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Engineered Interface Chemistry to Improve the Strength of Carbon Fiber Composites Cured by Electron Beam

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ABSTRACT: A reactive sizing was designed to achieve high levels of interfacial adhesion and improved mechanical properties with a carbon fiber−acrylate system cured by electron beam (EB). The sizing was made of a partially cured epoxy sizing with a high density of pendant functional groups (acrylate functionality) to facilitate covalent bonding with the matrix. The interlaminar shear strength improved from 61 to 81 MPa (+33%) without postprocessing, reaching a shear strength similar to that of the same system cured by a thermal treatment. Observation of the fracture profiles clearly highlighted a change in the fracture mechanism from a purely adhesive failure to a cohesive failure. To the best of our knowledge, such improvements of the mechanical properties of carbon fiber composites cured by EB, without any postcure, have not been reported previously. This constitutes a breakthrough for the industrial development of EB curing of composites.

I. INTRODUCTION

The development of lightweight composite materials is an area of active growth, driven by the need to reduce the weight of transportation vehicles for improved fuel efficiency and reduced oil consumption. Currently, high-performance composites are mainly cured by thermal treatment in an autoclave, which consumes relatively high amounts of energy and time. Electron beam (EB) curing of composite materials has gained interest as an effective out-of-autoclave composite manufacturing process. Its energy efficiency has been assessed to be around 10 times higher than that of thermal treatment in an autoclave.[1] Because fewer volatile organic compounds are involved and the use of toxic hardeners or radical initiators is eliminated, expensive treatment/disposal processes are minimized, and worker safety is improved. Overall, this process can be considered more environmentally friendly than autoclaving. Moreover, larger composite parts can be produced with EB curing. Nevertheless, composites cured by EB do not currently compete with the best composites cured by thermal treatment because the fracture resistance, interlaminar shear strength (ILSS), and transverse mechanical properties of composites cured by EB are typically inferior. One contributing factor to the poor performance of EB-cured composites that needed to be improved was the fracture resistance of the resins used as matrixes, and very significant improvements have recently been obtained with epoxy and acrylate resins.[2−4] The other major parameter directly responsible for the low performance of EB-cured composites is poor interfacial adhesion in comparison to that of thermally cured composites.[5−7] This issue is generally fixed with a postcure thermal treatment, which is an additional and undesirable processing step. In the case of a carbon fiber−acrylate system, it was shown that the differences in thermal history during curing were actually responsible for differences in interfacial adhesion.[8] Indeed, the generation of covalent bonding at the carbon fiber−matrix interface was found to be the result of the thermal postcure and not the EB curing, because the temperature reached within the composite during EB curing was not high enough. This explains why different carbon fiber surface oxidation treatments (electrochemical,[9] boiling nitric acid,[10] oxygen plasma[11]) do not lead to any significant improvement in interfacial adhesion with EB curing as they do for composites cured with a thermal treatment.[12,13] Some improvement was actually obtained when the fiber surface was functionalized with chemical groups that were able to generate covalent bonds with the matrix during its polymerization and using regular EB processing conditions. Those chemical groups were vinyl groups[14] and thiol groups.[15] However, the level of performance was still below that of a thermal cure. Some functionalities such as hydroxyl groups and amines were shown to strongly inhibit the EB cure of acrylate resins,[16] and those groups were still present at the surface of the fiber, potentially disturbing the cross-linking of the matrix in the vicinity of the fiber surface. Shielding of the fiber surface seems to be necessary. Moreover, volume shrinkage of the matrix during EB curing was around 5%, and it is known that high (5% or more) matrix cure volume shrinkage has a negative influence on interfacial adhesion.[17] This effect needs to be counteracted as well. Recently, a study involving plasma polymerization[18,19] led to high levels of interfacial adhesion because this approach potentially counteracts all negative effects at the same time. This study indicated that the following criteria have to be met in the design of the carbon fiber interface to reach levels of adhesion comparable to those achieved with a thermal cure (Figure 1):

- The carbon fiber surface needs to be shielded from the matrix, so the use of a polymer layer between them is necessary, which is also required for processability of the fiber (primary purpose of a sizing).
- The sizing needs to be covalently bonded to the carbon fiber surface and the matrix to ensure optimal transfer of the stress from the matrix to the reinforcement.

