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# Experimental determination of fracture toughness properties of nanostitched and nanoprepreg carbon/epoxy composites

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ABSTRACT

The interlaminar fracture toughness properties based on the double cantilever beam test of the multilayered stitched carbon/epoxy/multiwall carbon nanotube prepreg woven composites was investigated. The fracture toughness based on beam theory and modified beam theory of the stitched/nano and stitched composites showed 3-fold and 2-fold increases compared to the base and base/nano composites, respectively. The fracture toughness resistance to arrest the crack propagation in the stitched/nano composite was primarily due to out-of-plane directional stitching fiber bridging and was secondarily due to in-plane directional biaxial fiber bridging and multiwall carbon nanotubes. Fracture surfaces of the stitched/nano had multiple matrix and brittle tensile filament breakages in carbon stitching yarn and ductile filament breakages in the *para*-aramid stitching yarns where filament/matrix debonding and filament pull-out were identified.



## 1. Introduction

Fiber composites have been used in various space-aerospace, industrial and medical sectors because of their high stiffness to weight ratio and damage tolerance [1]. However, fiber composites based on two dimensional (2D) fabrics such as dry or prepreg forms suffer delamination. In order to develop a delamination free structure, Z-directional reinforced textile preforms were developed by 3D weaving [2], 3D braiding [3] and stitching techniques [4]. Recently, nanosphere, single wall (SWCNTs) or multiwall (MWCNTs) carbon nanotubes were employed in the fiber composites by dispersing the nano in the resin using various techniques such as shear mixing, ultrasonication, calendering, ball milling or ultrasonication-extrusion and transfer-printing [5]. The 3D woven structure was found to have low in-plane properties due to fiber formation in the in-plane direction. The nanosphere, nanotubes or nanofibers were all randomly distributed in the fabric structure based on layer sequences and they did not provide true out-of-plane reinforcement to the structure due to their discontinuous form. The crack propagation resistance of 3D composites was considerably higher than that of traditional laminated composites due to crack bridging in the transverse z-yarn in the structure [6]. Manual stitching causes a smaller amount of fiber damage and a resin rich pocket compared to machine stitching (lock stitch). Thus, untwisted Kevlar stitching yarn used in manual stitching showed higher mode-I interlaminar fracture toughness compared to that obtained by machine stitching [7]. It was revealed that stitching effectively impeded delamination growth by crack arresting and bridging. Additionally, subsurface damages were predominated by intralaminar matrix cracks, interlaminar delamination, and stitching

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fiber/matrix debonding [8]. Stitching topology and weave types of woven structure affected the mode-I failure of the composite due to interlacement and fiber bridging in the fiber/matrix debonding region [9,10].

When the carbon nanotubes (CNTs) are mixed into the base matrix, the agglomeration, lack of alignment, poor dispersion and damage to the CNTs occurred during mixing. This caused extensive mechanical property loss. Therefore, radially-aligned CNT technique, in which nanotubes are grown in-situ on the fibers in 2D woven fabric, was developed. This provided an important improvement in mode-I and tension-bearing [11]. A technique was developed to align CNTs in the through-the-thickness direction of the carbon fiber prepreg by transfer-printing [5]. Another method was employed to functionalize MWCNTs based on the silanization reaction. It was claimed that the fracture toughness of silane modified CNT composite was improved due to homogeneous dispersion and better interfacial bonding between the silane-modified CNT and epoxy [12]. On the other hand, it was found that the mode-I of the carbon fiber/epoxy/carbon nanofiber (CNFs) composites was 50% higher compared to base composite [13].

A model considering the bridging energy density and critical energy release rate was developed. They were analyzed by fiber pull-out in the matrix and fiber crossing in the bridging surfaces. It was found that the cohesive/bridging energy density and the peak cohesive/bridging traction influenced the delamination crack growth [14]. It was also shown that a crack was possibly to begin at the fiber/matrix interface and the crack-tip bluntness influenced the initial crack growth in the DCB test [15]. Several models were also developed to determine the mode-I behavior of the nanocomposites. These models indicated that CNT length, density, volume fraction and the interfacial shear strength between the CNT and matrix were the critical parameters to improve the mode-I fracture of nanocomposites [16,17].

The objective of this study was to develop one-dimensional stitched carbon/epoxy nano composites and to experimentally examine the fracture toughness of those structures by the double cantilever beam (DCB).

