibers

Polyacrylonitrile-based AS4 carbon fibers from Hexcel (Magna, Utah) were chosen for this study. The 12K (12,000 filaments per tow)-AS4-type fiber studied here was processed without any surface sizing, but it underwent a surface treatment to remove the original surface and alter its chemistry. This has the effect of increasing the surface chemical groups and fiber surface roughness. The carbon fiber modulus is reported from Hexcel product data as 228 GPa (33 Msi).

Polymeric Matrices

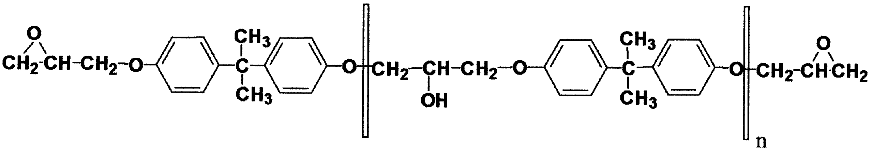
The epoxy resin Tactix 123® from Ciba Polymer (Tarrytown, New York) was selected as the matrix for composite fabrication. This resin is a diglycidyl ether of bisphenol A-based epoxy formulation. The viscosity of the resin is 5000 cps at 25°C. The structure of the monomer is shown in Scheme 1.

SarCat CD1012 cationic initiator from Sartomer was used to initiate the cationic polymerization. The active molecule is the diaryl iodonium hexafluoroantimonate that decomposes under electron beam irradiation [7], UV irradiation (240 nm to 300 nm range), or thermal heating (temperature higher than 140°C). The structure of the molecule is presented in Scheme 2.

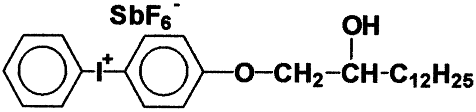
Epon 828® a diglycidyl ether of bisphenol A from the Shell Chemical Company (Houston, Texas), thermally cured with 14.5 phr of meta-phenylene diamine (m-PDA, Aldrich Chemical Company (St. Louis, Missouri)) was also used for comparison purposes. The resin was air-cured for 2 h at 75°C and 2 h at 125°C [8].

Electron Beam Processing

Electron beam irradiation was carried out using the Acsion Industry 1–10/1 electron linear accelerator (Acsion Industry, Pinawa, Manitoba, Canada). A nominal 10 MeV pulsed electron beam was configured with a horizontal horn to scan at a frequency of 2 Hz over a 30 cm wide path onto a variable speed conveyor belt. The beam current



SCHEME 1 Structure of the DGEBA molecule.



SCHEME 2 The diaryl iodonium hexafluoroantimonate molecule.

delivered during a single pulse was set at 70 mA and the pulse duration and beam period were 4 s and 3.3 ms respectively. As a result, the instantaneous dose rate delivered at the conveyor during a pulse and averaged onto the beam spot surface was on the order of 600 kGy/s for all the experiments.

The dose deposited per single pass under the beam, also called "dose increment," was varied from 5 to 20 kGy per pass by decreasing the conveyor speed from 0.84 to 0.21 cm $\times$ s^{-1}. The total dose was delivered to the material by accumulating successive passes under the beam. During passes under the beam, the temperature increased in the samples due to both exothermic polymerization and energy absorption. The samples were allowed to cool close to room temperature between each pass under the electron beam (natural conduction and convection). The temperature variation was continuously monitored in the samples and recorded during electron beam processing.

Sample Preparation

The initiator concentration used for the study was 3 parts per hundred parts of resin. Composite materials cured under the electron beam were small samples consisting of test tubes (2 ml, diameter of 9 mm, length of 3 cm) filled with 4 tows of AS4 12K carbon fibers and the matrix. The resin was heated to 60°C for 1 h before composite preparation to avoid crystallization but was allowed to cool to room temperature before electron beam processing. The neat resin samples for Dynamic Mechanical Analysis (DMA) and Fourier transform infrared (FTIR) analysis were 5 ml bars cast into silicone molds (1.2 cm $\times$ 7.5 cm $\times$ 0.03 cm). The temperature evolution was recorded during electron beam processing in the 5 ml DMA samples (thermocouples embedded in the resin).

Spectroscopic Monitoring

The chemical changes induced by repeated application of a 5, 10, or 20 kGy dose of accelerated electrons were quantitatively analyzed by transmission FTIR spectroscopy on powder extracted from the bulk material and pressed into KBr-based pellets (polymer concentration around 10 wt%). Infrared spectra were recorded using a Perkin Elmer FTIR System 2000 model with a conventional TGS detector. The spectrum obtained in transmission from uncured Tactix 123 is presented in Figure 1.

The 1509 cm^{-1} band was unchanged in the dose range applied and was used as an internal standard for comparing different samples. The

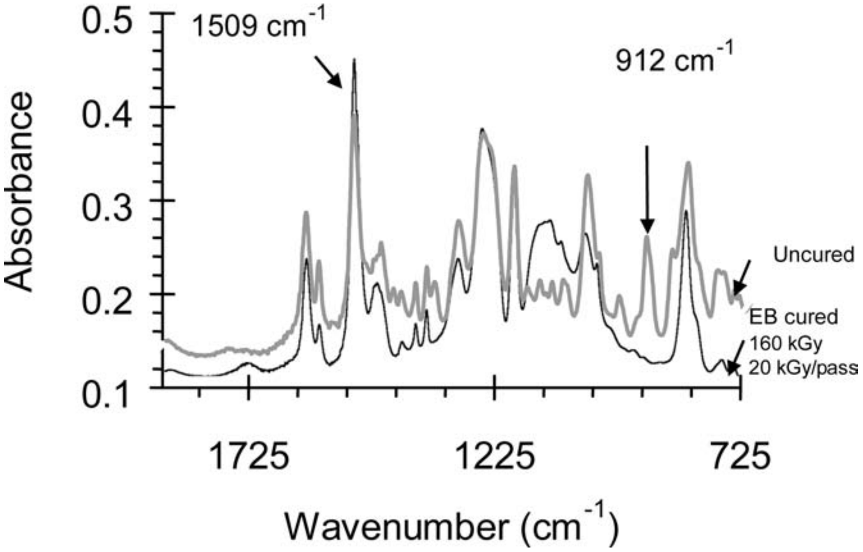


FIGURE 1 FTIR spectrum of uncured Tactix 123®–CD 1012.

