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Effects of carbon nanotube modified adhesive layer on low velocity impact and flexural properties of cork core sandwich structures

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Abstract

The traditional method of manufacturing sandwich structures using a structural adhesive to achieve face-sheets to core bonding maintains widespread use. Most research addressing experimental performance of sandwich structures focuses on core and face-sheet related parameters, and only marginal attention is directed to the mechanical properties of the thin, low content, adhesive layer – it usually suffices that it can provide effective face-sheet/core bonding. The present work studies sandwich structures with a cork agglomerate core and resin infusion processed skins consisting of +/-45º glass fibre fabric reinforced epoxy resin. A polyurethane structural adhesive was used to assemble the structure. The focus of the study was the influence on sandwich performance with respect to a modification of the adhesive with multiwall carbon nanotubes, exploring the possibility of an increase in both shear and adhesion strength of the modified adhesive. The sandwich structure was evaluated with respect to four-point bending and low velocity impact tests. In addition, scanning electron microscopy analysis was used to examine the adhesive layer morphology. The results were analysed to determine how the addition of ca. 0.4 wt.% of carbon nanotubes to the adhesive effectively influenced failure behaviour and damage events in both flexural and impact testing.

Keywords: Sandwich structure; carbon nanotube; cork core; adhesive; flexural properties; low velocity impact.

1. Introduction

Composite sandwich structures have found widespread application in automotive, aeronautic, aerospace, marine and civil industries, owing primarily to the high specific strength- and stiffness-to-weight ratios which can be achieved. They comprise a low bulk density core material and two comparatively thinner and rigid face-sheets. These are loaded primarily in tension or compression due to bending while the core resists most shear stresses [1].

When thermoset resins are involved, sandwich structures are usually constructed in either a two-step or a single-step process. The later involves a vacuum assisted resin infusion process (VARIM) where the impregnation of face-sheets and their bonding to the core is performed using the same resin. In the former and more traditional method, the face-sheets are processed in an initial independent step which is followed by bonding to the core using a structural adhesive.

Most research addressing experimental performance of two-step processed sandwich structures focuses on core and face-sheet related parameters. The interest on the adhesive component is generally confined to the materials selection phase where its elastic properties and adhesive bond strength to the main components are thoroughly analysed. Although there are tests specifically designed to address the face-sheet to core adhesion [2], the importance of the adhesive layer is

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often overlooked, and studies addressing the face-sheet/core interface focus primarily on surface preparation [3].

In a previous work, some of the authors studied the performance of sandwich structures when cork agglomerates are used as core materials instead of typical polymer foams [4,5]. The sandwich structures had VARIM processed skins consisting of +/-45º glass fibre fabric reinforced epoxy resin, and a polyurethane structural adhesive was used to assemble the structure.

The present work used a similar sandwich structure, with one of the previously studied cork agglomerate cores. The focus of the study was the influence on sandwich performance with respect to a modification of the adhesive with multiwall carbon nanotubes (MWCNT), exploring the possibility of an increase in both shear and adhesion strength of the modified adhesive [6-8].

The sandwich structure was evaluated with respect to four-point bending and low velocity impact tests, and the results compared to those previously obtained with the same core material and neat adhesive [4,5]. In addition, scanning electron microscopy (SEM) analysis was used to examine the adhesive layer. The results were analysed to determine how the addition of *ca.* 0.4 wt.% of CNTs influenced failure behaviour and damage events in both flexural and impact testing.

2. Experimental

The two sandwich structures under consideration were constructed using the same facing material, core thickness and material, and adhesive layer thickness. The parameter under study was a modification of the adhesive layer material composition.

2.1. Materials

The matrix material used in sandwich face sheets was a very low viscosity (170 mPa s) two component Biresin® system (Sika®, Germany) based on epoxy resin CR83 and amine hardener CH83-6; the reinforcing material was Multifab® (Lintex®, PRC) E BX 600, a double biaxial (±45°) E-glass fibre fabric with areal weight of 612 g/m^2, which includes the contribution from polyester yarn stitching.

The core material was a 12 mm thick cork agglomerate CoreCork™ NL25 (Amorim Cork Composites S.A., Portugal) – a product developed for composite applications, with finer grain and narrower size distribution, and lower density (250 kg/m^3) than general purpose agglomerates, and a surface treatment to improve adhesion.

A structural two-component, fast-curing polyurethane assembly adhesive − SikaForce®-7888 L10 (Sika®, Germany) − was used to bond the face sheets to the core materials. The adhesive components are a mixture of filled polyols and isocyanate derivatives, respectively, which must be mixed in a 1:1 volume ratio.

Multiwall carbon nanotubes (MWCNT) with reference Baytubes® C 70 P (Bayer® MaterialScience, Germany) were used to modify the structural adhesive. (*cf.* C 70 P MWCNT's properties in Table 1).

