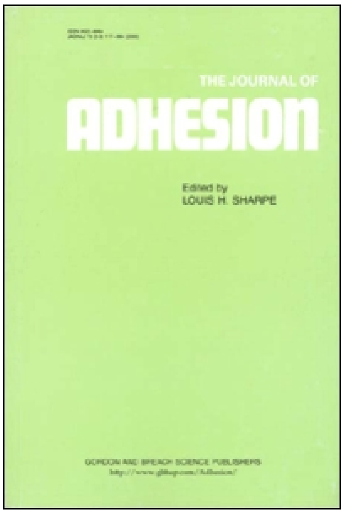

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Nanoreinforced Epoxy Adhesives for Aerospace Industry

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Adhesive joints of carbon fiber/epoxy laminates were studied using an epoxy resin as the adhesive. In order to enhance the mechanical and electrical properties of epoxy adhesives, they were modified by the introduction of carbon nanofibers (CNFs). Also, different surface treatments, such as grit blasting, peel ply, and plasma, were applied to the laminates.

The CNFs addition slows down the curing reaction of the epoxy adhesive although the final conversion is still high. The contact angle of nanoreinforced adhesives on the surface of treated laminates is lower than that of the neat epoxy resin. However, this increase of wettability scarcely modified the lap shear strength. Plasma treatment causes an important increase of the surface energy of laminates, markedly increasing the joint strength. The fracture mechanisms of the adhesive joints tested in the present study are strongly dependent on the surface treatment applied to the laminates.

Keywords: Carbon nanofiber; Composite; Epoxy; Surface treatment

1. INTRODUCTION

Carbon fiber reinforced polymers (CFRP) are a very common type of composite material. Although they find applications in several fields like the automobile industry, energy production, or sports, probably the most important is in the aerospace industry. CFRPs fulfil the strict requirements of this industry, especially the combination of good

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mechanical properties and low weight. In every new model of aircraft, the amount of composite material used to build the structure is higher.

Ideally, any structure should be designed without joints, as a monolithic entity. Joints are a source of weakness and they increase the weight of the structure, implying the use of more material. Also, the bonding process of several parts is usually less efficient and more expensive. However, size limitations on structures and the manufacturing process itself hinder the building of structures without joints. Thus, most structures consist of an assembly of different parts.

There are basically two ways of joining composite materials to build a structure: mechanically and with adhesives. Mechanical joints require the use of screws, bolts, or rivets. To make this kind of joint, it is not necessary to prepare the surface of the components and the joint can be easily disassembled for inspection and repair. A drawback of such techniques is the increase of the global weight of the structure. This fact is especially important in applications where the weight of the structure plays a key role, like the aerospace industry. Also, in the case of composite materials, the presence of localized stresses induced by fasteners can cause delamination, matrix crazing, and fiber failure [1].

Adhesive joints minimize stress concentrations, distributing the load over the overlap area. They do not require holes and usually present lower cost for large surface joints. The use of adhesives reduces the weight of the structure in comparison with mechanical joints. However, adhesive joints have some disadvantages. Joining surfaces must present surface properties which promote the adhesion. This requires the application of surface treatments, especially in the case of low surface energy materials, like polymers or polymer composites. In general, the aims of surface treatments are [2,3]:

- To remove any weak boundary layer on the surface of the adherend, such as contaminants, poorly adhering oxidized layers, or low molecular weight species, which can be the origin of adhesive failure of the joint.
- To improve wetting of the adherend by the adhesive.
- Chemical modification such as the introduction of different chemical groups into the surface which can form acid-base or stronger primary bonds with the adhesive. In CFRP, as the polymeric matrix usually has an important apolar character, surface treatments often aim to increase the polar part of the material in order to increase surface energy and, thus, enhance chemical adhesion.
- To increase the surface roughness, giving rise to improved mechanical interlocking or increased bondable surface area.

The intention of the surface treatments is to modify the chemistry and morphology of a thin surface layer without affecting the bulk properties. The effectiveness of any surface treatment is dependent upon the type of substrate and the extent of the treatment [2]. There is a wide variety of surface treatments, like solvent cleaning, acid etching, flame, plasma, or laser or peel ply, among others. In order to choose the most suitable treatment in every case, the properties of adherends and adhesive must be taken into account. The main surface treatments in the case of CFRP are grit blasting, peel ply, and plasma.

Grit blasting is the simplest surface treatment to improve adhesion. It modifies the surface morphology, increasing the roughness and, therefore, the effective surface area. This promotes mechanical interlocking. Also, it removes surface contamination. To ensure this and that no grit particles remain on the surface, it must be cleaned with a solvent, usually acetone. A drawback of grit blasting is that it causes visible damage to the composite, breaking carbon fibers even at low blast pressure and short treatment time [2].

Peel ply treatment is one of the most used surface treatments in the composite industry, due to its low cost and ease of use. It consists of a single ply placed on one side of composite material prior to the manufacturing process. During the cure cycle, this ply is progressively impregnated with the polymer matrix of the composite, remaining as fully part of the composite. Then, its removal leads to a rough surface, which is the negative of the peel ply used, increasing the surface free energy. In addition, peel ply contributes to protection of the surface until the adhesive is applied, preventing its contamination. However, the peel ply usually leaves residues of release agent on the surface of adherends. This is the main problem in the use of this kind of surface treatment. The peel ply can be made of different polymers, such as polyester, polyamide, or nylon. The chemical nature of the peel ply, as well as its morphology, induces some changes on the composite surfaces. For example, polyamide plies may bring some polar groups on the composite surface while polyester ones induce the predominance of apolar compounds [4].