decrease of the band at 912 cm^{-1} assigned to the epoxy function permits accurate evaluation of the monomer conversion. The fractional conversion of epoxy functions, Π, after exposure to a given dose, D, is thus calculated in Equation (1).

$$\Pi(D) = \frac{1 - \frac{A_{912(D)}}{A_{1510(D)}}}{\frac{A_{912(D=0)}}{A_{1510(D=0)}}} \tag{1}$$

Thermo-Mechanical Analysis

The thermo-mechanical changes (glass transition temperature (T_g), storage, and loss moduli) induced by repeated application of a 5, 10, or 20 kGy dose of accelerated electrons were quantitatively analyzed by dynamic mechanical analysis in the single cantilever mode, at a frequency of 1 Hz. DMA runs were recorded using a DMA 2980 Dynamic Mechanical Analyzer from TA Instruments (New Castle, Delaware). The glass transition temperature was measured at the maximum of the Tan(∂) curve.

Microindentation

The mechanical changes of the bulk matrix properties (Young's Modulus, Hardness) induced by repeated application of a 5, 10, or

20 kGy dose of accelerated electrons were quantitatively measured by microindention using a Nano Indenter from MTS Corporation (Eden Prairie, MN), equipped with a Berkovitch pyramid tip made out of diamond. The Shear Modulus of the material was deduced from the Young's modulus using a Poisson Ratio of 0.36.

Adsorption/Deactivation

The extent of adsorption/deactivation of the irradiated carbon fiber under electron beam conditions similar to those encountered during the conventional curing process was investigated as part of this study. Model compounds—Tactix 123 alone without initiator and CD1012 dissolved in acetone without resin—were electron beam processed in conditions similar to those encountered in the manufacture of the composite materials. The major differences between electron beam processing of model compounds and electron beam curing of the reactive formulation are the lower temperature rise of the model compounds during processing due to the absence of heat being released from exothermic polymerization, the absence of gelation and vitrification of the material, and the resulting increased mobility of the active species. The carbon fibers were carefully washed with acetone in a Soxhlet extractor for 24 h after electron beam treatment. X-ray Photoelectron Spectroscopy (XPS) examination of the composition of the carbon fiber surface was then used to determine the extent of any chemisorption [9]. Chemisorption studies have helped determine if the reaction of the matrix constituents with the carbon fiber surface was altered compared with a conventional thermal process. Surface analysis was performed using a Perkin Elmer Physical Electronics PHI 5400 ESCA Spectrometer equipped with a standard magnesium X-ray source operated at 300 W (15 kV and 20 mA). Survey and regional scans used pass energies of 79.6 and 22.0 eV, respectively. An asymmetric peak shape was used to fit the main C1s graphitic peak (referenced to 284.6 eV). Functionalized carbon peaks were assessed to carbon-oxygen groups and were fit with chemical shifts of 1.5 eV per C-O bond.

Adhesion

Adhesion investigations in composite materials require measurements that unambiguously evaluate fiber-matrix adhesion. Considerable previous work has been done with single-fiber fragmentation and single-fiber compression tests to measure the interfacial shear strength and transverse tensile properties between carbon fibers and the epoxy matrix. These methods not only provide a reproducible and quantifiable parameter for fiber-matrix adhesion, but also allow the interfacial failure mode to be determined [10, 11]. In the present study, adhesion in electron-beam-processed composites was measured using the fiber microindentation technique [12]. This procedure consists of mounting and polishing a section of carbon fiber/epoxy matrix composite in such a manner that the fiber ends are perpendicular to the polished surface and are distinctly visible using reflected light microscopy. The sample is then secured in an x, y, z-positioning stage that precisely moves the specimen in each direction. The sample is examined for fibers that are surrounded by nearest neighbors between one-half and 2 microns away from the selected fiber's edge. A conical indenter with a radius of curvature matched to the fiber diameter is placed in contact with the fiber and the stage is moved in the z-direction perpendicular to the fiber end. The load is monitored continuously. Periodically the fiber is unloaded and examined under the microscope for evidence of debonding. When a debond of 90 to 120 degrees along the fiber circumference is detected, the load is recorded as the failure load that is used to calculate the interfacial shear strength (IFSS) from Equation (2), where IFSS is the interfacial shear strength, G_m is the matrix shear modulus, d is the distance from the tested fiber to the nearest neighbor, D is the fiber diameter, E_f is the fiber Young's modulus, P is the maximum load, and A, B, C, and E are constants [13].

$$\mathrm{IFSS} = \mathrm{A}\frac{P}{D^2}\left[\mathrm{B}\left(\frac{G_m}{E_f}\right)^{1/2} - \mathrm{C}\ln\left(\frac{d}{D}\right) - \mathrm{E}\right] \tag{2}$$

Specimens for testing on the interfacial testing system (ITS) were cast in a cylinder (test tube, 3 ml). Sections of carbon fiber tows were cut to the length of the test tube and placed in the test tube. Tactix 123/CD 1012 mixture was poured around the fibers to fill the tube and then exposed to the electron beam at various dosages. The composite samples were cut into 1.5 cm segments using a water-cooled diamond saw and mounted in phenolic rings with a room-temperature processed epoxy and allowed to harden overnight. A Struers-Abramin polisher was used in the grinding and polishing to yield the flat surface necessary to conduct the ITS test. Final polish incorporated a rotating lap with a nap cloth and 1 μ Al_2O_3-water slurry. ITS measurements were conducted using a 4 μ radius diamond indenter, tested at 6 steps per s and 0.04 μ increments per step.

Fracture Surface

Composite material cast into syringes (1 ml) were fractured using a 3-point bending test at a rate of 0.5 cm/min and with a 3.8 cm span.

