International Journal of Adhesion & Adhesives 62 (2015) 139–145

Contents lists available at ScienceDirect

International Journal of Adhesion & Adhesives

journal homepage: www.elsevier.com/locate/ijadhadh

Toughening effect of carbon nanotubes and carbon nanofibres in epoxy adhesives for joining carbon fibre laminates

María R. Gude [a,*], Silvia G. Prolongo [b], Alejandro Ureña [b]

[a] Foundation for the Research, Development and Application of Composite Materials (FIDAMC), Avda. Rita Levi-Montalcini 29, Getafe, 28906 Madrid, Spain
[b] Department of Materials Science and Engineering, University Rey Juan Carlos, ESCET, c/Tulipán s/n, Móstoles, 28933 Madrid, Spain

ARTICLE INFO

Article history:
Accepted 21 July 2015
Available online 30 July 2015

Keywords:
Carbon nanotubes
Epoxides
Surface treatment
Fracture toughness
Carbon nanofibres
Scanning electron microscopy (SEM)

ABSTRACT

The effect of carbon nanotubes (CNTs) and carbon nanofibres (CNFs) on mode I adhesive fracture energy (G_{IC}) of double cantilever beam (DCB) joints of carbon fibre-reinforced laminates bonded with an epoxy adhesive has been studied. It was observed that the presence of carbon nanofillers in the epoxy adhesive results in a significant increase in the propagation value of mode I adhesive fracture energy with CNTs producing the largest increase. The toughening mechanisms, analysed using scanning electron microscopy (SEM), for the two nanofiller systems differed: pull-out with CNFs, and pull-out and crack bridging with CNTs. At the macroscopic level there was also a change in the failure mode, with an increased proportion of delamination occurring in the nanoreinforced joints in comparison with the unreinforced. Two different surface treatments were also applied to the laminates: grit blasting and atmospheric plasma. The highest fracture energy was obtained in the grit blasted joints.

1. Introduction

The addition of carbon nanotubes (CNT) to epoxy resins for the improvement of their mechanical, thermal and electrical properties has been widely researched in the past decade [1–6]. Among other applications, epoxy resins are often used as adhesives for joining different types of materials. It was reported that the addition of carbon nanotubes to epoxy adhesives can improve the lap shear strength of adhesive joints [7–9], but the most significant improvement is obtained in the electrical conductivity of these adhesives [10–13]. Carbon nanofibres (CNF) are a different type of carbon nanofillers. They present lower Young's modulus and tensile strength than carbon nanotubes but are less expensive [14] and can also improve the mechanical and electrical behaviour of epoxy resins [15,16] when added in lower contents than conventional microfillers, such as aluminium oxide, silicon oxide, copper or silver particles. The content of these microfillers can be up to 30 wt%, while the maximum content of nanometric fillers does not usually exceeds 5 wt%.

The presence of CNTs or CNFs can originate new micromechanisms of energy dissipation, increasing the fracture toughness of epoxy resins. Some of the toughening mechanisms reported for epoxy resins with nano-scaled reinforcements are inelastic matrix deformation and void nucleation, interfacial debonding, pull-out, crack bridging, crack deflection, crack pinning and plastic void growth around debonded CNTs [6,17–21]. However, it is not easy to find references in the literature about the toughening effect of carbon nanofibres or nanotubes in epoxy resins used for adhesive bonding [12]. Yu et al. [22] published a study of the CNT effect on the bonding strength and durability of the joints. The CNT addition into the adhesive induces a significant increase of the adhesive strength and fracture toughness, especially after immersion into water at high temperature in comparison with neat epoxy joint. On the other hand, recently Sydlik et al. [23] published the effect of the different chemical treatments applied over the surface of multi-walled CNT on the adhesive properties. They found that the enhancement of lap shear strength is higher when CNTs are functionalized, revealing that the fracture surface morphology change with the incorporation of functionalized CNTs. A deflection of the crack fronts at the site of embedded CNTs, as the mechanism accounting for increased adhesive strength.

This paper is the last of a series about the development of nanoreinforced epoxy adhesives for joining carbon fibre/epoxy laminates. In previous works we have published the effect of different surface treatment of these substrates (peel ply, grit blasting and atmospheric plasma treatment), analysing their surface properties [24] and the effect on the shear strength in dry [25] and hot/wet conditions [26]. We have also evaluated the correlation between surface properties and the mechanical properties and failure mode of the adhesive joints [27]. It was proved that the plasma treatment of carbon fibre/epoxy laminates provides the highest lap shear strength, among the surface treatments

* Corresponding author. Tel.: +34 916007772; fax: +34 916244639.
E-mail address: Maria.R.Rodriguez@fidamc.es (M.R. Gude).

http://dx.doi.org/10.1016/j.ijadhadh.2015.07.011
0143-7496/

evaluated, because of the important increase in the surface free energy of the laminates. The highest mode I adhesive fracture energy was obtained with grit blasted substrates, due to the high density of summits and mean summit curvature. In fact, it was concluded that the main adhesion mechanisms in the single lap joints (shear testing, mode II) are likely those influenced by the chemical composition of the surface (absorption and chemical bonding), while mechanical interlocking predominates in the double cantilever beam joints (mode I testing) [27]. Among the different surface treatments of the substrates that have been analysed, the joints with peel ply-treated laminates exhibit the best ageing behaviour. As it was explained elsewhere, they experience an increase in the strength of the joints from the dry to the hygrothermal-aged condition [26].