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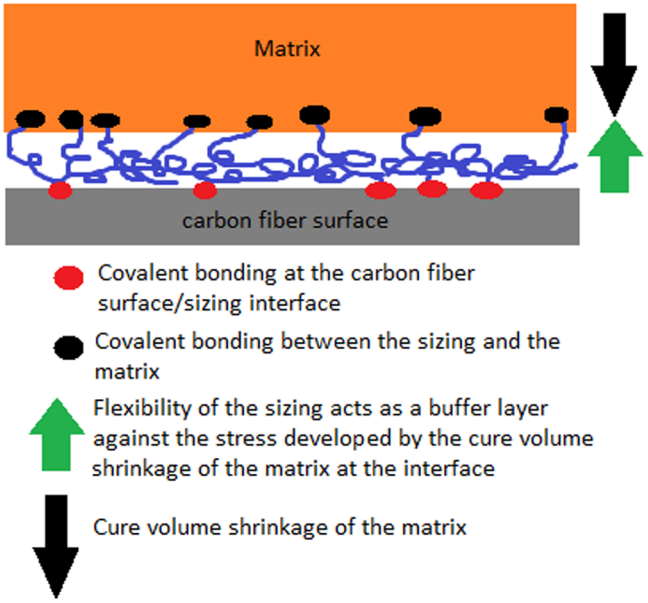

Figure 1. Engineered interphase for a carbon fiber composite cured by electron beam and with a matrix showing high cure volume shrinkage.

- The structure of the sizing needs to be flexible to counteract the stress developed by the cure volume shrinkage of the matrix.

If these criteria are not met, the interfacial adhesion will not be optimal. For example, the grafting of thiol groups at the surface of a commercial epoxy sizing (with no curing agent) was suggested. An improvement of the interfacial adhesion was obtained (more than 35% of the 90° flexural strength), but only after a postcure of 1 h at 160 °C, and no improvement was obtained with EB curing alone.[16] The thiol groups generated covalent bonding with the acrylate matrix, but the interfacial adhesion between the carbon fiber surface and the sizing was poor, which displaced the low interfacial adhesion issue from the carbon fiber−acrylate interface to the carbon fiber−epoxy sizing interface. Again, the low interfacial adhesion between the carbon fiber surface and the thiol/epoxy sizing was due to the thermal history of the sample during the cure, as shown by the beneficial influence of the postcure.

As mentioned before, plasma polymerization is a promising new approach for the surface treatment of carbon fibers that can produce an engineered interphase, as shown in Figure 1. However, the use of plasma polymerization, especially if pulsed and in vacuum, is still a technique that is relatively new, and its use for continuous surface treatment of carbon fibers is challenging. Even without plasma methods, it is still possible to mimic the engineered interphase depicted in Figure 1 using more common chemicals as the constituents of the sizing. This article describes how improved adhesion is obtained directly after EB curing by using a reactive sizing that contains pendant acrylate groups.

II. MATERIALS AND METHODS

II.1. Materials. The intermediate-modulus polyacrylonitrile-(PAN-) based Tenax IMS 5001 (12k) carbon fibers used in this study were manufactured by Toho Tenax Europe GmbH. These fibers were surface treated by electrochemical oxidation but not sized. According to single filament tensile testing results reported elsewhere,[9] their tensile modulus is 248 ± 20 GPa, their tensile strength is 4.51 ± 0.51 GPa, and their elongation at break is (1.6 ± 0.2)%.

Ebecryl 600 from Cytec was used as the matrix, and its chemical structure is displayed in Figure 2.

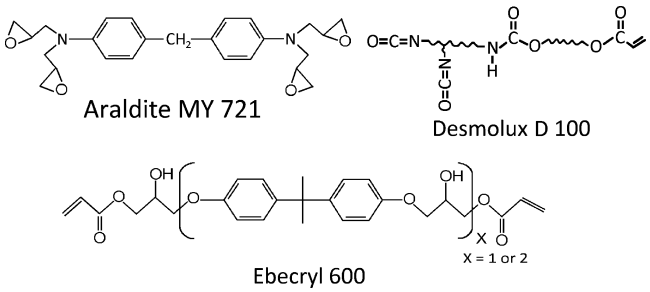

Figure 2. Molecular structures of the chemicals used in this study.

Araldite MY 721 (*N*,*N*,*N*′,*N*′-tetraglycidyl-4,4′-methylenebis-benzenamine) is a tetrafunctional epoxy resin (Figure 2) that was obtained from Huntsman Advanced Materials. Epon 828 epoxy resin (diglycidyl ether of bisphenol A, DGEBA) was obtained from Momentive. Desmolux D 100 is an isocyanate-bearing aliphatic urethane acrylate compound that was obtained from Bayer MaterialScience LLC. All chemicals were used as received. The formula of Desmolux D 100 is proprietary information, but according to the manufacturer, it has a functionality of 1 for the acrylate group and 2 for the isocyanate groups. A simplified molecular structure is displayed in Figure 2.