Analysis of the fracture surface of the composite was done by electronic scanning electron microscopy using the ElectroScan 2020 ESEM.

RESULTS AND DISCUSSION

Adsorption of Monocompounds onto the Carbon Fiber/Deactivation of Fiber Surface Chemistry

The objective of the chemisorption study is to investigate if the mechanisms of adsorption are altered during electron beam processing compared with conventional thermal processing.

Electron Beam Processing with Tactix 123 Alone

After electron beam processing, the epoxy resin was carefully removed from the AS4 carbon fibers *via* Soxhlet extraction with acetone for 24 h. The XPS analysis of the carbon fiber surface provides the atomic concentration of carbon, oxygen, and other atoms on the fiber surface. The atomic ratio of oxygen to carbon measured on the fiber for various processing conditions is presented in Figure 2. The reference (absorbed dose = 0 kGy) corresponds to a sample of carbon fibers that were in contact with Tactix 123 at room temperature for the same time

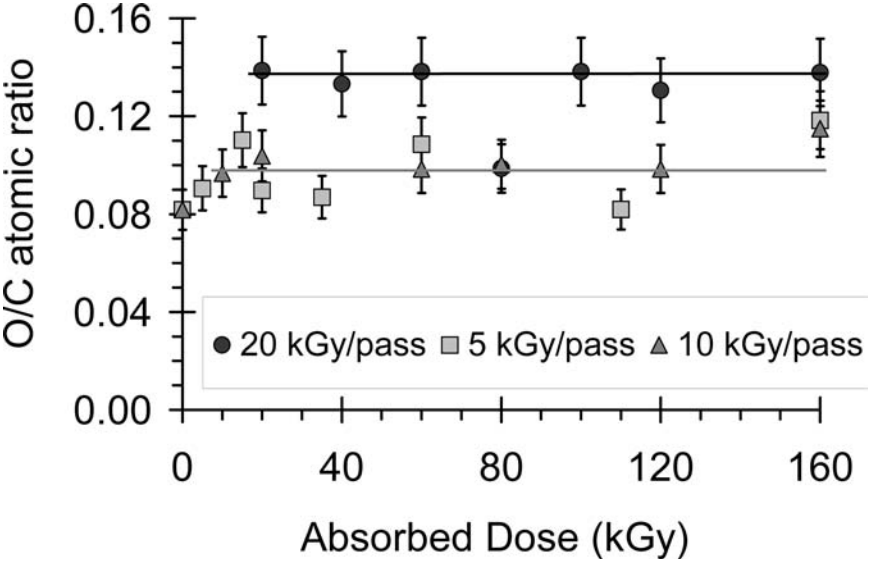


FIGURE 2 Oxygen/carbon atomic ratio on AS4 carbon fiber surface *versus* absorbed dose for AS4/Tactix123 model compounds processed at various dose increments.

TABLE 1 Oxygen/Carbon Atomic Ratio on AS4 Carbon Fibers Surface Versus Absorbed Dose for AS4/Tactix123 Model Compounds Electron Beam or Thermally Processed

Treatment	[C] (%)	[O] (%)	[O]/[C]
As received	91.7	7.5	0.08
20 kGy in one pass	85.1	11.8	0.14
10 min at 200°C	85.3	11.8	0.14

as the other samples, without any processing, and having been similarly washed with acetone. The oxygen/carbon ratio does not increase when the dose increases from 5, 10, or 20 kGy to 160 kGy when electron beam processing is performed at a constant dose increment at this dose rate. The average oxygen/carbon ratio is also about the same when the experiments are performed either at 5 or 10 kGy per pass, but it increases by a factor 1.4 when the samples are processed at 20 kGy per pass. It is worth noting that the energy deposition of 4 passes of 5 kGy does not have the same effect on the fiber surface as an energy deposition of 1 pass of 20 kGy. Furthermore, a similar level of oxidation of the carbon fiber surface is achieved by both a thermal treatment (10 min at 200°C) and application of 20 kGy as shown in Table 1.

As a result, it appears that the energy deposited on the fiber surface with dose increments of 5 or 10 kGy per pass is not sufficient to support the chemisorption of Tactix 123 onto the carbon fiber surface. The differences between conditions encountered during electron beam curing of the matrix and processing of the model compounds (absence of cationic species, lower viscosity, difference in temperature profile) may have an influence on the adsorption process, especially in the case of a fast electron-beam-initiated curing. The extent of monomer chemisorbed onto the fiber surface is lower when electron beam processing is conducted with low dose increments (5–10 kGy per pass). However, it seems that the adsorption/deactivation of the carbon fiber for electron beam and thermally processed materials have similar values when electron beam processing is conducted with dose increments of 20 kGy per pass.

Electron Beam Processing with CD 1012 Dissolved in Acetone

Since CD 1012 is a solid at room temperature, it was dissolved in acetone before performing monocompound experiments. The concentration of CD 1012 in acetone was 10wt%. After electron beam processing, CD 1012 and acetone were carefully removed from the

TABLE 2 Atomic Ratio on AS4 Carbon Fiber Surface for Model Compounds (CD 1012 in Acetone) Processed at Various Doses and Dose Per Pass

Dose (kGy)	Dose per pass (kGy)	[C] %	[O] %	[Sb] %	[F] %
0	0	91.7	7.5	0	0
5	5	89.3	7.7	0.3	0
25	5	79.4	14.0	4.4	0
60	5	81.4	11.1	2.3	0
160	5	79.7	14.2	2.0	0
20	20	80.0	14.5	2.9	0.4
160	20	78.8	15.4	3.6	0

carbon fibers *via* Soxhlet extraction for 24 h. The reference samples are carbon fibers that were immersed in the CD 1012/acetone mixture at room temperature for the same time but without exposure to electron beam. The first observation was a color change of the liquid mixture after electron beam processing. The solution turns a brown color. This color change does not occur in acetone alone in similar conditions and might be related to the decomposition of the initiator under the electron beam. The XPS analysis of the carbon fiber surface gives the atomic concentration of the different compounds present on the fiber surface after processing in various electron beam conditions, tabulated in Table 2.