On the other hand, we have also found that the addition of carbon nanofibres (CNFs) or carbon nanotubes (CNTs) to the epoxy adhesive used for bonding the laminates has a less noteworthy influence on the shear strength and durability under hot/wet conditions than the surface treatment applied to these laminates. In fact, the lap shear strength (LSS) is not significantly affected by the addition of carbon nanotubes [14] or carbon nanofibres [25]. In the adhesive systems evaluated, these nanofillers generally do not influence the variation of LSS after hygrothermal ageing. But in the joints with grit blasted laminates, they improve or maintain the joint strength after hygrothermal ageing [26].

Concerning the mode I adhesive fracture energy, the effect of modifying the epoxy adhesive with carbon nanofillers was only analysed in peel ply-treated joints [26]. The fracture energy was increased with the nanoreinforced adhesives due to the appearance of new mechanisms of energy dissipation.

In this work, the influence of surface treatment of the substrates and the addition of carbon nanofillers to the adhesive on the mode I adhesive fracture energy and failure mode of the adhesive joint of carbon fibre/epoxy laminates with epoxy adhesive is analysed. The values of G_{IC} have been calculated and the fracture surfaces have been analysed. The surface treatments applied were grit blasting and atmospheric plasma. Based on previous results, the CNF content selected was 0.5 wt% with respect to the epoxy precursor (diglycidyl ether of bisphenol A, DGEBA) [14,25]. In the case of CNTs, only 0.25 wt% with respect to DGEBA was added because of their greater effect on the viscosity due to their high specific surface area [29]. In particular, at 45 °C the addition of 0.5 wt% CNFs doubles the viscosity of the DGEBA, while the same content of CNTs increases the viscosity by 15. Moreover, the selected nanofiller contents provided the highest values of lap shear strength in a previous study performed with different surface treatments of the substrates [14,25].

The results obtained have been compared to those obtained with the peel ply treatment [28].

2. Experimental

2.1. Materials

The epoxy adhesive used is based on diglycidyl ether of bisphenol A (DGEBA), with 178 g/epoxy equivalent, cured with an stoichiometric amount of an aromatic amine (4,4′-diaminodiphenylmethane, DDM). This adhesive was modified with the addition of carbon nanofibres (CNF) and carbon nanotubes (CNT). The carbon nanofibres have been produced by produced by Grupo Antolin by chemical vapour deposition. Two main types of CNFs have been identified: platelet and cup-stacked. Their diameter ranges from 10 to 100 nm. An in-depth characterisation of these carbon nanofibres has been published elsewhere [30]. The multiwalled carbon nanotubes have a diameter smaller than 10 nm and length shorter than 1 μm, and they are amino-functionalized.

For the adhesive joints, unidirectional carbon fibre/epoxy laminates were used as substrates. These laminates were manufactured by the Instituto Nacional de Técnica Aeroespacial (INTA, Spain) using unidirectional prepregs (Hexply 8552/33%/268/IM7-12K, supplied by Hexcel). The fibre volume fraction of the composite is 57%. The curing was performed in an autoclave with vacuum bag at 180 °C for 2 h at a pressure of 6 bar. A caul plate was used during the curing process in autoclave to provide a smooth surface on the laminate.

2.2. Manufacturing of the nanoreinforced adhesives

The procedure applied for manufacturing the nanoreinforced adhesives was published in previous works [28,31]. For the dispersion of the nanofillers in the adhesive, they were first dispersed in chloroform. Then, DGEBA was added and mixed by ultrasonication. The hardener DDM was added after evaporating the solvent. The curing process for the neat and reinforced adhesives was performed in two steps: 3 h at 150 °C and then 1 h at 180 °C. The content of CNFs and CNTs in the nanoreinforced adhesives was 0.5 and 0.25 wt% respectively with respect to the mass of DGEBA.

2.3. Surface treatment of the substrates

Dry grit blasting (GB) was performed by hand using a Guyson (mod. Jetstream 22, North Yorkshire, England) grit blaster with 220 grit alumina (diameter in the range of 60–70 μm). Three passes were performed with the gun at an angle of approximately 45° and a distance of 10–15 cm from the surface of the composite. The grit blasted surfaces were then cleaned with acetone and compressed air to remove the alumina particles that remained on the surface after the treatment.

The atmospheric plasma treatment (PL) was performed using a plasma system supplied by PlasmaTreat (Elgin, IL, USA). A rotary nozzle was used, generating a conical beam. The samples were placed on a moving platform (1.2 m/min) in such a way that the distance between the surface of the laminate and the plasma nozzle was 7 mm. The treatment power was 615 W. Only one pass was made because the diameter of the plasma beam is the same as the width of the laminate substrate (25 mm). The substrates were cleaned with acetone prior to plasma treatment. Samples were bonded within the 72 h of plasma treatment. During this time, they have been wrapped in aluminium foil and stored at room temperature.

For the peel ply treatment, a dry polyester peel ply (Release Ply C, Airtech) was placed over the last prepreg layer of the laminate before curing. This ply was removed just before bonding, to generate a rough surface free of contamination.

2.4. Characterisation

Double cantilever beam (DCB) tests were performed to determine the mode I adhesive fracture energy of the adhesives joints, following the ISO 25217:2009 standard (Fig. 1). The substrates were 150 mm long, 25 mm wide and 3.3 mm thick. The thickness of the adhesive layer was 0.4 mm. A 75 μm thick polyethylene terephthalate (PTFE) film was inserted at one end of the specimen to act as a crack initiator. To perform the test, a pre-crack was generated from the nonadhesive insert, and then the DCB test was performed. To facilitate the detection of crack growth, one edge of the sample was coated with a thin layer of typewriter correction fluid. In the DCB test, the load was applied to the specimens at a constant cross-head rate of 1 mm/min. The measured displacement, δ, was corrected with the system compliance. Five specimens were tested for each combination of adhesive