ELECTRICALLY CONDUCTIVE STRUCTURAL ADHESIVES BASED ON BUCKYPAPERS

I.D. Rosca, S.V Hoa*
Mechanical and Industrial Engineering, Concordia University, Montreal, Canada
* Corresponding author (hoasuon@alcor.concordia.ca)

Keywords: *Structural adhesives; Carbon nanotube; Electrical conductivity*

1 Introduction

Structural adhesives are extensively used to build lightweight structures in aerospace and automotive industries. Electrical continuity and electrostatic dissipation capabilities are usually requested for these structures. Since all of these adhesives are electrical insulators, the structures must be grounded by time intensive operations like silver brazing or strapping. Recently, carbon nanotubes (CNTs) were intensively investigated as efficient fillers for electrically conductive composites [1-2]. However, homogeneous nanotube dispersions require time and energy intensive operations and the resulting adhesive displays high viscosity and insufficient electrical conductivity. These inconveniences can be addressed by using buckypaper (BP) technology.

2. Materials and methods

2.1. Buckypaper preparation

Two types of buckypares were prepared: one made of single wall carbon nanotubes (SWCNTs) named sBP and one made of a mixture of SWCNTs and multi walled carbon nanoubes (MWCNTs) called hybrid buckypaper (hBP) For a sBP preparation 0.5 g of SWCNTs from Nikkiso Co. were dispersed in N, N dimethylformamide by a horn sonicator for 30 min. For a hBP a mixture of 0.125 g (25%) of SWCNTs and 0.375 g (75%) of MWCNTs from Nanolab Inc, were dispersed in N, N dimethylformamide by a horn sonicator for 30 min. Next the CNT suspension was filtered on a nylon membrane-filter with pore size of 45 micron. After filtration the buckypaper and the membrane were placed between several filter-papers and lightly pressed between two aluminum plates to absorb the excess solvent. The wet buckypaper was then separated from the filter membrane and dried at 130°C for 12 hours to form a sheet of 140x140 mm^2 and 50 μm thick.

2.2. Impregnated BP preparation

The BPs were impregnated with resin using direct impregnation (DI) or solvent impregnation (SI). For direct impregnation patches of BPs were immersed in a mixture of epoxy resin (Epon 862) and hardener (26.4 wt% Epikure W) and placed in a vacuum oven at 80°C for 30 min. For solvent impregnation patches of BPs were immersed for 1 hour at room temperature in an acetone solution (25 %vol) of the resin and curing agent mixture. Next the impregnated patches were placed in a vacuum oven at 80 °C for 40 min to remove the acetone. The third way to produce impregnated BPs called one step impregnation (OSI) consists of dispersing CNTs directly in the acetone solution of the resin and curing agent followed by filtration and solvent evaporation.

2.3. Lap joint preparation

Aluminum (2024 alloy T3) were cut to dimensions as shown in Fig. 1, degreased in acetone and etched in chromic acid solution for 30 min at 65 °C.
Patches with desired dimensions were cut out from a buckypaper sheet and impregnated with resin as described in paragraph 2.2. The overlap area of both adherents was coated with a thin layer of adhesive. Next, the impregnated patches were placed on one adherent and the lap joint was tightened using a C-clamp. The lap-joints were cured in an oven at 175°C for 4 hours.

2.4. Measurements

The resistance of the bonded joint was measured by four-wire method using a current source (Keithley 6220 DC) and a nanovoltmeter (Keithley 2182A). The resistivity of the as produced BPs and the that of impregnated BPs were measured by a van der Pauw setup [1]

Single-lap specimen for the tension-tension fatigue test and shear strength is shown in Fig.1. The shear strength of the simple lap joints prepared according to ASTM D1002-01 was measured on an MTS 100kN testing machine at 1.3 mm/min strain rate. In order to expedite the fatigue tests the maximum loading was 50 % of the average shear strength and the load ratio was 0.1. The fatigue tests were carried out on an MTS 100kN testing machine at 10 Hz

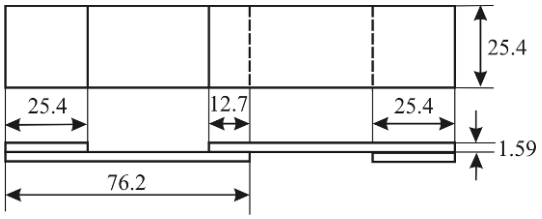

Fig1. Single-lap joint for tensile testing; dimensions in mm.

