Influence of the modification with MWCNT on the interlaminar fracture properties of long carbon fiber composites

Faustino Mujika, Gustavo Vargas, Julen Ibarretxe, Juan de Gracia, Ainhoa Arrese

Materials+Technologies Group, Department of Mechanical Engineering , University of the Basque Country(UPV/EHU)

Polytechnic School, Plaza Europa, 1, 20018 San Sebastian, Spain

ABSTRACT

This paper reports the processing of a carbon fiber reinforced epoxy composite with carbon nanotube integration and examines the potential improvement on the interlaminar toughness. Carbon nanotube enhanced composites were fabricated by spreading a solution of reinforcing nanoparticles between prepreg layers with the aid of an airbrush. The influence of MWCNTs incorporation has been studied by the End Notched Flexure (ENF) test by means of a new test methodology named “Beam Theory including Bending Rotation effects” (BTBR) proposed recently . This method allows the determination of the critical energy release rate at each point of the test when stable crack advance occurs, obtaining the R-curve. A maximum increase of 22% in initiation fracture toughness was observed in the samples with functionalized CNTs. Moreover, the propagation fracture toughness increased 14 %.

Keywords: A. Laminates; B. Fracture toughness; D. Mechanical Testing; R-curve

INTRODUCTION

In recent years a new generation of composite materials with reinforcements at nano-level has been extensively analysed. Owing to the exceptional properties provided by their aspect ratio, carbon nanotubes (CNT) have become one of the most studied types of reinforcement. However, although some breakthrough has been achieved, results of these studies are not satisfactory due to the wide range of factors determining the bonding between the matrix and the CNTs and hence, the stress transfer between them [1].

Some of the factors to be taken into account before using nanotubes as reinforcement are functionalization processes, alignment and dispersion. On the one hand, functionalization aims to minimize the aggregation tendency of CNTs by forming functional groups on their outer wall, thus increasing their solubility and facilitating a better interaction with other molecular species such as polymers [2,3]. On the other hand, alignment is a way to maximize an anisotropic property in the manufacture of a composite by conducting reinforcement in the desired direction, whereas a correct dispersion maximizes the effect of reinforcement both preventing the formation of aggregates of particles and distributing CNTs more efficiently.

Research is being done on a variety of methods to achieve uniform spreading of CNTs in different matrixes, including traditional techniques of powder mixing, such as the use of ball mills [4], calendering [5], ultrasonic dispersion [6], or other mechanical methods that involve kneading and extrusion [7].

The present work focuses on long carbon fiber laminates and the addition of multi wall carbon nanotubes (MWCNT) in the interlayer, since these materials have traditionally been known for their poor interlaminar mechanical properties. Several methods have been used to disperse the nanotubes in such composites. Although most of them involve initially mixing the polymer with nanoparticles for subsequent manufacture of prepregs [8], others are based on the growth of CNTs on carbon fibers themselves, which avoids carrying out dispersion [9,10]. Moreover, studies on the mechanical properties of laminates have been carried out, introducing a thin layer of nanotube reinforced matrix between two lamina [11].

The aim of this study is to improve the interlaminar toughness of a unidirectional composite by incorporating MWCNTs. A novel technique consisting in spreading a solution of reinforcing nanoparticles between the prepreg layers with the aid of an airbrush is presented.

The influence of MWCNTs incorporation has been studied by the End Notched Flexure (ENF) test by means of a new test methodology named “Beam Theory including Bending Rotations (BTBR) and proposed recently by Arrese et al. [12].

Usually the crack length in ENF tests is determined by optical measurements during the test, where it is very difficult to establish the difference between crack initiation and propagation. By the BTBR procedure the crack length determination is carried out at each point of the test, based on the variation of the compliance of the cracked specimen. The evolution of crack lenght is determined after testing the specimen by the load and displacement data provided by the testing machine. Therefore, this method allows the determination of the critical energy release rate at each point of the test when stable crack advance occurs, obtaining the curve that gives the toughness as a funcion of the crack length, named R-curve. Moreover, the difference between the initiation and the propagation of the crack is clearly appreciated in the R-curve. It is the first time that this methodology has been applied to the anlaysis of composites modified by CNTs.