Plasma surface treatment is another common technique for composite materials. During plasma treatment, the adherend surface is exposed to ionized gas, usually generated by radio frequency energy. The plasma region contains a high concentration of reactive species, such as ions and electrons, which are formed from the gas. Various studies have indicated that these energetic species interact with the surface and cause chemical and textural changes. The chemical changes that occur are dependent upon the gas used to create the plasma [2]. Some researchers have found that plasma treatment increases the concentration of polar groups on the surface, thus increasing the polar component of the surface energy [1]. This treatment is more complex and requires the adjustment of several parameters which affect the quality of the applied treatment, such as the plasma medium, the distance of the sample from the plasma, and the exposure time.

The properties of the adhesive also affect the mechanical properties of adhesive joints. Epoxy resins are the most used adhesives to join carbon fiber/epoxy composites. They present good mechanical properties and high chemical resistance, but have some limitations, such as low toughness and very high electrical resistivity. To overcome them, different reinforcements are added. In the recent past, the introduction of nanometric reinforcements has been widely studied. In epoxy resins, the addition of small amounts of carbon nanotubes (CNT) or carbon nanofibers (CNF) can increase mechanical properties and electrical conductivity [5–7]. CNTs present better properties than CNFs, due to their novel forms of crystalline carbon structures, which consist of concentric graphene cylinders with a diameter in the range of nanometers. However, CNFs are much cheaper, due to their manufacturing process by vapour phase growth. The application of both CNTs and CNFs as reinforcement in epoxy resins is limited by the difficulty of dispersing them and the lack of interaction between the reinforcement and the epoxy matrix. Many researchers are working to solve these problems by means of functionalization of carbon nanoreinforcements [8], the use of surfactants to aid dispersion [9] or different stirring techniques [5].

The application of these nanoreinforced epoxy resins as adhesives for joining carbon fiber/epoxy laminates would have as main advantages the enhancement of the mechanical strength and the increase of fracture energy in relation to the neat epoxy adhesive. Besides, nanoreinforced epoxy adhesives are electrically conductive, improving also the thermal behaviour with the incorporation of carbon nanofibers. On the other hand, the chemical similarity between carbon nanofiber/epoxy adhesive and carbon fiber/epoxy laminate could favour the wetting and improve the adhesion. Also, the very small diameter of the reinforcement used and its relatively high length could favour its penetration into the small hollows or voids of the adherend surface, enhancing the joint strength [10].

Several authors [10–12] have studied the effect of the addition of nanoreinforcements to adhesives. They separately found that the failure mechanisms radically change relative to the neat adhesive. However, no great enhancements were measured either in the joint strength [12] or in the fracture toughness [11]. In the present work, the viability of using nanoreinforced epoxy resins with CNFs as adhesives for bonding carbon fiber/epoxy laminates was studied. Different surface treatments of adherends were applied, studying their effect on the surface energy and the contact angle. The effect of nanoreinforcement content on the curing process of the adhesive was studied by differential scanning calorimetry. Also, the joint strength was measured as a function of surface treatment and carbon nanofiber content. Finally, the mechanism of failure was studied by scanning electron microscopy.

2. EXPERIMENTAL

2.1. Materials

The carbon fiber/epoxy laminates used as adherends were manufactured by Instituto Nacional de Técnica Aeroespacial (INTA, Madrid, Spain), using prepreg material from Hexel Corporation (Stamford, CT, USA), with the denomination HEXPLY 8552/33%/268/IM7 (12 K) which is made from intermediate modulus polyacrylonitrile (PAN)-based continuous carbon fibers (HexTow^{TM} IM7) manufactured in 12,000 filament count tows and an epoxy resin designated 8552 whose typical application is in aerospace structural parts (empennage, fighter wings). The unidirectional carbon fiber laminate ($[0]_{10}$) had a fiber volume fraction of 33% and was made by vacuum bag molding and autoclave curing.

As the adhesive, a basic formulation of epoxy resin was used. The epoxy monomer was the diglycidyl ether of bisphenol A (DGEBA), supplied by Sigma-Aldrich (St. Louis, MO, USA) with 178 g/epoxy equivalent. The curing agent 4,4′-methylenedianiline (DDM) was used, purchased from Sigma Aldrich. This epoxy adhesive was analysed in our lab by Charpy and flexural tests. It is relatively brittle and presents high flexural strength. The absorbed energy measured by the Charpy test is close to $2.3 \pm 0.2\,kJ/m^2$, the value of its elastic modulus is $3.2 \pm 0.2\,GPa$, its flexural deformation is around 4%, and its maximum flexural strength reaches 120 MPa.

CNFs were added as reinforcement to the epoxy adhesive. They were prepared by chemical vapour deposition (provided by Antolin, Burgos, Spain), with diameters ranging from 20 to 80 nm and an average length of 35 μm. The morphology of the nanoreinforcements was analyzed by Transmission Electron Microscopy (TEM), with the finding that CNFs are basically constituted of “platelet-like” or “fishbone” nanofibers, in which the CNFs have a helical disposition.