3. Results and discussion

Typical SEM micrographs of sBP and hBP are presented in Fig. 2. There are several reasons for producing hybrid BPs: (i) BPs made of SWCNTs are strong and highly conductive but too expensive; (ii) BPs made of MWCNTs are too fragile to handle and low display conductivity but are cheap. Using less than 0.25 weight fraction of SWCNTs it is possible to prepare strong BPs with good electrical conductivity and price. The electrical conductivity of the as-produced and impregnated BPs are presented in Table 1. During the impregnation process the buckypaper swells, and its thickness increases significantly (Table 1). Analyzing the three impregnation methods it is clear that direct impregnation is the most convenient as it avoids the difficulties related to solvent processing. Furthermore, direct impregnation results in the highest conductivity and swelling.

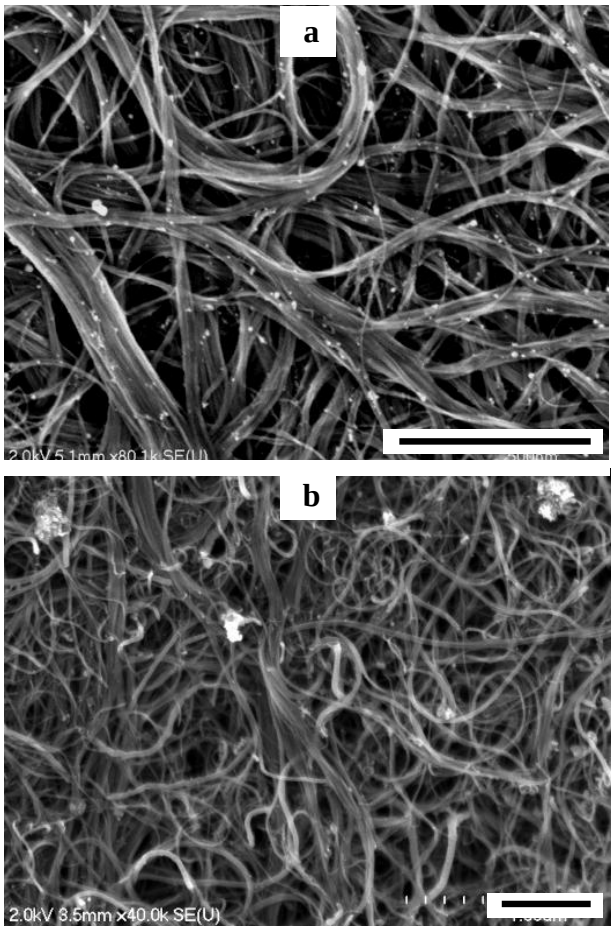

Fig 2 SEM micrograph of as produced sBP (a) and hBP (b); scale bar 500 nm.

Table 1 Electrical conductivity of the as produced and impregnated BPs

BP Type	PM	Conductivity, S/cm		TIF
		BI	AI	
sBP	DI	928	520	3.0
	SI		365	1.7
	OSI	NA	34	NA
hBP	DI	173	95	4.1
	SI		54	1.6

PM- BP production method; BI, AI – before and after impregnation; TIF- thickness increase after impregnation

However, the cross section of BPs impregnated using the DI process is not homogeneous i.e. resin rich layers are intercalated between CNT rich layers, as shown in Fig. 3 (regions marked with white circles). Furthermore, the cross section of impregnated sBPs is far more inhomogeneous than that of hBPs (Fig. 3). Two factors contribute to this: the considerable viscosity of the resin system and the BP morphology. In sBPs the CNTs are aligned and closely packed to form a stratified morphology with higher density (density of 700 kg/m^3, Fig 2a) than hBPs in which CNTs are more loosely packed into an entangled 3D structure (density 230 kg/m^3, Fig 2b) that allow a more uniform impregnation. Because of its layered structure, sBP is only in-plane entangled thus the viscous resin rather peels SWCNT layers than penetrates small pores.