Table 1. Properties of Baytubes® C 70 P.

C-purity (wt.%)	Outer mean diameter (nm)	Inner mean diameter (nm)	Length (μm)
> 95	~ 13	~ 4	> 1

2.2. Manufacturing

The sandwich structures were produced by sequentially producing the fiberglass/epoxy laminate face sheets by vacuum infusion, preparing the core, and bonding them together using the structural adhesive. Each fiberglass/epoxy facing had two layers of ±45° biaxial fabric. Two large laminates (*ca.* 2000×600 mm) were obtained by vacuum infusion, from which 500×200 mm face sheets were cut. These were bonded to the NL25 core using the two-component polyurethane-based neat adhesive in the sandwich structure previously characterized [4,5]. For the new sandwich structure, the adhesive was modified with the addition of 0.4 wt.% of MWCNTs. This was produced by adding the necessary amount of MWCNTs to the polyol component and combining sonication (UP200S, Hielscher Ultrasonics, Germany) at maximum amplitude and frequency of 0.5 Hz and mechanically stirring during two 4 min periods separated by a pause in sonication, to avoid excessive temperature build-up. Then the isocyanate component was added and manually mixed for about 1 min without further sonication, considering the low adhesive pot life (*ca.* 10 min) and the time required to evenly apply the adhesive to the face sheets prior to bonding. The procedure for MWCNT dispersion in the high viscosity adhesive was based on a previously developed one [9]. After assembly, weights were uniformly distributed on the sandwich structure so that a constant pressure was applied throughout adhesive curing/bonding, and adhesive layers with nearly constant thickness resulted along each of the sandwich bonded surfaces. Both structures had a nominal thickness of 15 mm, from which specimens for impact and four point bending were cut.

2.3. Scanning Electron Microscopy (SEM) analysis

Specimens of fracture surfaces for the adhesive material were obtained by peeling off the face sheet of small sandwich pieces cooled with liquid nitrogen. The fracture surfaces were mounted on a resin block and graphite coated for SEM analysis. The observations were performed using a FEI Quanta 400 ultra-high resolution field-emission Scanning Electron Microscope, with integrated EDAX Pegasus X4M microanalysis X-ray system - Energy Dispersive Spectrometer (EDS) and Electron Backscatter Diffraction (EBSD).

2.4. Mechanical testing

Four-point bending and low velocity impact tests of sandwich specimens were performed with an Instron® model 4208 electromechanical universal testing machine with a 5 kN load cell, and a Rosand® IFW 5 HV testing machine, respectively.

2.4.1. Flexural testing

The four-point bending tests were carried out according to ASTM C 393-00. Four sandwich specimens with nominal dimensions of 350×30 mm (length × width), were tested using a third-point loading configuration (Fig. 1). The span length was set to 300 mm. Loading was applied at a constant speed of 5 mm/min, and loading rollers with 20 mm diameter were used.

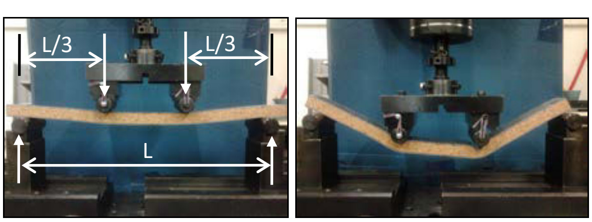

Fig. 1. Third-point loading configuration for four-point bending tests, according to ASTM C 393-00. Test of sandwich specimen with MWCNT-modified adhesive at an early stage (left) and after failure (right) due to core compression.

2.4.2. Impact testing

When the sandwich structure with neat adhesive bonding was being performed, standard ASTM D7766/D7766M-11, "Practice for Damage Resistance Testing of Sandwich Constructions" regarding low velocity impact testing of sandwich structures was not yet available. Therefore, based on the available information at the time, low velocity impact tests were carried out according to standards for polymers and laminates, such as ASTM D5628-96, ASTM D7136/D7136M–05, ASTM D7137/D7137M–05 or Airbus AITM1-0010, and considering restrictions imposed by the testing equipment.
Specimens with a square cross-section of 3600 mm^2 were used for low velocity impact testing. The tests were carried at impact energies of 10 J, 15 J, 20 J, 25 J, 30 J (three specimens) and 40 J, using a 3.774 kg mass impactor with a 16 mm diameter hemispherical tip. The impact energy was obtained changing the drop height, as summarized in Table 2.

Table 2. Impact conditions for low velocity impact testing.