Nanoreinforced epoxy resins were prepared by a dilution method [13,14], using chloroform as solvent in order to decrease the epoxy viscosity and to enhance the nanoreinforcement dispersion. First, a dispersion of CNFs in the solvent was prepared. In order to break nanoreinforcements sheets into tiny bundles, the obtained suspension was stirred at 40°C for 30 min (Magnetic stirrer, Agimatic-E, Selecta, Madrid, Spain). Next, the epoxy precursor was added. The DGEBA was mixed with the nanofibers suspension and subjected to high shear mixing (150 rpm) for 30 min at 40°C (AGV-8, Bunsen, Madrid, Spain). The resultant solution was then sonicated using a 50–60 Hz ultra sonicator (UP400S Hielscher, Teltow, Germany) for 45 min at 40°C. Then the solvent was slowly evaporated with continuous stirring at 90°C for 24 h. A stoichiometric amount of DDM was added to the epoxy/CNF mixture, followed by stirring at 130°C to dissolve the hardener. The applied curing treatment consisted of heating at 150°C for 3 hours and then postcuring at 180°C for 1 h. CNFs were added in different percentages: 0.25, 0.5, and 1 wt% with regard to the epoxy monomer mass. As a reference sample, the neat epoxy resin was also prepared, mixing DGEBA and DDM at 130°C for several minutes and then applying the same curing and postcuring treatment, 150°C for 3 h and 180°C for 1 h.

2.2. Surface Pretreatment

Some laminates were supplied with a peel ply layer, which was removed by hand. The weave of the polyester peel ply was observed by scanning electron microscopy. It consists of a web of interweaved fibers, whose diameter is around 15 μm. Groups of 20 fibers are interlaced, forming square domains of 0.08 mm^2.

Grit blasting was carried out in a Guyson (mod. Jetstream 22, North Yorkshire, England) grit blaster using 220 grit alumina. Three passes were made with the gun at a distance of 10–15 cm from the composite probe. The grit blasted surfaces were swabbed with acetone.

Atmospheric plasma treatment was carried out at 615 W of power. Plasma treatment was applied with a rotary nozzle, which generates a conic beam. Only one pass was made at a distance of 7 mm and at a speed of 1.2 m/min.

2.3. Characterization of the Joints

The curing process of the different epoxy/CNFs mixtures was analysed by differential scanning calorimetry (DSC). DSC measurements were carried out in a Setaram (Setsys 16/18, Caluire, France) apparatus, calibrated with indium and zinc. The scan was made from 20 to 250°C at 10°C/min under argon atmosphere, in order to measure the reaction enthalpy (ΔH) of the curing.

Contact angle analysis was carried out with a Ramé Hart 200 (mod. p/n 200-F1, Mountain Lakes, NJ, USA) contact angle goniometer equipped with a camera and video monitor. Different wetting liquids (water and glycerol) were utilized to obtain the surface free energy [1]. Also, the contact angle of non-cured neat epoxy resin and resin reinforced with different CNFs contents was measured. Drops of 2 μL were carefully placed on the substrate with a microlitre syringe. The obtained contact angle was the average value of ten measurements, at left and right sides, of two drops for each liquid.

The joint strength was determined by single lap shear test according to ASTM D5868. The thickness of the adhesive was 0.7 mm, and the overlap was $25 \times 25\,\text{mm}^2$. Five joints of each composition and surface treatment were tested.

Treated surfaces of laminates were observed with a Philips (Dawson Creek, OR, USA) ESEM XL30 scanning electron microscope (SEM). Energy dispersive spectroscopy (EDS) was used to determine the compositional changes induced by the different surface treatments. SEM was also used to observe the fracture surfaces of adhesive joints, in order to study the failure mechanism. All surfaces were coated by Au-Pd sputtering.

3. RESULTS

3.1. Characterisation of Adhesives

The addition of carbon nanofibers to the epoxy adhesive could modify the kinetics of the curing process, changing the degree of crosslinking reached and, therefore, its mechanical and thermal properties. The effect of CNFs on the cure of modified epoxy adhesives was analysed by DSC. Figure 1a shows the thermograms obtained by DSC in scanning mode for stoichiometric mixtures of DGEBA/DDM with different CNFs contents. All the curves present only one exothermic peak at high temperature, the maximum of which is in the range of 165–185°C, corresponding to the curing reaction between oxirane rings of DGEBA and aromatic amine groups of DDM. The reaction peak shifts to higher temperatures with the addition of nanofibers, hindering and retarding the curing process of the epoxy adhesive. This effect has been already observed by other authors [15,16], even with addition of carbon black [15]. This retardation can be explained by the possible adsorption of curing agent molecules into the nanofibers, which reduces its effective concentration.

The total area under the thermogram peak was used to calculate the total heat of reaction (ΔH). The extent of reaction (α) can be

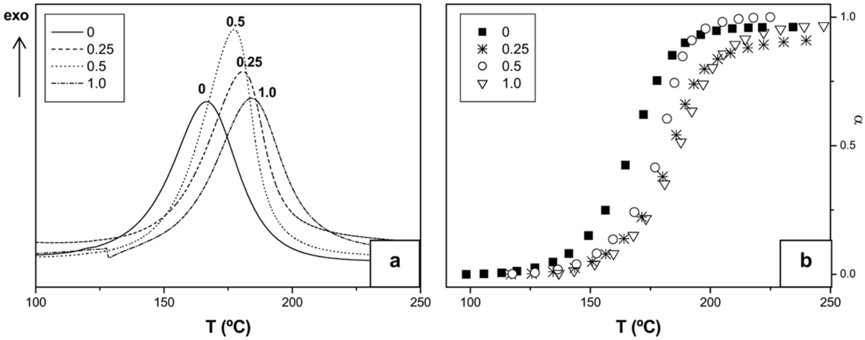

FIGURE 1 DSC results for epoxy/DDM mixtures with 0, 0.25, 0.5, and 1 wt% CNFs: (a) Dynamic DSC thermograms and (b) evolution of epoxy conversion with temperature.

defined as:

$$\alpha = \frac{\Delta H_i}{\Delta H_T}, \tag{1}$$

where ΔH_i is the partial area under the DSC trace and ΔH_T is defined as the total reaction when the crosslinking reaction is complete. The theoretical value of the total reaction enthalpy for epoxy/amine reaction is 100 kJ per epoxy equivalent [17].