EXPERIMENTAL WORK

Materials and apparatus

Carbon fiber (T300) / epoxy resin (F-593) prepregs kindly provided by Hexcel Composites were used to manufacture the laminates.

The volume-content of fiber in the prepregs was 50 %, which results in a longitudinal flexural modulus of around 100 GPa, and a shear modulus of around 4 GPa. The gel-time of the epoxy resin was determined by DMA to be close to 20 minutes at 120 ºC.

Twelve-layered unidirectional laminates ($[0]_{12}$) were prepared and tested. Some of the laminates were modified with MWCNT purchased from ARKEMA. As supplied by the manufacturer, the CNTs had diameters of 10–15 nm and lengths of 1–10 µm. The nanotubes were used as received or functionalized.

A universal testing machine MTS–Insight 10 with a load cell of 10 kN and standard test fixtures, was used to perform mechanical testing.

Preparation of the CNTS

Prior to using them for the modification of the laminates, the MWCNTs were dispersed in 50 ml of ethanol using a horn-sonicator working at 750 W, 20 kHz and 20% of amplitude for 30 minutes. The mass of nanofiller used corresponds to 0.1% of the mass of the matrix per laminate layer.

Afterwards, part of the MWCNTs were functionalized with carboxylic and alcohol groups. For this purpose, the nanotubes were oxidized in a solution composed of highly concentrated nitric and sulphuric acid, according to the method presented by Goyanes et al. [13], and Fernandez d'Arlas et al. [14].

Fabrication of modified laminates

The modification of the laminates was carried out by means of a simple manufacturing method: spraying a solvent dispersion of nanotubes. The spraying was performed using an airbrush A8-300, with a 0.2 mm exit diameter. It was applied between the two central layers of the laminate, i.e. at the central interlaminar plane, modifying only the interface between those two layers.

The solvent was evaporated before the prepegs were piled together. Then, the laminates were hot-pressed and cured according to the following procedure: Firstly, the non-cured laminate was introduced between two PTFE-covered copper plates in the hot-press and heated up to 120 ºC. The ensemble was maintained at that temperature for 35 minutes and thus the matrix cured beyond gelification. During this isothermal step, pressure was controlled in order to prevent excessive material flow towards the sides of the plates. Secondly, the laminate was compressed and heated up to a temperature of 180 ºC, at which it was kept for 2 hours. Finally, the laminate was slowly cooled down. When the temperature dropped below 60 ºC the pressure was removed and the laminate released from the copper plates.

Mechanical tests

In order to assess the effect of the modification of the laminates on the interlaminar strength, ENF measurements were performed considering the “Beam Theory including Bending Rotation effects” (BTBR) method presented by Arrese et al.

[12]. The BTBR method is a novel procedure that allows the determination of the mode II R-curve in ENF tests without optical determination of the crack tip position. The R-curve represents the energy release rate as a function of crack extension. For the calculation of the compliance and the energy release rate, this method takes into account shear, local deformation and bending rotation effects. Local deformation effects include the deformation of the specimen through the thickness under the application of the load and the compliance of the testing system.

For the laminates tested in the present work, the value of the stiffness constant accounting for the local deformation was 15900 N/mm. Prior to ENF measurements, the flexural modulus, E_F, of each specimen was independently determined, according to the method proposed by Mujika [15].

The nominal thickness and width of the specimens used in the ENF measurements were 2.1 mm and 15 mm respectively. The borders of the laminate were discarded for the preparation of the specimens. A span of 80 mm was chosen for the ENF measurements. In this way the span-to-thickness ratio was near 40, and shear effects could be considered negligible [12]. The initial crack length was around 32 mm, in order to obtain stable crack growth.

RESULTS AND DISCUSSION

Flexural properties

Results for flexural stiffness reveal that the modification of the laminates with MWCNT in the middle plane does not affect the flexural modulus. This was the expected behavior because the modified middle plane is the neutral plane of the laminate defined as the plane where the strain is zero.

