Composite Structures 111 (2014) 488–496

Contents lists available at ScienceDirect

Composite Structures

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

Impact and residual after impact properties of carbon fiber/epoxy composites modified with carbon nanotubes

Marcel Siegfried [a], Carmen Tola [b], Michael Claes [b], Stepan V. Lomov [a], Ignaas Verpoest [a], Larissa Gorbatikh [a,*]

[a] Department of Metallurgy and Materials Engineering, Katholieke Universiteit Leuven, Kasteelpark Arenberg 44, 3001 Heverlee, Belgium
[b] Department of Research and Development, Nanocyl S.A., Rue de I' Essor 4, B-5060 Sambreville, Belgium

ARTICLE INFO

Article history:
Available online 2 February 2014

Keywords:
Nano-engineered polymer composite
Compression after impact
Carbon nanotubes

ABSTRACT

The effect of carbon nanotubes (CNTs) on the impact and after impact performance of woven carbon fiber/epoxy composites is investigated. Three nano-reinforced epoxy systems that differ in the CNT dispersion and functionalization are used as a matrix material. The composites are tested for the resistance to an out-of-plane low velocity impact, the residual compressive strength, the mode II interlaminar fracture toughness and the interlaminar shear strength. The composite with the highest mode II fracture toughness is found to be the best performing system in the compression test. The resin in this composite contains a network-like structure of CNTs. Nanotubes are found to have a dual effect on composite properties: (1) they improve the mode II interlaminar fracture toughness and (with it) damage tolerance of a composite, but (2) they also make composites more susceptible to the onset of matrix cracks leading to a larger delamination area after impact.

1. Introduction

Fiber reinforced polymer composites offer remarkable in-plane mechanical properties combined with a low density but exhibit poor through thickness properties. In the absence of the out-of-plane reinforcement they are highly susceptible to impact damage in the form of matrix cracks and delaminations. Even if the damage is not visible on the surface it can still severely reduce the residual performance of these composites, including such a critical property as the compressive strength. The damage resistance during and damage tolerance after impact have received considerable attention in the literature over the years. It is generally agreed that composites with a superior interlaminar fracture toughness, interlaminar shear strength (ILSS) and interfacial shear strength (IFSS) perform better in compression after impact tests. In the past decade it has been successfully shown that these properties can be enhanced by additionally reinforcing composites with carbon nanotubes (CNTs) [1–3]. It can, therefore, be expected that with it the impact damage resistance will also be improved. However, little is known about the damage resistance under impact loading of such composites modified with CNTs.

In the open literature, only few articles were found addressing the compression-after-impact (CAI) property of CNT modified laminates [4–6]. These studies were conducted with carbon fiber/epoxy laminates and the CNTs were dispersed in the matrix. The differences between the research works is the use of different types: single wall CNTs [4], cup stacked CNTs [5] and multi wall CNTs [6].

In Asharfi et al. [4] 0.1 wt% of functionalized SWCNTs were dispersed in the epoxy matrix of carbon fiber laminates. The SWCNTs were chosen instead of MWCNT because of the higher aspect ratio, more efficient load transfer and better mechanical properties. The addition of the SWCNTs resulted in a decrease of the resin fracture toughness by 12%. However, the interlaminar fracture toughness of the composite increased by 13% in mode I and 28% in mode II. Also the results of the CAI test show the beneficial effect of the CNTs since the delamination area decreased by 5% and the compression after impact strength was 3.5% higher. The variance of the samples without CNTs was, however, greater than 3.5% and the results were not statistically analyzed by the authors.

A similar series of tests was conducted by Yokozeki et al. [5] where carbon fiber laminates were modified with different concentrations of cup-stacked CNTs (CSCNTs). By adding 5 wt% CSCNTs, the interlaminar fracture toughness in mode I increased by 97% and in mode II by 30%. The compression after impact strength increased by 0% and 7% with 5 wt% and 10 wt% of CSCNTs, respectively. A limitation of the study is that just two samples for each material configuration were tested and, therefore, the representativity of the results is limited.

* Corresponding author. Tel.: +32 16321235.
E-mail address: Larissa.Gorbatikh@mtm.kuleuven.be (L. Gorbatikh).

http://dx.doi.org/10.1016/j.compstruct.2014.01.035
0263-8223/

In Kostopoulos et al. [6] the epoxy matrix of a carbon fiber composite was reinforced with 0.5 wt% of MWCNTs. The CAI experiments were carried out with different impact energies. It was found that the delaminations area decreased for the doped samples but results showed a large standard deviation. It was also noted that the specific delamination energy (SDE) – the energy needed to develop a unit delamination area – was only at higher impact energy levels superior for the MWCNT doped samples. The authors attributed the improvements to additional energy dissipation effects like CNT pull-out, CNT breakage and crack bridging. They also concluded that the CNTs perform better at higher strain rates. A higher strength of about 12–15% for the CNT modified samples was reported.

It is interesting to note that the above works are similar in their observations that, while the interlaminar fracture toughness of a composite can be considerably improved by adding CNTs, the effect of these improvements on the CAI strength is less pronounced. In the present study the effect of CNTs on the impact damage resistance will be further investigated for different CNT reinforced epoxy systems. One of them was shown to suppress formation and development of transverse cracks in a woven carbon fiber/epoxy composite subjected to quasi-static tensile loading [7,8].