Figure 1b shows the evolution of epoxy conversion as a function of temperature. The curing reaction of the epoxy resins with amine crosslinkers is commonly called autocatalytic. This means that the epoxy/amine reaction is accelerated by hydroxyl groups which are formed during the cure by the opening of oxirane rings. This behaviour can be described by the following equation, defined by Kamal and Sourour [18]:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n, \tag{2}$$

where $d\alpha/dt$ corresponds to the reaction rate, k_1 is the kinetic constant of the auto-catalytic reaction, k_2 is the kinetic constant of the non-catalytic reaction, and m and n are the reaction orders of the non-catalytic and catalytic processes, respectively.

This equation presents numerous unknown quantities. That is why it is usual to make the simplification that the autocatalytic process is negligible at high temperatures due to the large difficulty of forming complex ternary molecules (epoxy-amine-hydroxyl) [19]. Applying this hypothesis and taking into account that the ratio between the kinetic constant and temperature is of the Arrhenius type, Eq. (2) is reduced to:

$$\ln\left[\frac{(d\alpha/dt)}{(1-\alpha)^{n}}\right] = \ln A - \frac{E_a}{RT}, \tag{3}$$

where A is a pre-exponential factor, E_a is the activation energy of the curing reaction, R is the ideal gas constant, and T is the temperature.

It is well known that the reaction order of the non-catalytic epoxy/amino reaction is two [18,19]. The experimental data of Fig. 1b were fitted with this equation and the activation energy of the non-catalytic curing reaction was determined. The obtained values are shown in Table 1 together with a summary of the DSC results. The addition of CNFs to the epoxy/amine mixture induces an increase of the activation energy of the curing reaction. Similar behaviour was found by Valentini *et al.* [16] in agreement with the shift of peak temperatures. It is worth pointing out that although all the obtained results confirm that the nanofiller causes a delay on the curing advance, the epoxy conversion at which the reaction rate is maximum is the same on all studied samples (neat epoxy resin and epoxy modified with different CNFs contents) [20]. This implies that the decrease of concentration of the curing agent due to their adsorption into nanofibers affects mainly at the end of process when the values of conversion is high, probably after gelification of the system.

In short, the addition of CNFs causes a decrease of the curing reaction rate although the final epoxy conversion reached is still high.

3.2. Characterisation of Adherends

Different treatments (peel ply, plasma, and grit blasting) were applied on the surface of carbon fiber/epoxy laminates in order to increase

TABLE 1 Summary of Curing Study by DSC of Epoxy Adhesives Reinforced with Different CNFs Contents

% CNFs	ΔH (kJ/ee)	T_P (°C)	E_a (kJ/mol)	α_{max}
0	96.5	166	110.8	0.43
0.25	91.3	181	135.6	0.42
0.5	99.6	177	138.7	0.42
1.0	96.8	184	136.6	0.42

ΔH = total heat of reaction in kilojoules per epoxy equivalent (kJ/ee).
T_P = maximum reaction peak temperature.
E_a = activation energy of curing reaction at high temperature.
α_{max} = conversion when the reaction rate is maximum.
ee = epoxy equivalence.

their wettability and adhesion capability and, therefore, to enhance the joint strength. The treated surfaces were observed by SEM in order to observe the induced changes in the surface profile. Figure 2 shows the collected micrographs. It is clearly observed that the peel ply treatment drastically modifies the surface texture of the adherend. In Fig. 2b, it can be seen that the last surface layer of epoxy matrix of the laminate rightly copies the texture of the peel ply tissue [4] as can be observed in Fig. 2e. Grit blasting induces an increase of surface roughness but the initial texture of the laminate remains since the surface texture of the oriented fibers is still visible (Fig. 2c). The surface treated with plasma also keeps the initial texture of laminates but, at high magnifications, it is possible to observe the hollows and marks generated by the application of the plasma beam (Fig. 2d).

A semi-quantitative analysis of the elemental composition of the laminates was carried out using an EDS detector, the results of which are shown in Table 2. The non-treated adherends are mainly constituted of C, although O and S are also detected in very low concentration. The elemental sulphur comes from the crosslinker of

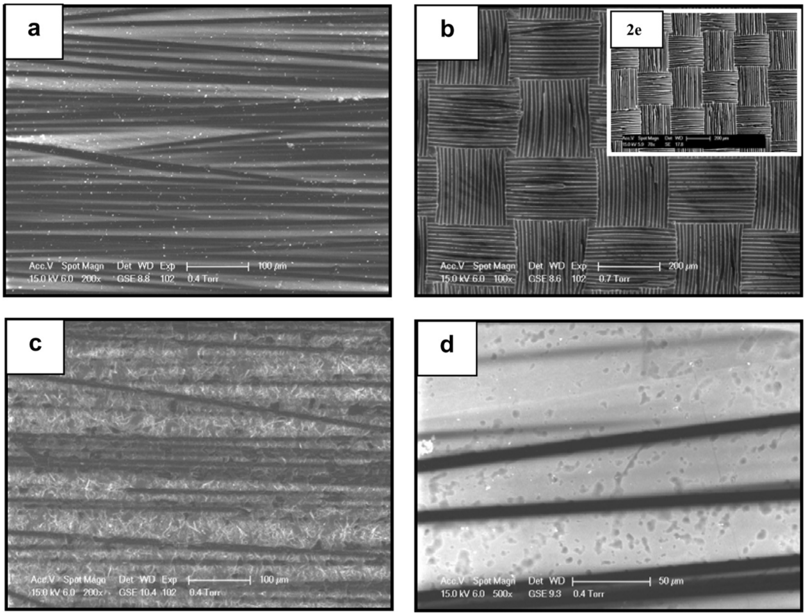

FIGURE 2 SEM micrographs of carbon fiber/epoxy laminates: (a) non-treated and surface treated with (b) peel ply, (c) grit blasting, and (d) plasma. The micrograph 2e shows the texture of peel ply tissue. The scale marker in a = 100 μm, b = 200 μm, c = 100 μm, d = 50 μm, and e = 200 μm.