II.2. Sizing of the Fibers and Composite Manufacturing. The sizing solution was prepared by adding 37.3 g of Desmolux D 100 to 15.3 g of Araldite MY 721 and thoroughly mixing the components. Considering that the weight per epoxide for Araldite MY 721 is 113 and that the weight per isocyanate for Desmolux D 100 is 328, the ratio of the concentration of isocyanate groups to the concentration of epoxide groups was 0.84 (isocyanate groups were in excess). The mixture was left for 30 min at room temperature before being dissolved in 4 L of acetone, giving a sizing solution at 1.6 wt % of epoxy−isocyanate mixture. The fibers were then sized with the solution using a sizing unit made of mirror-finished stainless steel rollers, a scraper to remove excess sizing, and a multigallon-capacity bath. After passing through the sizing bath, the fibers were dried in a tubular furnace at 200 °C for 15 min. The dried fibers showed good handleability, and the tow was flexible. A thermogravimetric analysis found that the final content of sizing was 0.9−1.0 wt %.

Ebecryl 600 was degassed under vacuum before use. A temperature of 90 °C had to be set during the degassing to reduce its high viscosity (80 Pa·s at 30 °C).

The carbon fibers were wound around a steel frame and placed in a two-piece mold so that unidirectional composites were obtained. The fibers were impregnated with an excess of resin by layup with the use of a roller made out of Teflon. Ebecryl 600 was at 90 °C when the process was started. The impregnated fibers and the bottom part of the mold were left under primary vacuum at 90 °C for a few minutes to remove trapped air. Excess resin was expelled when the mold was closed. The top of the mold was made of aluminum, and its thickness was limited to 2.0 mm (0.08 in.), so that the EB could go through it and cure the composite sample. The bottom part of the mold was made of steel. The dimensions of the free

space in the mold controlled the dimensions of the composite samples, which were constant. The concentration of fibers was 60 vol %.

EB curing of the sample was carried out by Acsion Industries (Pinawa, Manitoba, Canada) with a 10 MeV electron gun and a total dose of 100 kGy (four passes of 25 kGy). The cure was done using a dynamic mode. The dose was adjusted by varying the translation speed of the sample carrier.

For each carbon fiber reference, three composite panels were made.

II.3. Analysis and Testing. *II.3.1. Differential Scanning Calorimetry.* Differential scanning calorimetry (DSC) analysis was used to study the reactions occurring between the components of the sizing when heated. A TA Instruments Q2000 apparatus was used with liquid cells. The heating rate was 5 °C min^{-1} from room temperature to 250 °C, and the analysis was done under nitrogen.

II.3.2. Fourier Transform Infrared Spectroscopy. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was also used to characterize the reactions occurring between the components of the sizing when heated and, more particularly, the fractional conversions of the epoxide and isocyanate groups. IR spectra were recorded using a Perkin-Elmer Spectrum 100 FTIR spectrometer equipped with a universal attenuated total reflectance accessory (with a single-bounce diamond crystal) and a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector. Prior to FTIR measurements, the spectrometer and the ATR accessory were purged with industrial-grade nitrogen gas to remove moisture and carbon dioxide contaminants. All spectra were recorded with a resolution of 2 cm^{-1} and were the averages of 16 scans.

The fractional conversion of epoxide groups was determined by measuring the area under the peak located at 908 cm^{-1} (asymmetric stretching of the epoxy ring). The peak located at 1189 cm^{-1}, characteristic of C—H aromatic stretching, was used as an internal reference. The fractional conversion of epoxide groups α was calculated as

$$\alpha = \frac{(A_{908}/A_{1189})_t}{(A_{908}/A_{1189})_{t=0}} \quad (1)$$

where A_{908} and A_{1189} are the areas of the peaks located at 908 and 1189 cm^{-1}, respectively.

The fractional conversion of isocyanate groups β was similarly calculated using eq 2 by measuring the area under the peak located at 2264 cm^{-1} (asymmetric stretching of the isocyanate group)

$$\beta = \frac{(A_{2264}/A_{1189})_t}{(A_{2264}/A_{1189})_{t=0}} \quad (2)$$

where A_{2264} and A_{1189} are the areas of the peaks located at 2264 and 1189 cm^{-1}, respectively.

II.3.3. Mechanical Testing. Short-beam shear tests were performed according to ASTM D2344. The dimensions of the specimens were 19.2 mm × 6.4 mm × 3.2 mm, and the span-to-depth ratio was 4. An MTS Alliance RT/5 twin-screw load frame was used with a 5 kN load cell. The testing device was controlled by the software Testworks 4. Twelve samples were obtained from each panel. All samples failed according to a shear mode.

