

CARBON NANOFIBERS REINFORCED ADHESIVES FOR JOINING CARBON FIBER EPOXY COMPOSITES

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ABSTRACT

The modification of epoxy adhesive by the introduction of very low amounts of carbon nanofibers (CNFs) has been studied. Carbon fiber/epoxy composites were used as adherends, applying different surface treatments, such as grit blasting, peel-ply and plasma. The curing reaction of nanoreinforced adhesives was studied by DSC, founding that the addition of CNFs causes a shift at higher temperatures, due to the absorption of crosslinker molecules although the final reached conversion follows being high. The wettability was determined by the measurements of contact angle. Plasma treatment widely increases the wettability, decreasing the contact angle in half. Therefore the measured lap shear strength is much higher with regard to peel ply substrates. Although grit blasting treatment scarcely modifies the wettability, the adhesive strength with grit blasted adherends is so high, due to the increase of the roughness. The addition of CNFs on the epoxy adhesive causes the decrease of contact angle. However the contact angle of nanoreinforced epoxy adhesive decreases with the increase of CNFs content. Not great differences are observed in the adhesive strength with the CNF addition due to the presence of defects generating by the evaporation of dispersion solvent during the thermal curing treatment of the adhesive.

1. INTRODUCTION

Nowadays composite materials are used in many industries fields because of their high specific mechanical strength and stiffness and high corrosion resistance. These characteristics make them suitable for structural applications such as aircraft, automobiles, space and marine vehicles and any application which requires a high degree of performance [1,2].

Ideally, a composite structure would not contain any joints and should be manufactured as one monolithic entity because the joint is a source of weakness. Also, the bonding process is usually less efficient and more expensive. However, limitations of size of design on structures hinder the manufacturing of the structure without any joints. In fact, the majority of composite structure is manufactured by smaller components which are later assembled.

The join of composites can be carried out through classical mechanical techniques, such as bolting, riveting or screwing. Unfortunately, such techniques can drastically increase the global weight of composite assemblies [1]. Mechanical joint involves the use of screws, pins, rivets and/or bolts. Its main limitation is the presence of localized stresses induced by fasteners, which can cause delamination, matrix crazing and fibre failure. The necessary holes in the composite may cut fibres, decreasing the strength of the material. In contrast, this kind of joint does not require surface preparation of adherends and its disassembly is easy, without incurring significant damage.

The adhesive joint minimizes stress concentrations, distributing the load over the overlap area. It does not require holes and has higher fatigue resistance. Also, adhesive bonding reduces the weight of the structure and usually present lower cost for large

area joints. However, the adhesive joint requires careful surface preparation of the adherends in order to get a strong and durable joint. The surface treatments mainly aim to improve specific parameters, such as roughness, chemical modification, surface free energy, etc [1]. The objective is to modify the chemistry and/or morphology of a thin surface layer without affecting the bulk properties. There are numerous kinds of surface treatments for composite materials but their effectiveness depends upon the specific substrate nature, the geometry of joints, the extent of the treatment and the requirements during its service. There is not an unique ideal surface treatment, all present advantages and disadvantages.

Owing to its low cost and ease to use, peel ply treatment is one of the most widely spread surface treatments in the composite industry. Peel ply treatment consists in a single ply placed on one side of composite material prior to 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 removing leads to a rough surface, which is the negative of the peel ply used, increasing the surface free energy. One of the main problems is the transference of contaminations by silicones [3]. This contamination is most serious when the peel ply has polyester nature [1].

Plasma surface treatment is other common technique for composite adherends. In the plasma process, the surface is exposed to ionized gases, usually generated by radio frequency energy in air or a low pressure chamber. The plasma contains a high concentration of reactive species, such as ions and electrons, which interact with the surface and cause chemical and texture changes. 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.

Some surface treatments act through surface roughness, such as the grit-blasting, affecting the wetting of the composite. This treatment modifies the surface morphology and removes some surface contamination. It has been found that grit-blasting can cause visible fibre damage in the composite at even low blast pressures and short treatment times. The abrasion can carry out with alumina or silicon carbide [3].