TABLE 2 Elemental Composition (Atomic %) on the Surface of Treated Adherends Measured by EDS-SEM

Elemental %	As received	Grit blasting	Peel ply	Plasma
C	83.7	78.4	79.4	75.3
O	12.4	15.3	14.4	20.0
S	3.9	4.9	5.9	4.7
Al	–	1.4	–	–
Si	–	–	0.3	–

the matrix, 4,4′-diaminodiphenylsulfone. Although the epoxy matrix also contains N, this element is not detected due to its low concentration. Similar elemental compositions were found for the adherends treated with grit blasting and peel ply. In the case of grit blasting, a very low concentration of aluminium was also detected, which comes from alumina abrasive used in the surface treatment. The adherends treated with atmospheric plasma present a higher concentration of O than for the other treated laminates, indicating an important modification of its surface composition. As was commented on above, the atmospheric plasma treatment consists of exposing the surface to ionized gases in order to enhance its adsorption. Finally, the compositional analysis of peel ply showed a very low concentration of Si, whose origin probably is the silicone release agent applied to the polyester ply [4,21].

Figure 3 shows the contact angle of the studied epoxy adhesives. The highest values of contact angle were measured on the as-received adherends, without any treatment, justifying the necessity of surface pretreatment. However, no great differences were observed as a function of the applied treatment.

The contact angle of the neat epoxy adhesive is similar to those reported for other commercial epoxy adhesives [1,4] and it decreases with the addition of CNFs. This could be explained by the nano-scale size of the nanofiber and the higher chemical compatibility between the carbon fiber/epoxy composite and the nanoreinforced epoxy adhesive. However, the increase of CNFs percentage added causes an increase of contact angle although the measured value is lower than that of neat epoxy adhesive in most cases, except for the epoxy adhesive reinforced with 1 wt%. This increase could be associated to the worse dispersion of the nanofiller when its content is higher, possibly forming agglomerations of CNFs which increase its effective size. In previous works [14,22], it was observed that the epoxy nanocomposites with 0.25 wt% CNFs present suitable dispersion of filler, although at very high magnifications it was possible to observe that nanofibers tend to

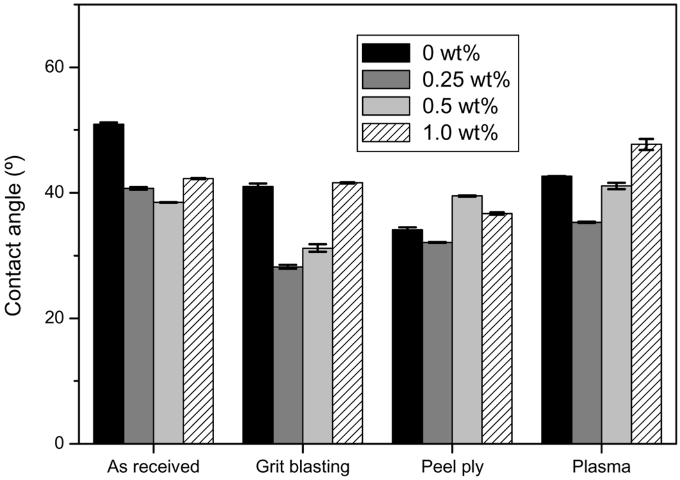

FIGURE 3 Contact angle of neat epoxy adhesive and modified adhesives reinforced with 0.25, 0.5, and 1 wt% CNFs on carbon fiber/epoxy laminates (non-treated and treated with grit blasting, peel ply, and plasma).

be tangled. Higher contents cause the appearance of aggregates, whose size and amount grow as the proportion of nanofibers increases.

The measurement of contact angle on a substrate with different liquids allows one to calculate the surface free energy of this material by the method of Dynes and Kaelble [23]. This allows determination of the dispersive and polar components of the surface free energy. Taking into account Kaelble's approach, the total surface energy can be calculated as the sum of both. Figure 4 shows the values obtained for these parameters calculated with the contact angles of water and glycerol for the carbon fiber/epoxy substrates as received, without any treatment, and superficially modified with different treatments, peel ply, grit blasting, and plasma. The surface energy of non-treated adherends is low ($38\,\mathrm{mJ/m^2}$). Dynes and Kaelble [23] reported values of surface energy for various graphitic and carbon materials ranging from 37 to $58\,\mathrm{mJ/m^2}$. Also, the main component of surface energy on the substrates used, carbon fiber/epoxy laminates, is the polar one.