II.3.4. Observation of the Fracture Profiles by Scanning Electron Microscopy. A Hitachi S3400 variable-pressure scanning electron microscope was used in high vacuum and secondary electron mode for observation of the surfaces of the fractured composites. The samples were previously coated with gold and fixed on the sample holder with carbon tape. The acceleration voltage was 5 kV, and the intensity of the emission current was 60 μA.

III. RESULTS AND DISCUSSION

III.1. Reactions in the Sizing Leading to an Engineered Interphase. Because the acetone used as the solvent in the sizing solution evaporated quickly—even before reaching the drying furnace—it can be considered that the reaction between the Araldite MY 721 and Desmolux D 100 during the drying step corresponds to a reaction in bulk. There is considerable debate in the literature about describing the reactions occurring, as they strongly depend on the temperature (ranging between 40 and 250 °C), the type of catalyst (if any), the presence of impurities, and the relative concentrations of the reactive chemicals. A reaction between diisocyanates and multifunctional epoxies can produce polyoxazolidones and trimeric isocyanurates by cyclization of isocyanate groups[20] (Figure 3).

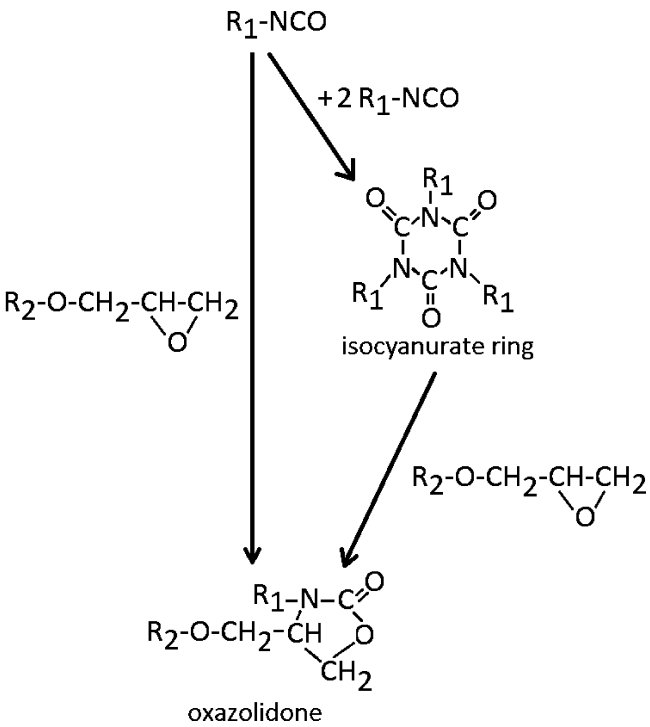

Figure 3. Possible reactions in a system containing epoxide and isocyanate groups.

Senger et al.[21] reported that the trimerization of isocyanate groups occurred rapidly (a few minutes only) at 150 °C when using DGEBA and diphenylmethane-4,4′-diisocyanate with 2-ethyl-4-methylimidazole as a catalyst and that the reaction could start at a temperature as low as 50 °C. Then, gradually, oxazolidone was formed. The trimerization of isocyanates was favored with all of the catalysts tested. Oxazolidone was also produced from the reaction of the isocyanurates with epoxide groups at higher temperatures. Caille et al.[22] demonstrated that the relative concentrations of the two monomers had a major influence on the type of generated groups and that an excess of isocyanate groups favored the reaction occurring at lower temperature, that is, the trimerization of isocyanates. Dileone[23]

showed that oxazolidones could be produced at 150 °C with the appropriate catalyst. DeMeuse et al.[24] claimed that tertiary amines are suitable for the high-yield synthesis of oxazolidones at temperatures between 80 and 150 °C, but at a lower rate: from 30 min to 8 h.

Studies on the reactivity between epoxy and isocyanate monomers without the use of catalysts are rare. Kadurina et al.[25] studied the reactivities of different epoxy−isocyanate systems as a function of the structures of both monomers (aliphatic or aromatic). They concluded that, with no catalyst, a reaction was occurring and could be divided into two steps. First, there was the generation of a urethane bond within the range of 45−90 °C if the epoxy monomer had secondary hydroxyl groups, and the second reaction was the generation of oxazolidone groups.