The adsorption of initiator on the fiber surface is low, and no influence of the total absorbed dose or the dose increment was observed in the investigated range. Another observation is the presence of antimony on the fiber surface after electron beam processing even though no fluorine was detected. This phenomenon is surprising considering the chemical composition of the initiator. Since the ratio of sensitivity factors of fluorine to antimony is close to 1 to 5 and as there is 6 times as much fluorine in the initiator, it was expected that fluorine would be detected as clearly as antimony in the XPS spectra. When the diaryl iodonium hexafluoroantimonate molecule dissociates under electron beam, dissociation of the Sb and F bonds was not expected, but a degradation of the molecule under electron beam might lead to this result. The concentration of antimony does not significantly depend either on the total dose or on dose increments and is limited to a few percent (less than 4.5%).

Adhesion of the Epoxy Matrix to Carbon Fibers

Thermally cured epoxy amine/unsized carbon fiber composite presents better interfacial properties than an equivalent electron-beam-cured material. The difference in shear modulus between electron-beam-cured Tactix 123 and thermally cured Epon 828 with 14.5 phr of m-PDA is as high as 60% as shown in Table 3. The difference between electron beam and thermally cured composites can be even higher in terms of interfacial properties, depending on the matrix formulation [6]. During thermal curing, chemical bonding takes place between the epoxy and amine groups of the matrix and carbon fibers. The amine function has been shown to be more reactive than the epoxy function and as little as 3% of chemical bonding can account for as much as 25% increase of interfacial shear strength in some cases, as shown by Drzal *et al.* [14].

Furthermore, if thermally initiated cationic curing of the same formulation as the one used for electron beam processing (no amine, polymerization initiated by thermal dissociation of CD 1012) is conducted, the resulting adhesion is superior to the adhesion in electron-beam-cured materials. A 30% increase in adhesion was measured for thermally cured Tactix 123 and CD 1012 (170°C for 3 h) compared with samples e-beam cured at 5 kGy per pass (Table 3). This result seems to indicate that the thermal stresses produced in the matrix during curing may have a positive effect on the fiber adhesion measured by the microindentation test or/and that a chemical reaction supported by a treatment at high temperature for a certain time might happen at the fiber/matrix interphase. The temperature profile during processing is expected to have a significant influence on the interfacial stress. In the electron-beam-cured

TABLE 3 Interfacial Shear Strength, Thermally and Electron-Beam-Cured Composites

Matrix	Curing process	G_m* (Gpa)	IFSS** (MPa)
Tactix 123/CD 1012	Electron beam, 160 kGy at 5 kGy per pass	1.45 ± 0.02	31 ± 4.1
Tactix 123/CD 1012	Electron beam, 160 kGy at 10 kGy per pass	1.38 ± 0.03	33.6 ± 5.5
Tactix 123/CD 1012	Electron beam, 160 kGy at 20 kGy per pass	1.39 ± 0.01	34.7 ± 4.5
Tactix 123/CD 1012	Thermal, 3 h at 170°C	1.33 ± 0.01	40.7 ± 8.7
Epon 828/m-PDA	Thermal, 2 h at 90°C and 2 h at 125°C	1.31 ± 0.01	49.4 ± 5.4

*The shear modulus of the matrices (G_m) was measured by the nanoindentation technique for each sample and used for IFSS calculation.

**The carbon fiber modulus used for the IFSS computation was 228 GPa.

materials, the temperature rise during curing lasts only a very short period of time and at the same time as the vitrification of the material (Figure 3), limiting thermal stresses compared with a thermally initiated process. In the microindentation test we performed, the IFSS value takes into account the increase of adhesion due to the stress in the matrix, which could be part of the reason for the increased adhesion in thermally cured composites. The importance of the thermal treatment was further investigated by thermally postcuring electron-beam-cured samples. It is most likely that a long time/high temperature treatment induces a chemical reaction between some epoxy functions left unreacted in the matrix and the carbon fiber surface [15].

Finally, it seems that the initiation mechanism of the polymerization associated with electron beam processing does not have any specific negative effect on adhesion. On the other hand, the absence of amine compounds in the formulation, the relatively limited temperature rise, and the short high temperature exposure time might all have detrimental effects on both the chemical and mechanical fiber-matrix bonding.

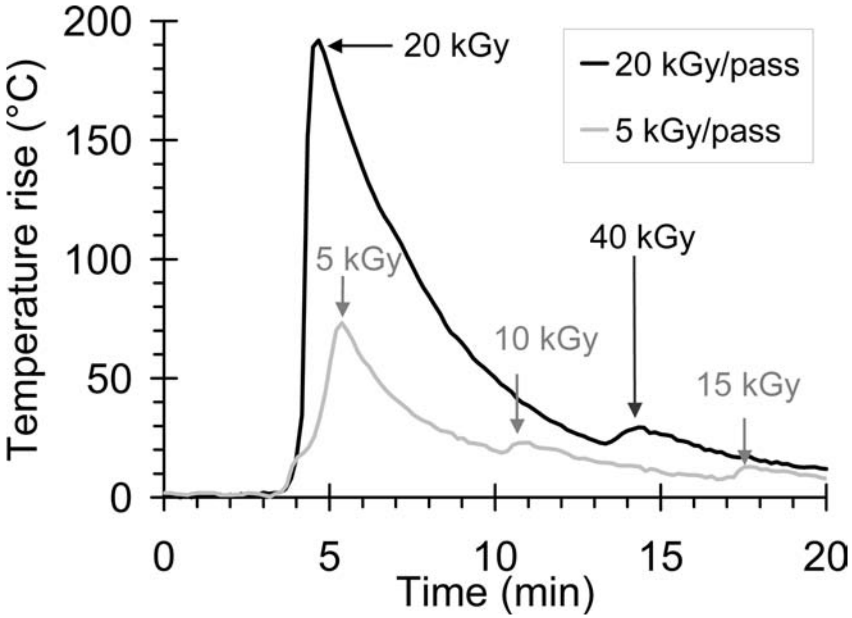


FIGURE 3 Temperature rise during electron beam curing of Tactix123/CD 1012 at 5 or 20 kGy per pass.