Except for the plasma, the total surface energy is scarcely modified by the surface pretreatments applied. However, the ratio between the polar and dispersive components of the free surface energy changes. While the non-treated laminate presents a very low dispersive component, this increases considerably after applying grit blasting and peel ply treatments, while the polar component proportionally decreases. This behaviour could be associated with the found differences in the

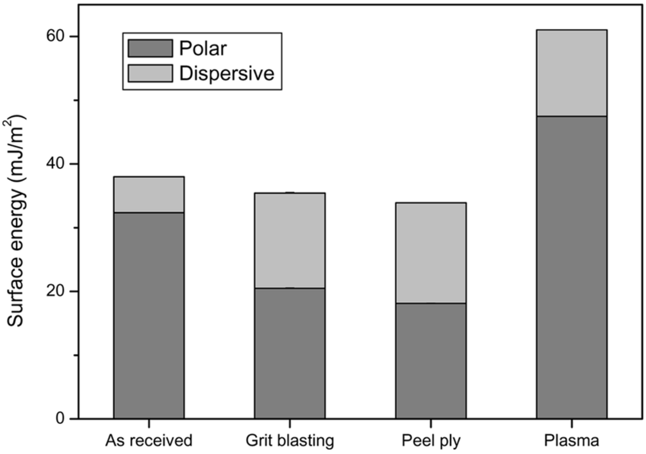

FIGURE 4 Polar and dispersive components of surface energy of carbon fiber/epoxy laminates non-treated and treated with grit blasting, peel ply, and plasma.

roughness, surface texture, and chemical composition of composites when peel ply and grit blasting are applied. In fact, Bénard *et al*. [4] showed that polyester plies induce a predominance of apolar compounds on the composite surface. This is in agreement with our results obtained by EDS-SEM, which confirm the presence of silicon (from silicone release agent) on the peel ply treated surface.

After plasma treatment, the total surface energy of the composite is strongly enhanced. Figure 4 shows that this enhancement is mainly generated by the increase of the polar energy component, indicating an increase of polar element concentration on the surface of the adherend. This is explained by the fact that the atmospheric plasma treatment increases the concentration of oxygen in the surface [1].

3.3. Characterisation of Joints

The joint strength of neat epoxy and nanoreinforced resins was determined by single lap shear test following the ASTM D5868 standard, using the carbon fiber/epoxy laminate adherends treated by plasma, grit blasting, and peel ply. Figure 5 shows the obtained results. The failure mode is highly dependent on the applied surface treatment. While the joints with peel ply presented adhesive failure, grit blasted joints broke in a mainly cohesive mode through the first laminate of the adherend. The failure mode of plasma treated joints was partially cohesive-adhesive. Here, it is necessary to note that the cohesive

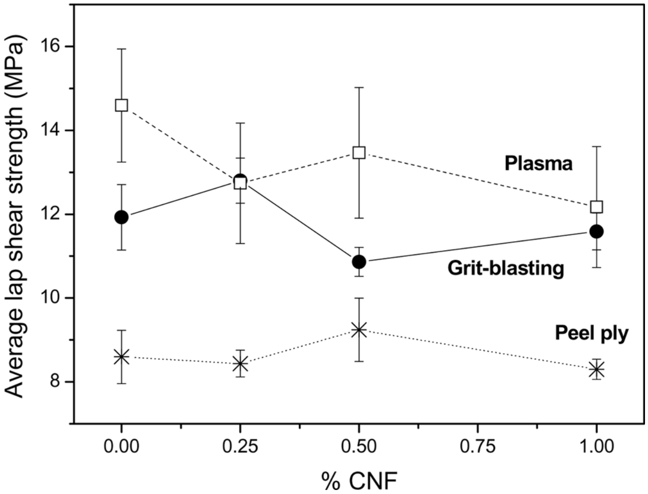

FIGURE 5 Average lap shear strength [maximum force/(width × overlap)] of neat epoxy adhesive and modified adhesives reinforced with 0.25, 0.5, and 1 wt% CNFs with carbon fiber/epoxy laminates, treated with grit blasting, peel ply, and plasma.

failure through the adherends implies that the maximum strength of the adhesive is not tested.

It is observed that the addition of CNFs scarcely affects the joint strength in spite of the decrease in contact angle (Fig. 3), enhancing the wettability of the laminates.

In contrast, the measured lap shear strength strongly depends on the surface treatment applied to the composite. The highest strength is obtained for the composite treated by plasma. One of the reasons is the higher wettability of the adhesives on these surfaces. Although the surface energy of grit blasted adherend is not significantly modified, the measured lap shear strength is quite high. This must be related to the increase of roughness generated. It is worth noting that the failure mode of these joints, the adherends of which were treated by grit-blasting, was totally cohesive in the substrate. This means that the strength of the composite adherends is lower than the adhesive strength. Peel ply treatment gives low values of lap shear strength. It has been reported [4] that peel ply treatment based on polyester tissue leads to a decrease of mechanical performance, mainly as a consequence of a decrease of adhesion between the adhesive and the adherend due to the contamination with silicone.

The mechanisms of failure were studied in depth by SEM. Figure 6 shows some micrographs of the fracture surface of failed joints, the

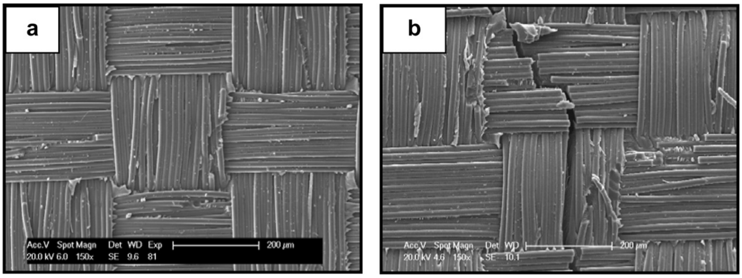

FIGURE 6 SEM micrographs of the fracture surface of tested joints with peel ply treated adherends (failure mode: adhesive at the interface): (a) non-modified epoxy adhesive and (b) epoxy adhesive reinforced with 0.5 wt% CNFs. The scale marker is 200 μm in both.