A DSC analysis of the mixture used for the sizing solution is shown in Figure 4. An exothermic reaction occurred between

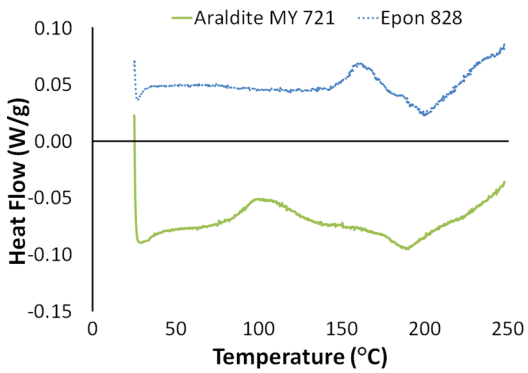

Figure 4. Differential scanning calorimetry analysis of epoxy−Desmolux D 100 systems.

80 and 140 °C. For comparison, the same DSC analysis with DGEBA was performed with the same weight concentrations. The weight per epoxide for Epon 828 is 170. The ratio of the concentration of isocyanate groups to the concentration of epoxide groups is 1.26. Kadurina et al.[25] showed that DGEBA did not react with an aromatic isocyanate in that range of temperatures. Nevertheless, they also claimed that an aliphatic isocyanate could be more active. Therefore, it is assumed that the exothermic peak at 150 °C corresponds to the formation of isocyanurates and the peak starting at 200 °C corresponds to the generation of oxazolidones. This can be seen as a model reaction, as the structure of DGEBA does not show any functionality other than the epoxide groups and the ether linkages (Figure 5). The Araldite MY 721 monomer structure is different because of the presence of the tertiary amines, which could potentially change the reaction mechanism.

Kadurina et al.[25] also reported that the presence of a tertiary amine in the epoxy monomer provoked the isomerization of the isocyanate groups at 100 °C. This explains the exothermic peak centered at 100 °C (Figure 4) because the MY 721 monomer contains tertiary amines in its structure (Figure 2).

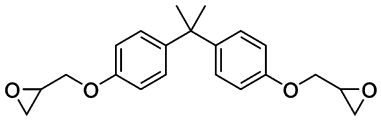

Figure 5. Chemical structure of DGEBA monomer.

Further heating at 200 °C leads to oxazolidone structures, which can be seen in the DSC curve by the beginning of a second exothermic peak at 190 °C. Nevertheless, as reported by other authors, oxazolidone can be expected to form at lower temperatures as well, although at a very low rate. An FTIR analysis of the same Araldite MY 721−Desmolux D 100 mixture as used for DSC analysis, after an exposure to 200 °C for 15 min, is displayed in Figure 6. The fractional conversions of epoxide and isocyanate groups were $\alpha = 0.05$ and $\beta = 0.15$, respectively. Overall, the sizing was partially cured after the drying step, with some of the isocyanate groups giving isocyanurate rings and a limited part of the epoxide groups having reacted with the isocyanate groups to give oxazolidone structures. The beginning of a three-dimensional structure was generated.

As described in the Introduction, the sizing also has to generate covalent bonding with both the carbon fiber surface and the acrylate matrix to ensure covalent bonding between the fiber surface and the matrix.

As demonstrated in a previous study,[14] isocyanate groups will react readily with hydroxyl groups and carboxylic acids located at the surface of the IMS 5001 fibers. A previously reported[7] X-ray photoelectron spectroscopy analysis of the IMS 5001 fiber surfaces showed that the oxygen atomic content was 15% and that the nitrogen atomic content was 2%. The fitting of the C 1s and O 1s peaks is reproduced in Table 1. It reveals that the oxygen is involved in a significant amount of hydroxyl and carboxylic acid functionalities. The generation of isocyanurates in the sizing allows the density of pending acrylate groups to be greater than obtained when single monomers were grafted directly onto the carbon fiber surface.

As shown in another study,[8] acrylate groups can generate covalent bonds with pendant amine functionalities located at the surface of the fibers through an aza-Michael reaction when the composite is heated at 150−160 °C. At these temperatures, the epoxide group of Araldite MY 721 reacts with those amines as well. It is unknown at this stage whether the tertiary amines of the Araldite MY 721 monomer can facilitate its grafting on hydroxyl groups or carboxylic acids. Also, it was demonstrated that some of the carboxylic acids can decompose at 150 °C and higher,[26] generating radicals at the surface of the fibers, which will create covalent bonds with acrylates.[8] Overall, there is a complex list of competing reactions for the generation of covalent bonding at the interface between the fiber surface and the sizing. The potential reactions for generating covalent bonding at the surface of the fiber with the sizing during the drying step are displayed in Figure 7.