## 2. Experimental

### *2.1. One-directional stitched multilayer woven carbon/epoxy/carbon nanotubes prepreg based preform and composite*

Polyacrylonitrile (PAN) carbon woven fabrics (Spinteks A.S., TR) were used to make multistitched preform. Carbon fabric was made from 800 tex (12 K, AKSACA, TR) fibers for both warp and weft which were coated by standard epoxy coating (DO12, 1.0–1.5%, wt.). Average density and melting temperature of carbon fiber were 1.78 g/cm$^3$ and over 1200 °C, respectively. Tensile strength, modulus and elongation at break of the carbon fiber were 4.2 GPa, 240 GPa and 1.80%, respectively. Two kinds of carbon fabric were utilized as twill (2/2 Z) and satin (1/4) weave. The warp-weft densities of both carbon fabrics were all the same, namely 38 ends/10 cm. The warp-filling crimp ratios of both carbon fabrics were less than 1% (0.20–0.36%). The carbon fabric unit area weights were 590 g/m$^2$ for twill (2/2 Z) and 585 g/m$^2$ for satin (1/4), and the fabric thicknesses were 0.81 mm for twill and 0.98 mm for satin weaves. The number of interlacements for both fabrics was almost equal but their placements in the fabrics were inhomogeneously distributed. Epoxy resin (Araldite LZ 5021, Biesterfeld Spezialchemie GmbH, DE) was used as matrix. Its average density and melting temperature were 1.1 g/cm$^3$ and 115 °C, respectively. Tensile strength, modulus and elongation at break of the epoxy resin were 0.8 GPa, 3.3 GPa and 5–8.5%, respectively.

The multiwall carbon nanotubes (MWCNTs, Nanothinx, GR) were selected based on compatibility with the carbon fabric, better mechanical properties and commercial availability. The average sizes of the MWCNTs varied from 15 to 35 nm for diameter, 10 μm for length and 1–2 nm for wall thickness [18]. Its density, surface area and purity were 1.74 g/cm$^3$ [19], over 100 m$^2$/g and over 97%, respectively. The tensile strength and modulus of the MWCNTs were 200 GPa and 1 TPa, respectively.

Basically, four types of carbon structures were developed: (1) base (unstitched, CTU, CSU) in which CTU was a four layer $[(0°/90°)]_4$ carbon twill (2/2 Z) preform, whereas CSU was a four layer carbon satin (1/4) structure; (2) stitched (CT-CS, CS-CS, CT-TS, CS-TS) in which CT-CS and CS-CS were four layer twill (2/2 Z) and satin (1/4) woven, one-directionally carbon stitched in warp (0°) structures, respectively, whereas CT-TS and CS-TS were four layer twill (2/2 Z) and satin (1/4) woven, one-directionally Twaron CT stitched in warp (0°) structures, respectively; (3) base/nano (unstitched/nano, CTU-N, CSU-N) in which CTU-N and CSU-N were four layer twill (2/2 Z) and satin (1/4) woven structures with added MWCNTs, respectively; (4) stitched/nano (CT-CS-N, CT-TS-N, CS-CS-N, CS-TS-N). When the MWCNTs were added to all the stitched structures which are described above, they were defined as stitched/nano structures. One-directional stitching was manually made on the layered woven structures using the carbon and Twaron CT stitching yarns as shown schematically in Fig. 1(d) and (e). The fiber diameter, density and yarn linear density of the carbon fiber (PAN, AKSACA, TR) and the Twaron CT (Para-aramid, Teijin, JP) stitching yarns were 6 μm, 1.78 g/cm$^3$, 6 K (TOW) and 12 μm, 1.45 g/cm$^3$, 3360 dtex, respectively. In addition, tensile strength, modulus and breaking elongation of the carbon fiber and the Twaron CT stitching yarns were 4200 MPa, 240 GPa, 1.8% and 3200 MPa, 115 GPa, 2.9%, respectively.

Stitched/nano multilayer carbon woven preforms were consolidated to make stitched/nano carbon composites. Fig. 2 shows the processing steps for one-directional stitched carbon/epoxy and stitched/nano carbon/epoxy composite.

MWCNTs (0.03125,%wt., Nanothinx, GR) were added to epoxy resin (Araldite LZ 5021, Biesterfeld Spezialchemie GmbH, DE). In order to conduct pre-mixing to prevent of possible heterogeneous dispersion and early agglomeration, they were stirred by a magnetic mixer (Wisestir ®, Witeg, DE) at 240 revolution per minutes (rpm) for 15 min. After that, the resin/