adherends of which were treated by peel ply. The shown surface corresponds to the face of the substrate where the adhesive remains. It is observed that in both cases the adhesive copies the peel ply texture of the adherend. Despite the fact that the measured values of lap shear strength are similar, the fracture surfaces generated by the neat epoxy adhesive and the reinforced ones present some differences. While the surface of the non-reinforced adhesive scarcely shows deformation (Fig. 6a), the surfaces of the epoxy adhesives reinforced with CNFs present long cracks on the peel ply texture (Fig. 6b) and even micro-scale zones of cohesive failure (small pieces of pulled out epoxy matrix of the laminates). This could indicate higher adhesion ability of the reinforced adhesives.

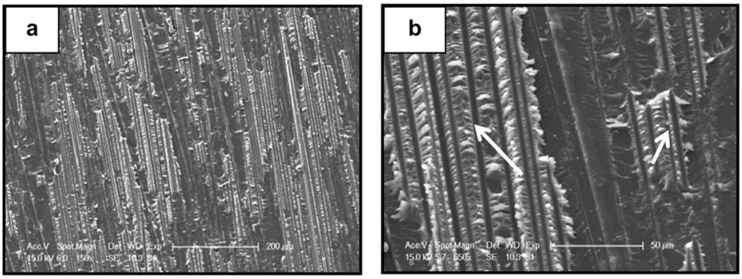

FIGURE 7 SEM micrographs at relatively low magnifications (<1000×) of the fracture surface of joints whose adherends were treated by plasma and whose adhesive was epoxy resin reinforced with 0.5 wt% CNFs. The failure mode was mixed adhesive and cohesive (in the composite). The scale marker in a = 200 μm and b = 50 μm.

SEM images of broken surfaces obtained from plasma treated adhesive joints (Fig. 7) show a mixed failure mode adhesive–cohesive. The cohesive failure happened in the composite adherend and it is marked with white narrows in Fig. 7b.

Figure 8 shows some micrographs obtained at higher magnification for fracture surfaces of epoxy adhesive reinforced with 0.5 wt% CNFs, whose adherends were treated by plasma. Figures 8a and 8b correspond to the cohesive failure zones while Figs. 8c and 8d show the adhesive failure zones. This detailed study of fracture surfaces shows some interesting points. The cohesive failure zone (Figs. 8a and 8b) in the composite adherend can be distinguished by the presence of the fiber imprints [24]. Within the imprints of the carbon fibers, it is possible to observe striations, which are the bright bands. These striations, running along the fiber axis, correspond to the characteristic surface roughness of PAN-based carbon fibers (intermediate modulus, IM7) used to manufacture the laminate. These marks on the epoxy matrix of the composite are generated during the test and provide a clear indication of the adhesive

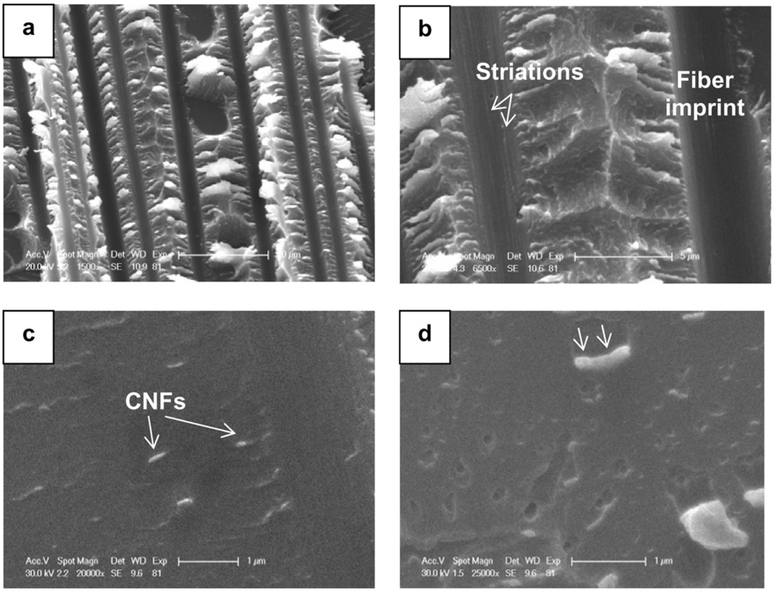

FIGURE 8 SEM micrographs at high magnifications (1500–25000×) of joints whose adherends were treated by plasma (failure mode: mixed adhesive-cohesive) and whose adhesive was epoxy resin reinforced with 0.5 wt% CNFs. Cohesive failure zones (a and b) and adhesive failure zones (c and d). The scale marker in a = 20 µm, b = 5 µm, c = 1 µm, and d = 1 µm.