The generation of covalent bonding with the matrix is ensured by the pending acrylate groups of the Desmolux D 100 monomers. In the case that not all of the isocyanate groups in the vicinity of the matrix react to give isocyanurate rings, the remaining ones can react with the hydroxyl groups located on the Ebecryl 600 monomer or with the acrylate groups during the radical polymerization.

The purpose of the design proposed in this study is to create a partially cured reactive sizing able to create covalent bonding with both the carbon fiber surface and the acrylate matrix, as shown in Figure 1. It is not known at this point whether the epoxy monomers experience extra cross-linking during the EB curing.

III.2. Mechanical Testing of Unidirectional Composites. The ILSS values obtained with nonsized fibers and sized fibers are reported in Table 2. Among the three samples made

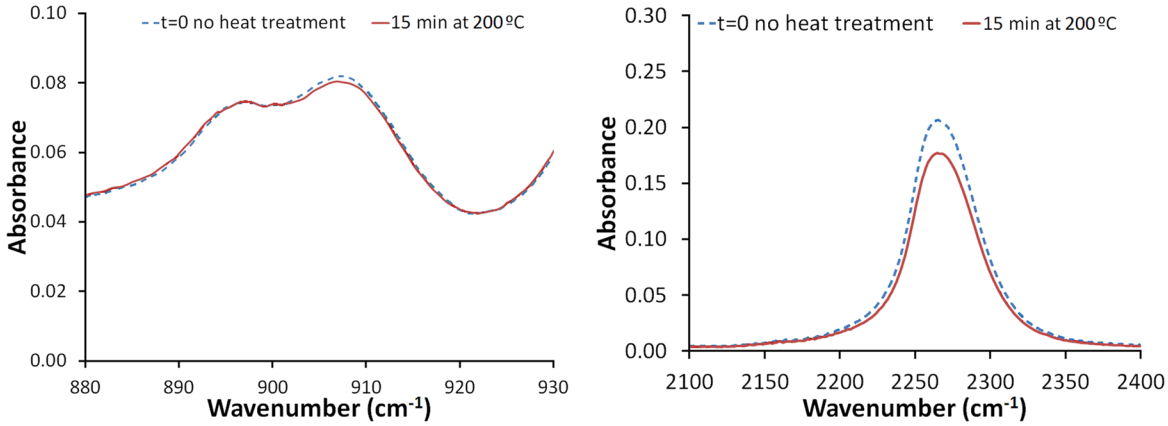

Figure 6. FTIR spectra of the mixture used for sizing before and after exposure to a temperature of 200 °C for 15 min. Enlargements of the peaks corresponding to (left) epoxide and (right) isocyanate groups.

Table 1. Fitting of the C 1s, O 1s, and N 1s Peaks of the X-ray Photoelectron Spectra of the IMS 5001 Carbon Fiber Surface[a]

C 1s		O 1s		N 1s	
C sp^2	76	Ph=O, Ph—C=O	32	amines, amides, nitrile	42
C sp^3	4	C=O, COOH	12	pyridine	10
C—O—R	5	R—OH, C—O—C	44	pyrrolidine, pyridone	40
C=O	3	Ph—OH, C—O	10	protonated N, pyridinium	8
COOH	5	H_2O	2		
C—COOR	5				
C—N	2				

[a]Reproduced from ref 7 with permission. Copyright 2012, Elsevier.