Influence of Total Absorbed Dose and Dose Increments on Adhesion

The influence of electron beam processing conditions on adhesion of carbon fibers to the epoxy matrix was investigated using the micro-indentation test. The values of the interfacial shear strength are plotted in Figure 4 *versus* the total absorbed dose and for different applied dose increments.

The maximum level of adhesion obtained for composites that absorbed doses higher than 60 kGy is almost the same regardless of dose increment. Furthermore, for dose increments of 10 and 20 kGy per pass, the adhesion level is the same regardless of absorbed dose in the 10 to 160 kGy range. In these two cases, there is no significant change in adhesion with dose or dose per pass. When dose increments of 5 kGy are applied, the interfacial shear strength is higher for absorbed doses lower than 60 kGy. The IFSS also decreases linearly between 5 and 60 kGy. These results show that the differences in the chemisorption of Tactix 123 onto carbon fibers with dose increments of 5, 10, and 20 kGy per pass (Figure 2) do not affect the adhesion measured with the indentation testing system. However,

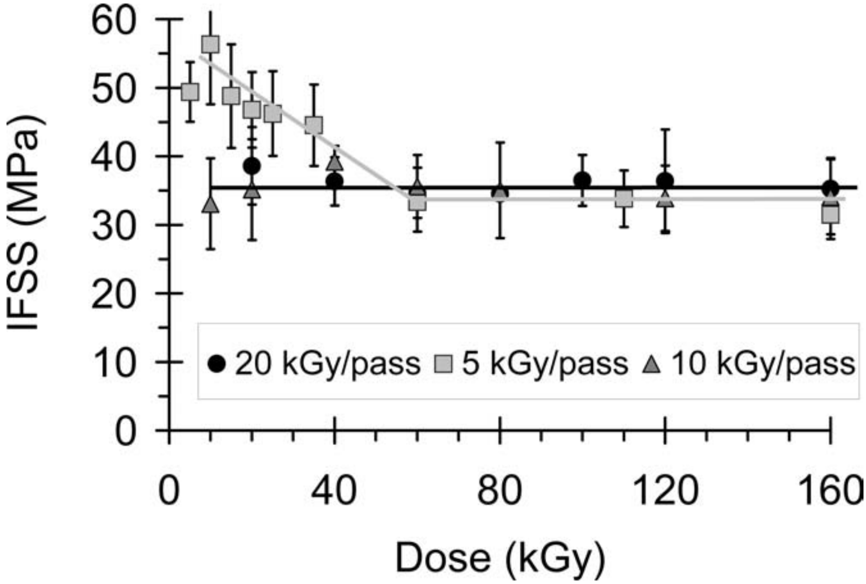


FIGURE 4 IFSS of AS4/Tactix 123-CD 1012 composites *versus* absorbed dose, at various dose increments.

there appears to be a difference in adhesion dependent on the processing conditions.

These results raised questions about the causes of the higher adhesion in composites that received a low dose at a dose increment of 5 kGy per pass. It would have been expected that a composite that absorbed only 5 kGy would have had lower adhesion because of an expected lower matrix stiffness and because of the limited adsorption of epoxy onto the fibers compared with processing at 20 kGy per pass. Therefore, it is important to investigate the matrix properties and to relate bulk matrix properties and adhesion of the matrix to carbon fibers.

Relationship between Bulk Matrix Properties and Adhesion

Fiber-matrix adhesion depends on physical and chemical interactions between the matrix and the fibers, but it is also highly sensitive to the bulk matrix material properties [16]. It has been shown that the electron beam processing conditions can have a strong influence on the properties of composite materials. But, is this due to the bulk matrix properties or is there a specific interaction at the fiber/matrix interface? In order to answer this question, one needs to understand the evolution of the chemical and physical matrix network properties as a function of electron beam processing conditions (dose, dose increments) and to relate this to the adhesion at the fiber-matrix interface. The neat resin polymerization kinetics were monitored by FTIR, DMA, and thermal analysis. More details are provided elsewhere [17]. The evolution of the glass transition temperature of the matrix upon curing is shown in Figure 5.

The final glass transition temperature attained by all the processed samples is high, around 175°C. In the case of 10 or 20 kGy/pass, a glass transition temperature close to 175°C is obtained immediately after the first pass under the beam, showing a very quick reaction. But with dose increments of 5 kGy, a total dose of about 60 kGy is required to reach a T_g of 175°C. The particular behavior of the curing kinetics at 5 kGy/pass is due to the vitrification of the material between the first and the second pass under the beam. The material reaches a glass transition temperature of 80°C after the first irradiation increment, and is allowed to cool down to 40°C after this first pass (temperature profile in Figure 3). At the application of the second dose increment, the temperature of the material is close to 40°C whereas its T_g is 80°C. The matrix is vitrified, and the polymerization rate is significantly reduced due to the reduced molecular mobility in the glassy state. Under these

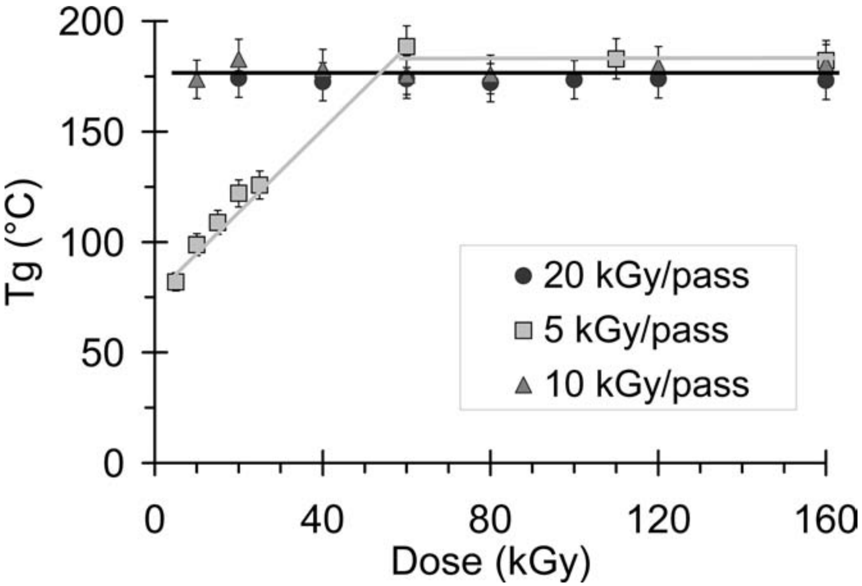


FIGURE 5 T_g of Tactix 123-CD 1012 resin *versus* absorbed dose, at various dose increments.

conditions the reaction rate is very slow, and so a higher dose is needed to reach the same conversion/T_g level.