shear failure mode at the matrix/fiber interface. The presence of shear forces at the crack tip causes the delamination of the interface, sliding the fiber surface over the matrix. It is known that the fracture energy in Mode II is higher than in Mode I for thermosetting carbon fiber/epoxy composites [25]. On the other hand, the epoxy matrix of the composite present the typical pattern of shear cusps or *hackles* (Fig. 8b) characteristic of Mode II shear failure observed by other authors both in epoxy carbon fiber laminates [26] and in adhesively bonded CFRP joints [27] during shear testing. The cusps are oriented perpendicular to the fibers, bent over along them with a width approximately equal to the distance between the fibers. Figures 8c and 8d correspond to the adhesive failure zone. In particular, they are SEM micrographs at very high magnifications of the face with nanoreinforced epoxy adhesive. In the adhesive surface, the characteristic pattern of shear cusps is also observed. Contrary to the case of the neat epoxy adhesive, where damage is characterized by the presence of small and poorly developed shear cusps, well developed and plastically deformed shear cusps were observed in the case of the nanoreinforced epoxy adhesive. A higher proportion of river markings and microflow was also found on cusp surfaces formed from Mode II crack propagation across the nanoreinforced adhesive. Observation at higher magnification showed the role played by CNFs in the crack propagation and final formation of shear cusps. Small voids with sizes in the range of the nanofiber diameters found on surfaces of the cusps could show the participation of these carbon nanofibers in pull-out mechanisms from the adhesive matrix. The shear sliding of those CNFs oriented on the fracture plane (white arrows in Fig. 8d) favour the matrix deformation in Mode II.

Figure 9a shows the fracture surface of the joints whose adherends were treated by grit blasting. The texture and morphology is radically different from that observed for the joints with other surface treatments. The failure occurred mainly cohesively in the first ply of the laminate. It seems that the first layer of polymer matrix was pulled out leaving marks of long carbon fibers of the laminate. The diameter of these marks was measured and a value of 4–6 μm was obtained, which agrees with the diameter of the long carbon fibers of the laminate used. This failure mechanism is called light-fiber-tear failure (LFT), according to the classification of failure modes published in the ASTM D5573 standard. This failure (Fig. 9b) is characterized by the crack propagation through the epoxy matrix of the composite. Some single fibers were also seen on the fracture surface rather than completely pulled-out fiber bundles. The fibers were usually covered with little resin remains. This is a clear difference from the joints treated with plasma, where the surface of these fibers was smoother. Shear cusps are relatively

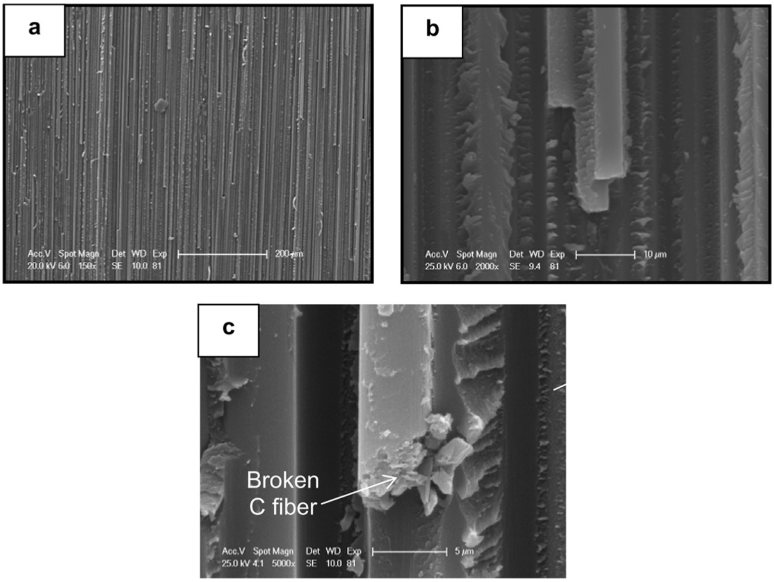

FIGURE 9 SEM micrographs of fracture surfaces of grit blasted joints which failure mode was cohesive in the substrate. The scale marker in a = 200 µm, b = 10 µm, and c = 5 µm.

common but they are quite small and less defined than those observed in plasma treated specimens. At high magnification (Fig. 9c), it can be seen that most of the adhered carbon fibers are broken. The origin of this failure could be the applied surface treatment. It is known [2] that grit blasting can cause damage to the composite, breaking carbon fibers even at low blast pressure and short treatment time. The effect of the incorporation of nanoreinforcement in the adhesive is less clear than in previous cases. The damage caused in the laminate by the grit blasting is the dominant factor which controls the shear strength and toughness of the adhesive joints. Although surface roughness generated by the treatment improves the bond with all the tested adhesives (neat and nanoreinforced epoxy) in relation to peel-ply treatment, no significant differences were observed among them.

4. CONCLUSIONS

The modification of an epoxy adhesive by the addition of different contents of CNFs was studied. Carbon fiber/epoxy composite adherends were used. Three surface treatments were applied: peel ply, grit blasting, and plasma. The treated surfaces of composites were characterised by SEM, EDS, and measurements of contact angle and surface energy. On the other hand, the curing process of adhesives was studied by DSC, analysing the effect of the addition of carbon nanofibers. Finally, the strength of the studied joints was determined by lap shear tests and the fracture surfaces were analysed by SEM.

The curing temperature increases with the addition of CNFs while the epoxy conversion remains high. The addition of nanoreinforcements causes a decrease of contact angle over the laminates indicating a higher wettability. However, high carbon nanofibers contents increase it up to the values obtained for neat epoxy resin. In spite of these differences, the lap shear strength is not influenced by the addition of nanoreinforcement to the epoxy adhesive.

The applied surface treatments modify the surface energy of the adherends. Atmospheric plasma treatment induces an important increase of the surface energy which is explained by the presence of polar elements in the surface, increasing its polar component. Peel ply and grit blasting treatments scarcely affect the total energy but they induce an increase of the dispersive energy component.

It was shown that the surface treatment applied to adherends has a great influence on the failure mode and the fracture mechanisms. That is why they give different joint strengths. Between the applied treatments, plasma is the one which gives the highest strength while peel ply provides the lowest values.

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