Impact energy (J)	10	15	20	25	30	40
Impact height (m)	0.270	0.405	0.540	0.675	0.811	1.081
Impact velocity (m/s)	2.30	2.82	3.26	3.84	3.99	4.60

Each specimen was held in place by a pneumatic lever arm with a reversible ring, at a clamping pressure of 3 bar - a higher clamping pressure would be excessive for the low compressive strength cork agglomerate core. The impactor was capturing after rebound, thus preventing multiple striking.

3. Results and Discussion

3.1. Scanning Electron Microscopy (SEM) analysis

SEM micrographs of fracture surfaces show evidence of the presence of well dispersed CNTs, although not homogeneously distributed throughout the surface (Figs. 2 and 3), *i.e.*, areas with CNTs and others of neat adhesive. It appears that, although sonication was effective in dispersing the nanotubes, more effective mechanical mixing or simply longer mixing time would be required.

3.2. Flexural tests

The flexural test results are shown in Fig. 4, where the results for the neat adhesive based structure [4,5] have been reproduced for better comparison.
The yield values for displacement, load, core shear stress and facings bending stress, for both sandwich construction types, are presented in Table 3.

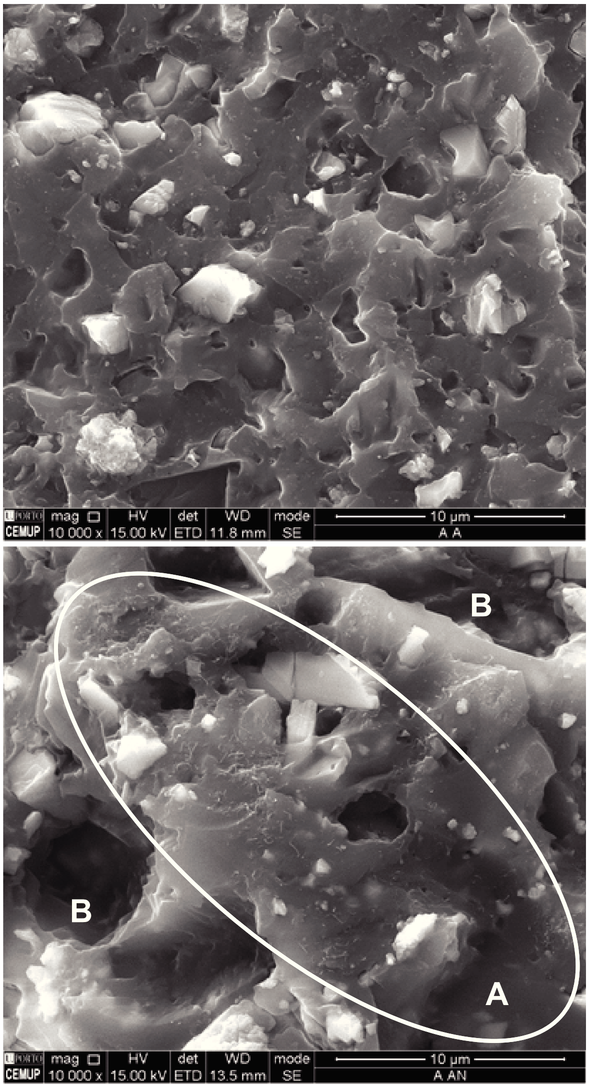

Fig. 2. SEM micrographs obtained at 10000x magnification for both neat (above) and MWCNT-modified (below) adhesives. In the lower picture MWCNT rich (A) and poor (B) areas are identified.

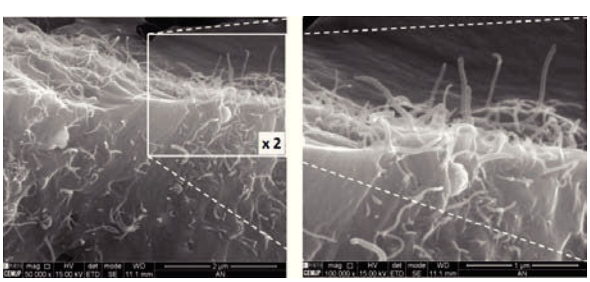

Fig. 3. SEM micrographs obtained at 50000x and 100000x magnification MWCNT-modified adhesive showing CNT rich and poor areas in the foreground and background, respectively.

The sandwich structures, with either neat or MWCNT-modified adhesives, exhibited similar behaviour under flexural load. The cork agglomerate core with low compressive modulus caused considerable local compression, which was the observed cause for failure (*cf.* Fig. 1). As a result, failure occurred at low core/adhesive shear stresses, preventing the observation of any improvement at in adhesive shear strength.

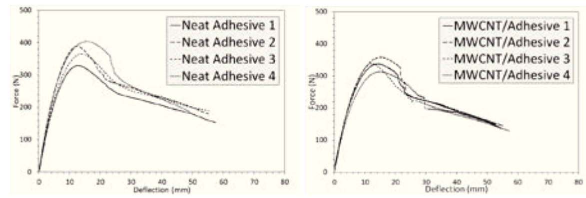

Fig. 4. Load-deflection curves for four-point bending of sandwich structures with (left) neat and (right) MWCNT-modified adhesives.