The DMA experiments show a significant beta transition around 80°C when processing is done with passes of 5 kGy. This is due to the vitrification after the first pass under the beam. During the following passes, the polymerization takes place in a vitrified medium and, even at the high values of T_g (170/180°C) reached for a high total dosage, there is still a significant secondary relaxation at a lower temperature in most cases. It can be expected that the structure of the network is slightly different when a sample is cured with small *versus* large dose increments. Despite the complexity of the network structure, the T_g and the epoxy conversion can be considered as average values characterizing the whole network.

In order to correlate the interfacial shear strength with the cure level of the bulk matrix, plots of the interfacial shear strength *versus* the epoxy conversion and *versus* the glass transition temperature of the matrix are presented in Figures 6 and 7. The relationships between the IFSS and the T_g and between the IFSS and the epoxy conversion are independent of the electron beam processing history, namely dose and dose increments, and depend only on the bulk matrix

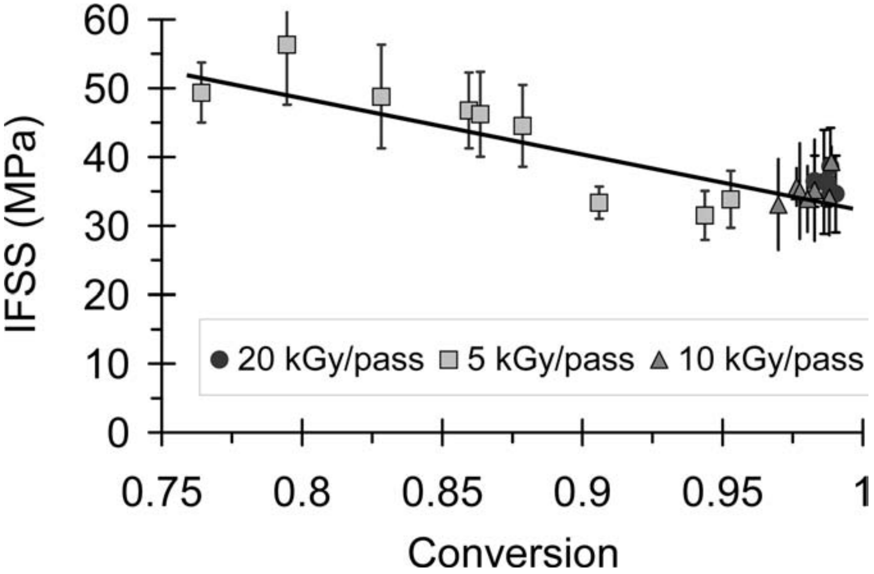


FIGURE 6 IFSS of AS4/Tactix 123-CD 1012 composites *versus* bulk matrix epoxy conversion, for processing at various dose increments.

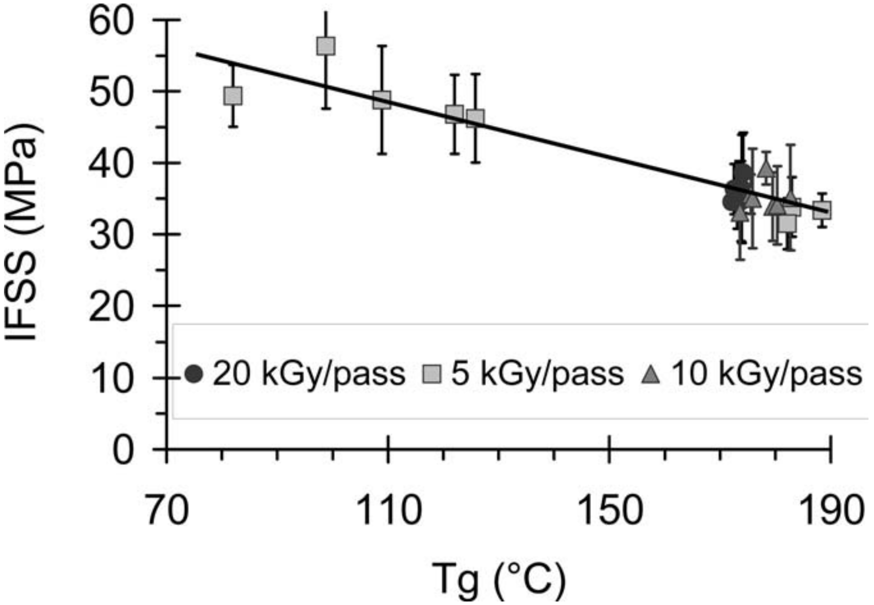


FIGURE 7 IFSS of AS4/Tactix 123-CD 1012 composites *versus* T_g of the matrix, for processing at various dose increments.

properties for those AS4 carbon fiber composites investigated. The variation of thermal profiles for the different curing processes (Figure 3) tends to indicate that this relationship is independent of the curing temperature also.