Properties of Interlaminar fracture in mode II

The R-Curve of the unmodified material, considered as the reference material, is presented in Figure 1.

As mentioned previously, the solvent was used for two purposes: as a dispersive medium and as a liquid vehicle for spray application of the nanotubes. Once sprayed on one of the prepegs, the solvent could interact with the resin, affecting its curing behavior, possibly resulting in a detrimental effect on interlaminar fracture properties. Therefore, the influence of the solvent has been studied considering laminates modified only with sprayed solvent, i.e. without including carbon nanotubes. The considered solvent was ethanol. Figure 2 shows the R-Curve of laminates modified only with ethanol.

Figures 3 and 4 whow the R-Curves obtained for laminates modified with CNTs. Figure 3 corresponds to laminates with non-functionalized CNTs and Figure 4 corresponds to laminates with functionalized CNTs.

In all cases the values of initiation fracture toughness have been determined at Δa = 0.25 mm and the propagation toughness values at the crack propagation plateau of the R-curves. Figures 5 and 6 shows the mean values corresponding to the different test conditions. In the case of the reference material, the initiation fracture toughness was 674 J/m^2, and the propagation fracture toughness was 906 J/m^2.

In the case of modification with ethanol, the results of initiation fracture toughness and propagation fracture toughness are very similar to those of the reference. It can be concluded that the use of ethanol has no influence on the interlaminar thoughness.

In the case of laminates modified with non-functionalized CNTs here is no appreciable difference in fracture toughness values with respect to the reference material, probably due to both the lack of adhesion between the nanotubes and epoxy matrix, and the insufficient dispersion of the CNTs. As mentioned, the improvement of fracture mechanics properties depends on an adequate transmission of stresses between the matrix phase and the reinforcement phase. In the case of non-functionalized carbon nanotubes, the polarity difference between the nanotubes and the epoxy matrix prevents a good dispersion of the nanotubes even after sonication and spraying. Besides, those non-functionalized nanotubes have no affinity for the epoxy matrix and therefore the sought reinforcement effect is not achieved.

In the specimens in which functionalized CNTs were used, both the initiation and the propagation fracture toughnesses were increased. The results presented in Figures 5 and 6 reveal that initiation fracture toughness increases up to values around 824 J/m^2, which means an increment of about 22 % with respect to the reference material. Moreover, the propagation fracture toughness reaches values of 1034 J/m^2, which represents an increase of 14 % with respect to the reference material. The functionalization of CNT improves the dispersion in the solvent and also promote the adhesion between matrix and nanotubes due to the dipole-dipole and even the hydrogen bonding forces that appear between the CNTs and the epoxy resin.

SUMMARY AND CONCLUSIONS

A novel method for the inclusion of nanoparticles in the interlaminar region of long-fiber composite laminates is shown in this paper.

In order to assess the quality of the proposed technique, the influence on fracture mechanics properties of the modification of epoxy/long carbon fiber laminate composites by the addition of functionalized and non-functionalized MWCNTs was studied. The laminates were modified by spraying the nanotubes at the central interlaminar layer by means of an airbrush.

Interlaminar fracture experiments were done by End Notched Flexure (ENF) tests, and the Beam Theory including Bending Rotation effects (BTBR) was used as data reduction method. This is a novel method that allows obtaining the R-curve without the use of optical devices.

The sample prepared using non-functionalized CNTs did not show any appreciable effect on the studied properties. An inefficient dispersion and the lack of interaction with the epoxy matrix are the cause of the observed lack of reinforcement.

However, results regarding the modification with functionalized MWCNTs show that the inclusion of 0.1 %w functionalized MWCNT in the central interlaminar layer, results in an increase of 22 % in the initiation fracture toughness with respect to the reference material, and an increase of 14 % in the propagation fracture toughness. On the one hand, this reinforcement effect takes place due to the better dispersion of the functionalized nanotubes compared to the non-functionalized ones. On the other hand, the intermolecular attraction forces between the functionalized nanotubes and the epoxy resin are also appreciably enhanced, resulting in an increased stress transfer between them.

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