Table 3. Four-point bending average test results at yield point.

Adhesive material	Deflection (mm)	Load (kN)	Core shear stress (MPa)	Facing bending stress (MPa)
Neat	13.7	0.372	0.434 (0.04)[1]	28.9 ± 3.1
MWCNT-modified	13.9	0.337	0.400 (0.02)[1]	25.9 ± 1.7

[1] standard deviation

3.3. Impact tests

No evidence of severe core crushing was apparent in contrast with what usually occurs in structures with more brittle cores, based on polymer foams such as PUR or PMI [4,5]. The impact force-time plot histories of both types of sandwich specimens for all tested energy levels, and characteristic impacted specimens for five energy levels, are shown in Fig. 5 and Fig. 6, respectively.

A similar behaviour in force development is observed for both structures up to 25 J. Matrix cracking begins to show at 25 J but the force maintains a steady evolution. At 30 J, the profiles differ, with the structure bonded with neat adhesive showing a much more irregular force evolution, although impacted laminates show similar damage. At 40 J, the disparity in force evolution of both structures accentuates, with the neat adhesive based structure exhibiting a very severe drop in force, a feature which is absent when MWCNTs are present. Damage also differs considerably at this energy level, being much more severe on the impacted surface of the structure with neat adhesive (*cf.* Fig. 8). This may be an indication of adhesive toughening by the presence of MWCNTs, improving the structure performance towards higher energy impact events, in particular, damage tolerance.

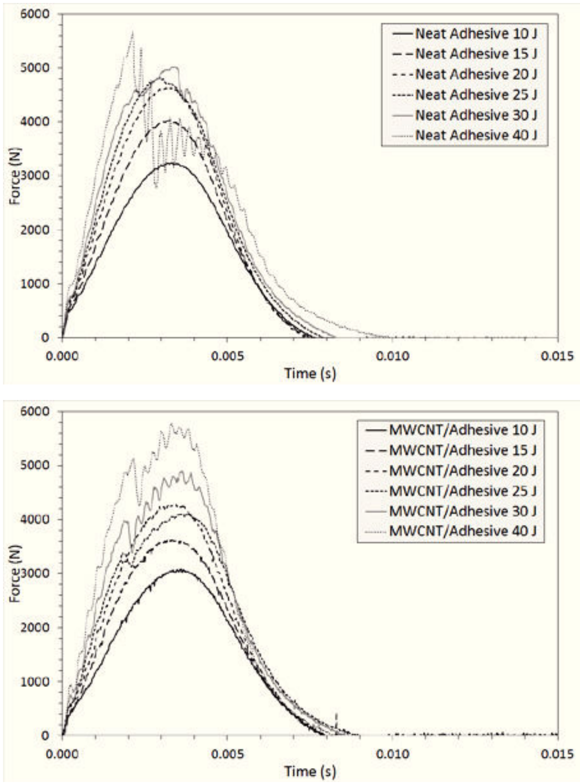

Fig. 5. Force-time plot histories of low velocity impacts for all energy levels, of sandwich specimens with neat (top), and modified (bottom) adhesives.

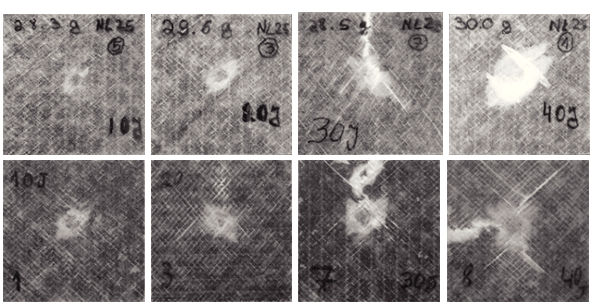

Fig. 6. Specimens impacted at 10 J, 20 J, 30 J and 40 J (left to right) for neat (above) and MWCNT-modified (below) adhesives.

4. Conclusions

The influence of the presence of MWCNTs on the adhesive layer of sandwich structures with a cork agglomerate core was investigated, regarding both flexural and impact performance:

– Flexural behaviour was dominated by the highly flexible core, resulting in premature structure failure due to compression at still moderate shear stresses, which prevented evaluating the influence of MWCNTs in adhesive ultimate shear strength;

– Impact behaviour only differed at the higher energy levels investigated – 30 J and 40 J – and the combined results of impact force curves and structure damage, indicate toughening of the adhesive by the MWCNTs;

– The CNTs, while well dispersed, are not homogeneously distributed - optimizing this parameter could result in improved performance.

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