The strength of the joint strongly depends on the surface treatment applied but also on the adhesive nature. The most used adhesives to joint epoxy reinforced carbon fibre composites are epoxy resins. They present high adhesive strength, good fatigue strength and high thermal and chemical resistance. Their main limitations are their low toughness and poor electrical conductivity [4]. Numerous researches [5-8] have been recently reported about the use of carbon nanotubes (CNTs) or carbon nanofibers (CNFs) as reinforcement of glassy polymeric materials. The addition of these nanoreinforcements in a very low percentage causes the enhancement of the mechanical and electrical properties of epoxy resins in spite of a good dispersion has not been obtained yet. CNTs present better properties than CNFs, due to its novel forms of crystalline carbon structure that consists of tiny concentric grapheme cylinders. However, CNFs are much cheaper, due its manufacturing process by vapor phase grown. Taking into account the studied application as adhesives, we have studied the use of CNFs as nanoreinforcements of epoxy resins. The main problem of this reinforcement is that CNFs tend to agglomerate, decreasing the mechanical properties of the nanoreinforced polymer. It is necessary the application of careful procedures of dispersion, which usually implies several stirring techniques, such as magnetic stirring, high shear mixing and sonication.

In this work, we analysed the viability of using epoxy resins reinforced with CNFs as adhesives for epoxy/carbon fibre laminates. Different surface treatments of laminates have been evaluated. The effect of nanoreinforcement content on the curing process of the adhesive was studied by differential scanning calorimetry (DSC). Finally, the adhesive strength was measured by lap shear test.

2. EXPERIMENTAL

2.1 Materials

The epoxy/carbon fiber laminates used as adherends were manufactured by *Instituto Nacional de Técnica Aeroespacial* (INTA, Spanish institute). The unidirectional carbon fiber laminate ([0]₁₀) used had a fiber volume fraction of 33%.

As adhesive, a basic formulation of epoxy resin was used. The epoxy monomer was diglycidyl ether of bisphenol A (DGEBA), supplied by Sigma-Aldrich with 178 g / epoxy equivalent. As curing agent, 4,4'-methylenedianiline (DDM) was used, purchased from *Sigma Aldrich*.

CNFs were added as reinforcement of epoxy adhesive. They were prepared by chemical vapour deposition (provided by *Grupo Antolin*, Spanish company) with diameters ranging from 20 to 47 nm and an average length of 35 μm . The morphology of nanoreinforcements was analyzed by transmission electron microscopy (TEM), founding that CNFs are basically constituted by "platelet-like" or "fishbone" nanofibers, in which the CNFs have a helical disposition.

Nanoreinforced epoxy resins were prepared by diluted method [9,10], 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 is prepared. In order to break nanoreinforcements sheets into tiny bundles, the obtained suspension was stirred at 40°C for 30 min. Next, the epoxy precursor is added. DGEBA was mixed with the nanofibers suspension and subjected to high shear mixing (150 rpm) for 30 min at 40 °C. The resultant solution was then sonicated using a 50-60 Hz sonicator for 45 min at 40 °C. Then the solvent is slowly evaporated with continuous stirring at 90°C during 24 h. A stoichiometric amount of DDM was added into the epoxy/CNF mixture, followed by stirring at 130°C to dissolve the hardener. The applied curing treatment consisted on a heating at 150 °C during 3 hours and then a postcuring process of 180 °C for 1h. CNFs were added in different percentages: 0.25, 0.5 and 1 wt % regard with epoxy mass. As a reference sample, the neat epoxy resin was also prepared, mixing DGEBA and DDM at 130°C several minutes and then applying the same curing and postcuring treatment, 150°C for 3h and 180 °C for 1h.

2.2 Surface pretreatment

Some laminates were supplied with a peel ply layer, which was removed by hand. Then the surface was cleaned with acetone and dried with nitrogen. The weave of polyester peel ply fabric was observed by scanning electron microscopy (SEM). It is constituted by a web of fibers interweaved, whose diameter is around 15 μm . Groups of 20 fibers are interlaced forming square domains of 0.022 mm².

Grit blasting was carried out in a *Guyson (mod. Jetstream 22)* 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 was carried out at 615 W of power. Plasma treatment was applied with rotary nozzle, which generates a conic beam. Only one pass were made at a distance of 7 mm and at a speed of 1.2 m/min.