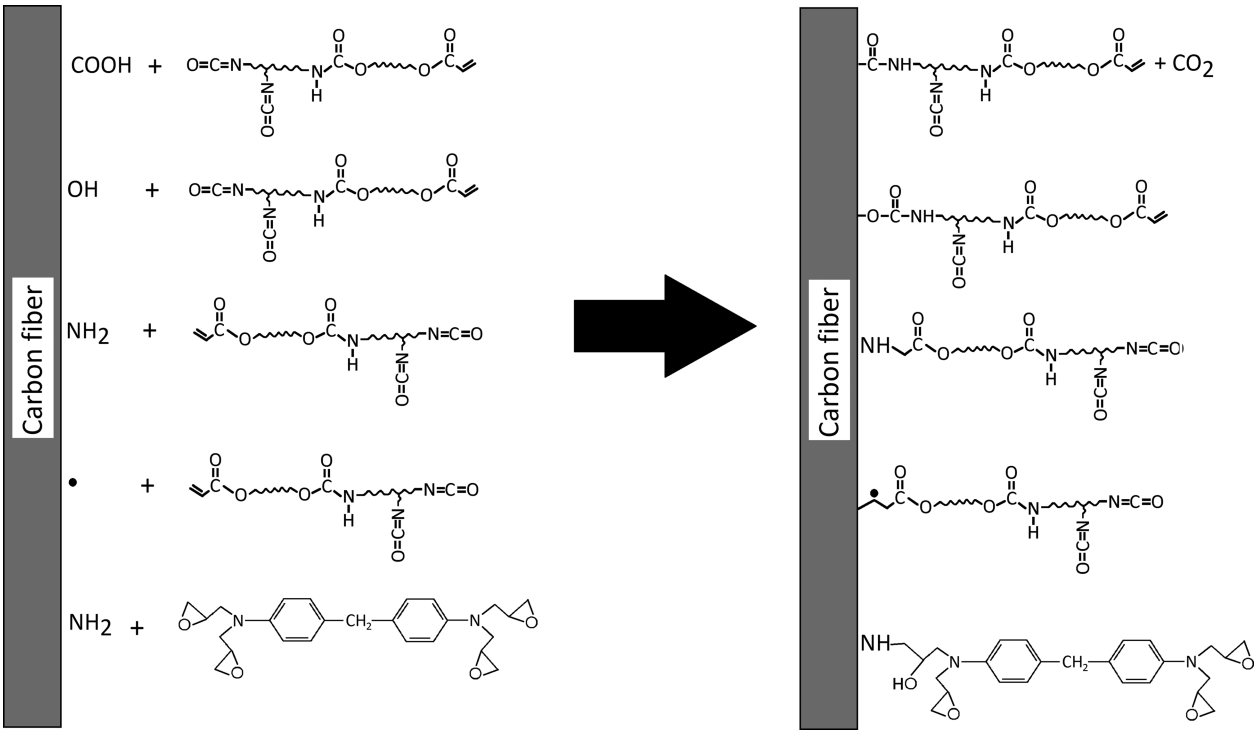

Figure 7. Possible reactions of grafting at the fiber surface−sizing interface.

from nonsized fibers, one showed a significantly lower value (52 MPa), which can be attributed to a higher void content; the short-beam shear test is very sensitive to the presence of voids. The values obtained with the reactive sizing were similar for the three samples. The improvement of the ILSS generated by the reactive sizing was clear (+33%), which is attributed to an improvement of interfacial adhesion. This was confirmed by scanning electron microscopy (SEM) characterization of the fracture surfaces (Figure 8). With nonsized fibers, the surfaces of the fibers showed only a few scattered pieces of matrix,

Table 2. Interlaminar Shear Strength (ILSS, MPa) Values of IMS 5001-EB 600 Composites Cured by Electron Beam with and without Sizing

no sizing	reactive sizing
60 ± 3	81 ± 3
62 ± 2	81 ± 3
52 ± 8	80 ± 2

which highlights a clear interfacial failure attributable to low interfacial adhesion. With sized fibers, the amount of matrix remaining at the surface of the fibers was much greater. Moreover, a typical fracture profile with hooklike protuberances can be seen (shown by the white arrows in image C). This is typical of a cohesive failure of the matrix under shear forces. The fracture mode switched from purely interfacial to cohesive, confirming the sharp improvement in interfacial adhesion with the reactive sizing.

The value obtained with the reactive sizing was also identical to that obtained with a thermal cure[8] (83 ± 5 MPa). To the best of our knowledge, no improvement like this one has been reported so far. Moreover, the parameters of the sizing have not been fully optimized. The architecture of the monomers (aliphatic/aromatic, number of functional groups per monomer), the thickness of the sizing, and the temperature of drying can be modified to improve the interfacial adhesion even further. Based on the work documented here, use of this reactive sizing with a reinforced version of the EB600 will lead to high mechanical performance, similar to that obtained with a thermal cure, which represents a true breakthrough in the development of EB curing technology. Finally, both epoxy and isocyanates (through blocked isocyanates technology) can be provided in water-based emulsion form, which potentially enables a scale-up according to current carbon fiber manufacturing practices. One concern about the use of isocyanate groups is that they can react with moisture to give amine groups. In this case, the production of amine groups will actually benefit the cross-linking of the sizing. By adjusting the relative concentrations of epoxide and isocyanate groups, it is possible to generate a reactive sizing that survives a significant time of storage under ambient conditions. Otherwise, the use of blocked isocyanates technology can also be a response to stability under ambient conditions.