Since fiber-matrix stress transfer operates mostly in shear, there should be a dependence of the IFSS on the shear modulus of the matrix. Figure 8 is a plot of the bulk shear modulus measured by microindentation *versus* the absorbed dose applied to the material whether it is applied at 5, 10, or 20 kGy per pass. The shear modulus of the matrix cured with dose increments of 5 kGy/pass is slightly higher than the shear modulus of the matrix cured at 20 kGy per pass for similar absorbed doses ranging from 100 to 160 kGy, probably indicating slight differences in the network structure. Furthermore, the shear modulus of the matrix is even higher when the matrix is undercured (conversion lower than 100%, *Tg* Lower than 150°C), that is to say when the matrix received a dose ranging from 5 to 60 kGy at 5 kGy per pass. The shear modulus of the matrix was expected to be lower for material that presents lower conversion and lower network density. This surprising result can only be explained by a different network microstructure or by heterogeneities of the network.

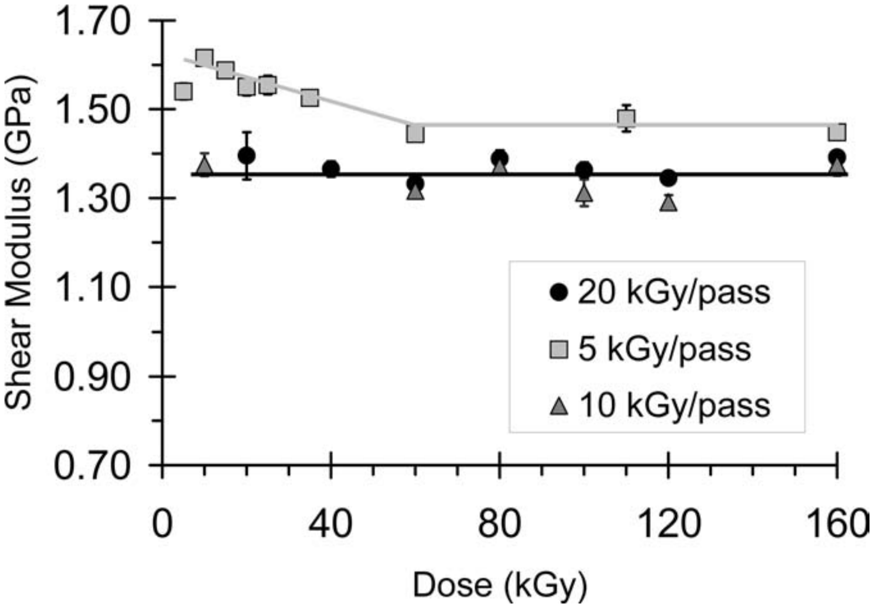


FIGURE 8 Shear modulus of the bulk matrix *versus* absorbed dose, for processing at various dose increments.

The interfacial shear strength is plotted as a function of the square root of the matrix shear modulus in Figure 9. From theoretical considerations, a linear dependency between the square root of the bulk matrix shear modulus and the interfacial shear strength is expected. It can be seen that all the data points fall on a single smooth curve that shows increasing interfacial shear strength with increasing shear modulus of the matrix, as would be expected. The relationship is not linear over the entire matrix shear modulus range investigated. For a shear modulus lower than 1.40 GPa, the interfacial shear strength is the same regardless of the shear modulus. In fact, for all fully electron-beam-cured material (100% epoxy conversion), the adhesion is the same even if there are small variations in shear modulus. It is also worth noting that the unexpectedly higher adhesion of the materials that received a low dose at 5 kGy per pass can be explained by their surprisingly high bulk matrix shear modulus.

Due to a higher matrix modulus, this higher adhesion to carbon fibers for undercured electron beam matrices was qualitatively confirmed by analysis of the fracture surface, as shown in Figures 10 and 11. The fracture surface of a material that is fully cured (high matrix properties) shows very little resin attached to the fibers and a

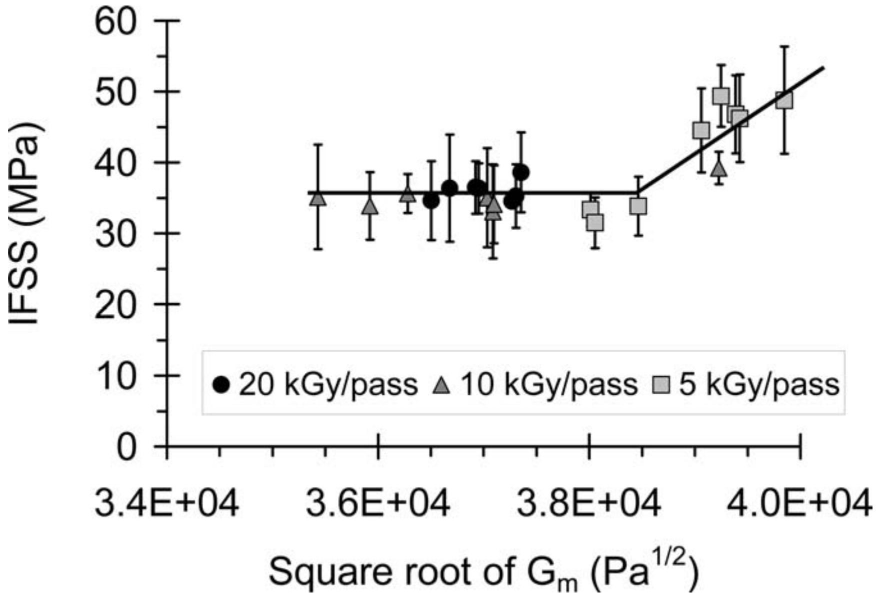


FIGURE 9 IFSS of AS4/Tactix 123-CD 1012 composites *versus* shear modulus of the bulk matrix processed for processing at various dose increments.