2. Materials and methods

2.1. Materials

The primary reinforcement used in this study is a balanced twill 2/2 woven carbon fiber fabric produced by Hexcel under the commercial name HexForce G0986 Injectex. The areal density is 285 g/m^2 and the fabric is made of HTA carbon fibers with a Young's modulus of 238 GPa, tensile strength of 3950 MPa and strain to failure of about 1.7%. The epoxy resin used to produce composites is Epikote 828LVEL (Bisphenol-A type) together with a 1,2-diaminocyclohexane (Dytek DCH-99) hardener.

The CNT reinforced epoxy was supplied by Nanocyl S.A. (Belgium) in the form of masterbatches. There were three masterbatches used in this study. They are based on a liquid Bisphenol-A epoxy resin and contain a high concentration of multi-wall CNTs with an average diameter of 9.5 nm, specific surface of 250–300 m^2/g and carbon purity >90%. Two of the masterbatches are the same commercial product EpoCyl NC R128-02 with the difference of the storage time. One of them was stored for less than three months prior to the current study whereas the other one was prepared almost three years earlier.

As described in Aravand et al. [9], a longer storage time may influence the CNT dispersion state in a dramatic away. From the rheological analysis it was found that the aged masterbatch had a significantly higher shear storage modulus compared to the fresh one. It also did not exhibit the anticipated recovery of the shear storage modulus over time, as it was in the case of the fresh master batch. From characterization during the curing reaction (after dilution and addition of the hardener) using an optical microscope, it was found that CNTs in the aged system formed an interconnected network with clear and well defined borders, while CNTs in the freshly prepared system aggregated into individually distinguishable clusters without formation of any network. Comparing results of the electrical impedance spectroscopy, it was found that the CNT-reinforced epoxy prepared from the aged masterbatch had a significantly higher specific conductivity (by five orders of magnitude) in comparison with the one made from the freshly made masterbatch. The diagrams of impedance vs. frequency revealed that the material from the aged masterbatch exhibited electrical percolation while this was not the case for the freshly made version, although both systems contained equal amounts of CNTs. The dispersion state in the resin will also then determine localization of CNTs in the composite and may affect its mechanical properties. As found in Gorbatikh et al. [10], for the case of small isolated CNT agglomerates (the case of the freashly prepared masterbatch), CNTs are able to enter fiber bundles. For the state of dispersion where CNTs form a network with large features (the case of the aged masterbatch), it is found that CNTs tend to localize in resin rich zones without (or hardly) entering fiber bundles. The composites produced with the three masterbatches are further referred in this report as "CF/epoxy/CNT" and "CF/epoxy/CNT**a**" ("a" stands for "aged").

The third type of the master batch is produced with functionalized multi-wall CNTs of the same type (this product is not commercially available). The surface of the CNTs is treated with a NH2 plasma to incorporate amino groups onto the surface of the nanotubes. Data provided by the supplier of the CNTs indicate that the amino content measured by X-ray photoelectron spectroscopy (XPS) was 0.7 at% of N and 3.4 at% of O. In general it is expected that the functionalization will promote a better dispersion of the CNTs and the amino groups will react with the epoxy matrix, resulting in an improved matrix–CNT interface [11]. The composite laminates containing the functionalized CNTs are referred in the text as "CF/epoxy/CNT**f**" ("f" stands for "functionalized").

The purpose of using these different masterbatches is to better understand how the CNT dispersion state influences the impact and after impact properties of composites.

2.2. Production of composite plates

Composite laminates were produced with the resin transfer moulding process (RTM). The stacking sequence was $[(+45/-45)/(0/90)]_{4S}$ and the targeted thickness was 4 mm. Before injection, the CNT masterbatches were diluted with the Epikote 828LVEL epoxy to obtain a CNT content of 0.25 wt% and mechanically stirred for 5 min. Afterwards the hardener was added in a ratio of 100 g resin/15.2 g hardener, resulting in a CNT content of 0.227 wt% for the resin. The resin was then degassed in a vacuum chamber for 10 min and subsequently injected into the mould with a spacer of 4 mm. The injection procedure was done with a changing pressure: starting at one bar and increasing about one bar every five minutes till a final pressure of four bars. Plates produced by this injection procedure were of high quality and showed no sign of dry areas, voids or other defects. The curing and post-curing conditions were 70 °C for one hour and 150 °C for one hour, respectively. Table 1 provides information about the average thickness and fiber volume fraction of the produced plates. The fiber volume fraction was calculated based on the thickness of the composite, the areal density of the carbon fabric and the number of plies.

2.3. Impact testing

The experimental setup for the impact test was chosen according to the ASTM D7136 standard. The purpose of the test is to introduce damage into the specimen without penetration. Five specimens for each material system with dimension of $100 \times 150 \times 4$ mm^3 were tested. All specimens were impacted on an in house built drop weight impactor. A hardened steel striker with a hemispherical tip of the diameter 16 mm was used. The weight of the impactor was adjusted to 5.536 kg. With a drop height of 0.49 m, an impact energy of 26.8 J was achieved. This corresponds to an impact energy of 6.7 J per mm sample thickness as recommended by the standard. During the impact event the contact force, impactor displacement and time were recorded at a sampling rate of 200 kHz. The damage threshold load (F_1), maximum contact force (F_{max}) and contact duration (t_T) were processed for further analysis. The damage threshold load (F_1) is the maximal load (F_{max}) before the first drop in the load–displacement history.