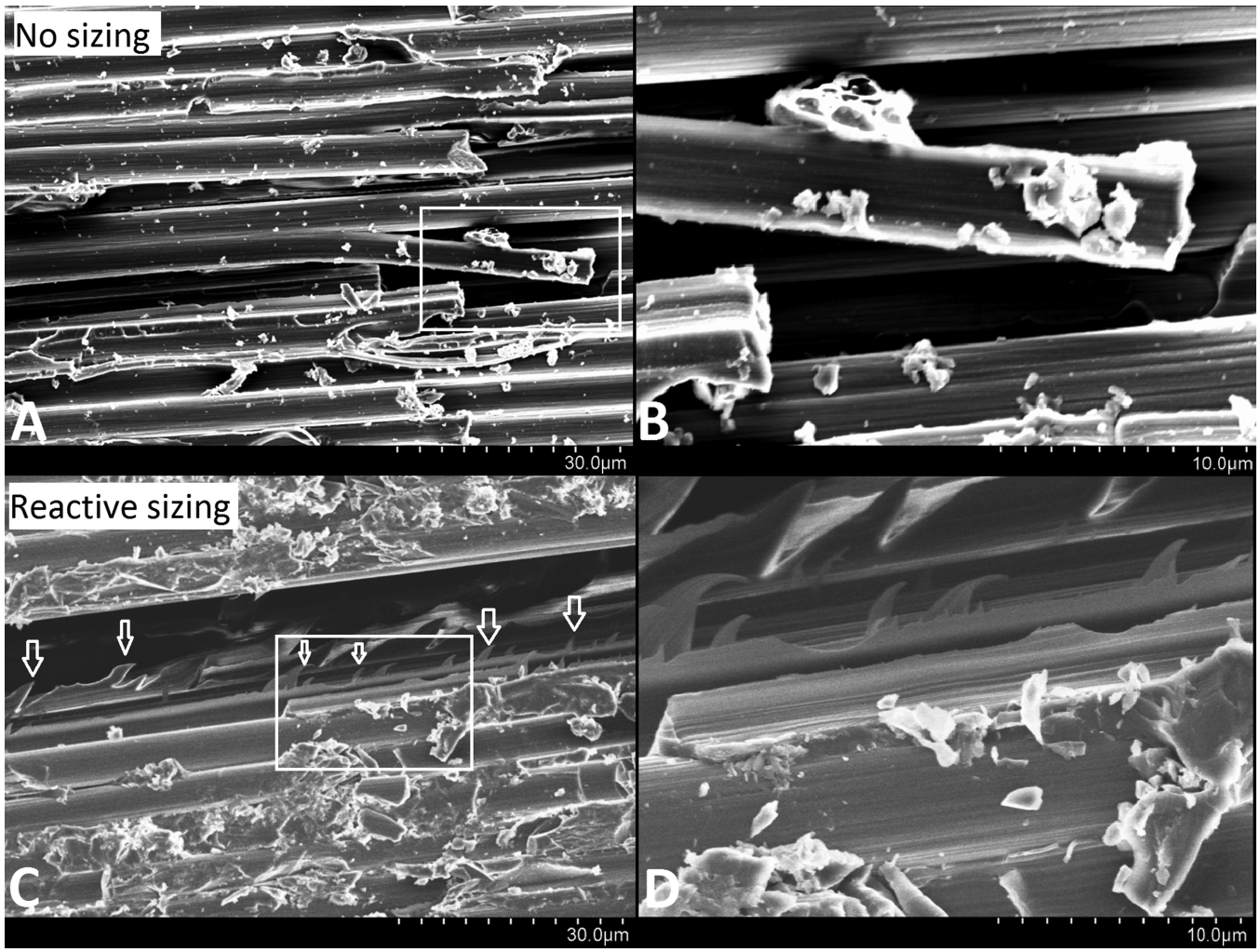

Figure 8. Scanning electron microscopy observations of the fracture profiles corresponding to the interlaminar shear strength values given in Table 2: (A) nonsized fibers, low magnification; (B) nonsized fibers, high magnification; (C) fibers with reactive sizing, low magnification; (D) fibers with reactive sizing, high magnification. Images B and D correspond to a magnification of the zone delimited by the white rectangles in images A and C, respectively.

IV. CONCLUSIONS

The use of a designed reactive sizing led to improvements in the mechanical properties of carbon fiber−acrylate composites cured by EB. The ILSS value was increased from 61 to 81 MPa (an increase of 33%) without postprocessing. This performance matches the value obtained with a thermal cure. A change in the fracture profile from adhesive to cohesive failure also highlighted the sharp improvement in interfacial adhesion. Obtaining a cohesive failure with the processing conditions imposed by EB curing is a true breakthrough. The production of high-performance carbon fiber composites by a fast, environmentally friendly, and energy- and cost-effective process seems to be attainable.

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Notes

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