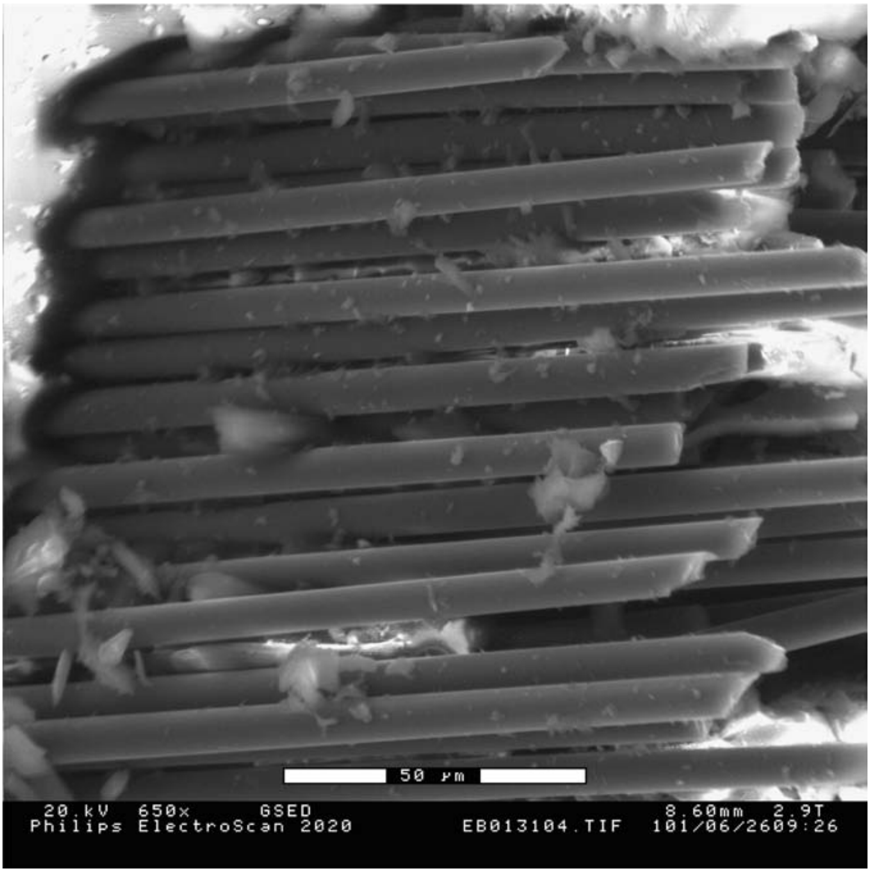


FIGURE 10 ESEM picture of the fracture surface of AS4/Tactix 123-CD 1012 composites e-beam cured, 20 kGy at 20 kGy per pass.

lot of fiber pullout. In contrast, the sample that received only 5 kGy at 5 kGy per pass does not exhibit bare fibers or appreciable fiber pullout and the resin adheres to the fibers.

The effect of processing conditions on the interfacial properties can be summarized as primarily due to the effect of the electron beam processing conditions on the bulk matrix properties. Assuming that the electron beam polymer at the carbon fiber surface is the same as in the bulk, the absorbed dose, the dose increments, and the thermal history do not seem to have a direct influence on the adhesion. In other words, matrix properties determine fiber/matrix adhesion for the unsized carbon fiber/Tactix 123 composites.

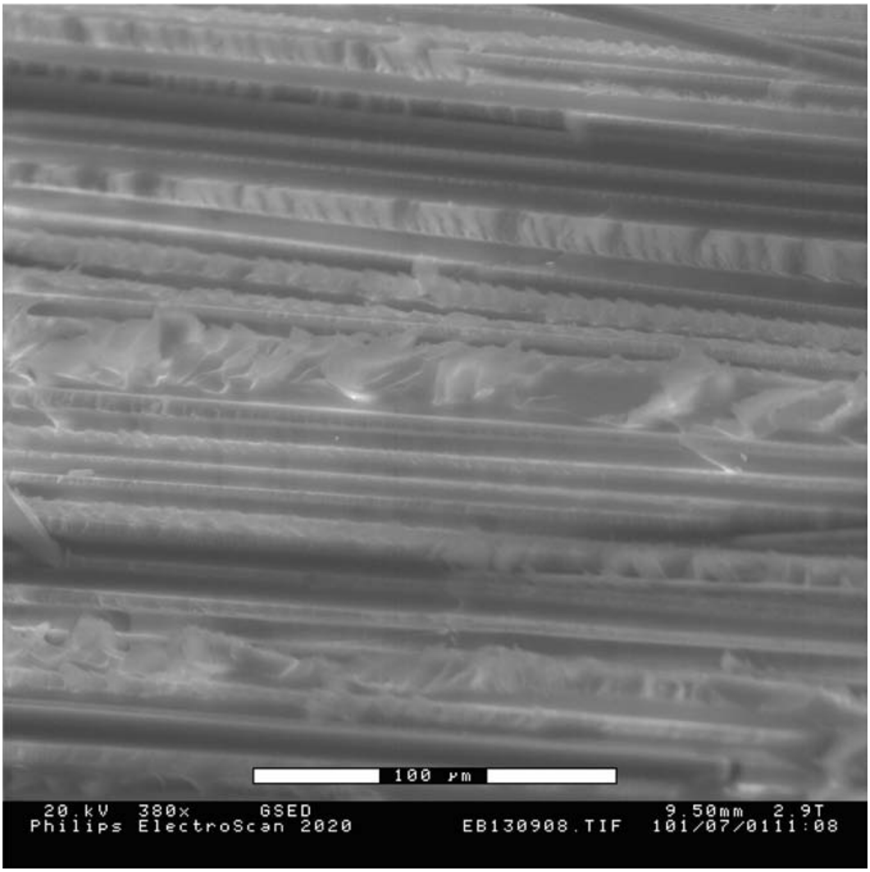


FIGURE 11 ESEM picture of the fracture surface of AS4/Tactix 123-CD 1012 composites e-beam cured, 5 kGy at 5 kGy per pass.

CONCLUSION

The initiation mode of electron beam processing is not responsible for the low adhesion of epoxy to carbon fibers, but both the chemistry of this system (absence of amine) and the absence of high temperature treatment have a negative effect on the fiber-matrix adhesion properties. The relationship between the processing conditions—expressed in terms of dose and dose per pass on the one hand and the matrix properties and the resulting interface properties to carbon fiber on the other—permit significant advances in understanding the whole composite. These results will provide the foundation to solve the issue of the poor adhesion in electron beam processed, high performance composites, and the development of specific solutions to improve the carbon fiber/epoxy matrix properties is currently under investigation.

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