2.3 Characterization

The curing process of the different epoxy/CNFs mixtures was analyzed by DSC. DSC measurements were carried out in a *Setaram (Setsys 16/18)* 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 (p/n 200-F1)* contact angle goniometer equipped with a camera and video monitor. Different wetting liquids, water and glycerol, were utilized to obtain the surface free energy [2]. Also, the contact angle of non-cured neat epoxy resin and 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 is the average value of ten measurements, at left and right sides, of two drops for each liquid.

The joining strength was determined by single lap shear test according to ASTM D5868. The thickness of the adhesive was 0.7 mm, and the lap shear overlap was 25x25 mm^2 .

3. RESULTS

3.1 Curing reaction

Figure 1 shows the curing thermograms obtained by DSC in scanning mode for stoichiometric mixtures of DGEBA/DDM with different CNFs contents. All the curves only present one peak at high temperature, in the range of 175 – 185 °C, which corresponds to the curing reaction between oxirane rings of DGEBA with aromatic amine groups of DDM.

The temperature of peak maximum depends on the CNFs contents: 175 °C for neat DGEBA/DDM mixture and 181, 178 and 185 °C for the mixtures with 0.25, 0.5 and 1.0 wt % CNFs, respectively. Therefore, the reaction temperature is increased by the addition of CNFs, meaning that the nanoreinforcements hinder the curing process. It is worthy to stand out that the nano-scale size of CNFs, whose average diameter is around 30 nm. This implies that the small DDM molecules could introduce inside of nanofiber. However, the size of DGEBA molecule is higher, making more difficult its absorption. The selective absorption of crosslinker molecules hinders the advance of curing reaction, shifting the peak at higher temperatures.

The reaction enthalpies measured as the integrated peaks area are 92.3, 91.0, 99.9 and 97.3 kJ/epoxy equivalent for the mixtures with 0, 0.25, 0.5 and 1 wt % CNFs, respectively. Taking into account that the theoretical value of the reaction enthalpy for epoxy/amine reaction is 100 kJ per epoxy equivalent [11], the reached conversion for all samples is very high.

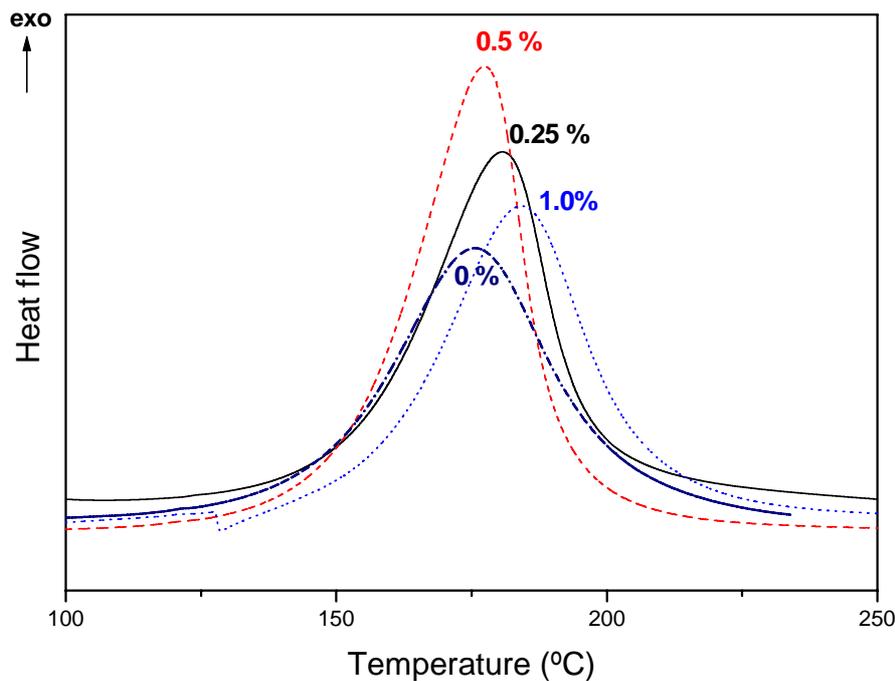


Figure 1: DSC thermograms (first scan) of DGEBA/DDM mixtures with different CNFs contents: 0, 0.25, 0.5 and 1 wt %.

The reaction enthalpy of the samples with high CNFs contents (0.5 and 1 wt %) is higher than the one of neat epoxy resin. In previous works [12,13], it was demonstrated the appearance of large CNF agglomerations in resins with nanoreinforcement contents higher than 0.5 wt %. The worse dispersion obtained for these samples hinders the DDM absorption and therefore enhances the curing reaction.

3.2. Wetting

The contact angle was measured for the epoxy/carbon fiber laminate adherends with different liquids, between them the used epoxy adhesives. The table 1 collects these results. A lower value of contact angle implies higher wettability. For all studied liquids, the highest value of contact angle was measured for the as received adherend, without any treatment, justifying the necessity of surface pretreatment.

The grit blasting treatment lightly enhances the wettability, indicating that it is not appropriated technique for the surface treatment of epoxy/carbon nanofibers laminates, in spite of being the most common treatment for metal adherends [14] due to its simplicity, low cost and the good results contributed. Peel ply treatment neither significantly affect to contact angle of the studied liquids. In spite of it, it is a surface treatment widely used in composites adherends due to its high simplicity.

Plasma treatment enhances the wettability of adherend due to significant changes in surface chemistry [2]. On the other hand, the contact angle of the studied adhesive is low compared with water or glycerol but it is a similar value of the other commercial epoxy adhesives [1, 2]. The contact angle markedly decreases with the addition of CNFs. This is explained by the nano-scale size of the nanofiber and the higher chemical compatibility between epoxy/carbon fiber composite and nanoreinforced epoxy adhesive. However, the increase of CNFs content causes a light increase of contact angle although the measured value is always lower than one of neat epoxy adhesive.

This increase is justified by the presence of agglomerations at high CNFs contents which increase its effective size.

Table 1. Contact angles for surface pretreated laminates with different liquids: water, glycerol, neat epoxy adhesive (0%) and epoxy adhesive reinforced with 0.25, 0.5 and 1 wt % CNFs.

Treatment	Water	Glycerol	0 %	0.25 %	0.5 %	1.0%
As-received	70.53 ± 0.05	73.06 ± 0.05	50.90 ± 0.03	40.70 ± 0.20	38.47 ± 0.07	42.27 ± 0.07
Grit blasting	73.14 ± 0.07	64.90 ± 0.30	41.00 ± 0.50	28.20 ± 0.30	31.20 ± 0.60	41.60 ± 0.10
Peel ply	76.20 ± 0.10	66.84 ± 0.05	34.10 ± 0.40	32.09 ± 0.06	39.50 ± 0.10	36.70 ± 0.20
Plasma	35.88 ± 0.06	39.18 ± 0.06	42.63 ± 0.05	35.30 ± 0.10	41.10 ± 1.50	47.70 ± 0.90

Table 2 shows the dispersive and polar components of the composite surface free energies calculated with the contact angle of water and glycerol by the method of Dynes and Kaelble [15]. The total surface energy is calculated from the sum of the dispersive component and the polar or non-dispersive component. The surface energy of non-treated adherend is low (38 mJ/m²). Dynes and Kaelble reported values of surface energy for various graphitic and carbon materials ranging from 37 to 58 mJ/m².

Except to plasma, the surface energy is not modified by the surface pretreatments applied. The plasma treatment doubles the value of total surface energy. This increase is mainly generated by the increase of polar energy component, indicating an augment of polar element concentration in the surface of the adherend. This is explained because of the atmospheric plasma treatment increases the concentration of oxygen and nitrogen at the surface [2].

Table 2. Surface energies (in mJ m⁻²) of epoxy/carbon fiber laminates

	γ_s^D	γ_s^P	γ_s
As-received	5.63 ± 0.01	32.35 ± 0.02	37.98 ± 0.01
Grit blasting	14.94 ± 0.11	20.48 ± 0.08	35.42 ± 0.03
Peel ply	15.77 ± 0.03	18.13 ± 0.04	33.90 ± 0.01
Plasma	13.57 ± 0.01	47.47 ± 0.01	61.04 ± 0.01

γ_s^D = dispersive component of surface energy

γ_s^P = polar component of surface energy

γ_s = surface energy, obtained via Kaelble's approach, $\gamma_s = \gamma_s^P + \gamma_s^D$

3.3. Lap shear strength

The adhesive strength of neat epoxy and nanoreinforced resins was determined by single lap shear test following ASTM D5868 standard, using the epoxy/carbon fiber laminate adherends treated by plasma, grit-blasting and peel-ply. Figure 2 shows the obtained results. The main observed result is that the addition of CNFs scarcely affects to adhesive strength. However it was determined that the wettability of the adhesive is enhanced with the presence of CNFs. This is associated to the presence of defects on the nanoreinforced adhesives. The broken surface of the nanoreinforced adhesives presented numerous microscopic voids, independently the CNFs content. However,

these defects were not appreciated in the surface of neat epoxy adhesive. This porosity is associated to the evaporation of chloroform, used in the dispersion of carbon nanofibers, during the thermal curing treatment applied to the adhesive, which does not rightly remove before.

The measured lap shear strength strongly depends on the surface treatment applied to the adherend. The highest strength is obtained for the composite treated by plasma. This is explained by the low value measured of contact angle between adhesive and substrate. Although the free energy of grit blasted adherend is not significant modified, the measured adhesive strength is so high. This must be related to the increase of roughness generated. Peel ply treatment gives low values of lap shear strength, due to the low wettability of the adhesives over these surfaces. Also, peel ply treatment based on polyester tissue leads to a decrease of mechanical performance, mainly as the consequence of a decrease of chemical adhesion between the adhesive and adherent due to the contamination with silicone [1].

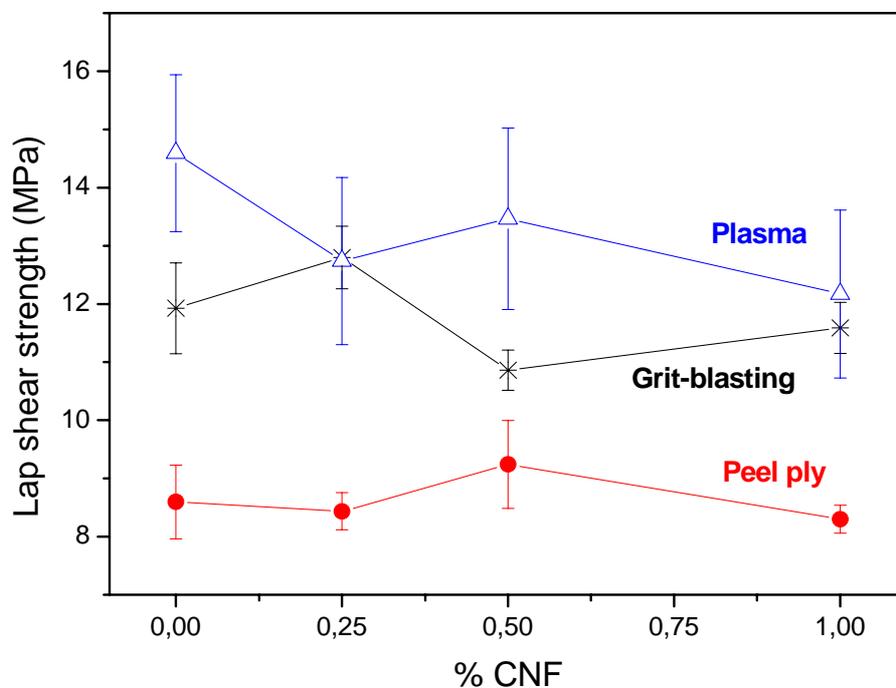


Figure 2: Single lap shear strength of epoxy resins reinforced with different CNFs contents (0, 0.25, 0.5 and 1 wt %) and composite adherends treated with different surface treatments: plasma, peel-ply and grit-blasting

4. CONCLUSIONS

The modification of epoxy adhesive by the addition of different content of CNFs has been studied. As adherend, epoxy/carbon fiber composite was used. The curing temperature is increased by the presence of CNFs while the reached epoxy conversion remains so high. The addition of nanoreinforcements scarcely affects to the contact angle, which lightly increases with the CNFs content. Therefore the adhesive strength is not affected with the CNFs addition.

The applied surface treatment modifies the surface energy of the adherend and therefore the adhesive strength measured. Atmospheric plasma treatment causes an important decrease of the contact angle of the adhesive and a high increase of adhesive strength. This is explained by the presence of polar elements in the surface, which increase the polar surface energy component. Grit blasting treatment also gives high lap shear strengths while peel ply is the worst surface treatment applied.

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