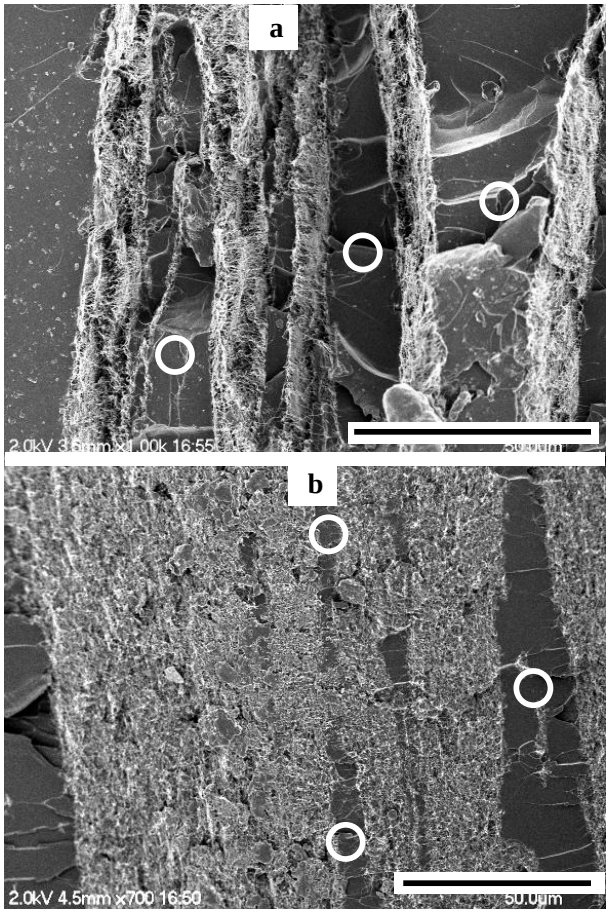

Fig. 3 SEM images of sBP (a) and hBP (b) cross sections produced by DI; circles mark resin rich regions; scale bar 50 μm.

The main advantage of using BPs in adhesive bonding is a reduction by 11 orders of magnitude of the electrical resistance compared to the neat resin, and 10 to 100 times compared to classical nanotube dispersions (Table 2).

As the CNT content in the BP adhesive is high (over 20 wt%) we expected improved mechanical properties, but when the whole overlap area was covered by sBP or hBP (Fig. 6a) the shear strength decreased by 57% and 20 % respectively, compared to the neat resin (Table 2). In a first instance we attributed the large decrease in shear strength in the case of sBP to the inhomogeneous impregnation. In consequence we have opted for solvent impregnation, as a much lower viscosity is expected to lead to a more uniform impregnation. Indeed, the cross section of sBP and hBP is uniformly impregnated as shown in Fig. 4.

Table 2 Mechanical end electrical properties of lap joints

BSC	CM	PM	SS MPa	FL cycles	R Ω
NA	**Neat resin**	**NA**	**20.7±1.5**	**24350**	**4.0.10^{12}**
100% (Fig. 6a)	MWCNT dispersion [3]	2%	19.3±1.8	19860	120 ±10
	sBP	DI	9.1±2.5	-	2.7±0.4
		SI	9.1±1.1	-	2.8±0.2
		OSI	8.2±0.7	-	6.0±0.5
	hBP	DI	16.5±4.0	-	4.5±0.5
		SI	15.9±1.7	-	3.2±0.2
50% (Fig. 6b)	sBP	DI	20.6±2.8	5020	3.9±0.4
	hBP	DI	19.4±2.0	26330	5.8±0.4

BSC-bond surface coverage by the conductive medium; CM-conductive medium; P-MWCNT loading in wt % or BP production method; SS-apparent shear strength; FL-fatigue life; R-electrical resistance

The most uniform impregnation was achieved by OSI (Fig. 5), as SWCNT bundles wrapped in resin are stacked during the filtration forming in one step the impregnated BP. The tradeoff of a very uniform impregnation is a significantly lower conductivity compared to the BPs produced by DI and SI procedures (Table 1).

Unexpectedly, the shear strength of lap joints made with sBPs impregnated by SI and OSI remained the same as for DI (Table 2). This suggests that not the uniformity of the resin impregnation is the determinant factor but BP morphology. BPs made of SWCNTs display a stratified structure with low strength in the normal direction because of the lack of the CNT entanglement in the normal direction. Hybrid BP displays a 3D entanglement that explains their higher shear strength.

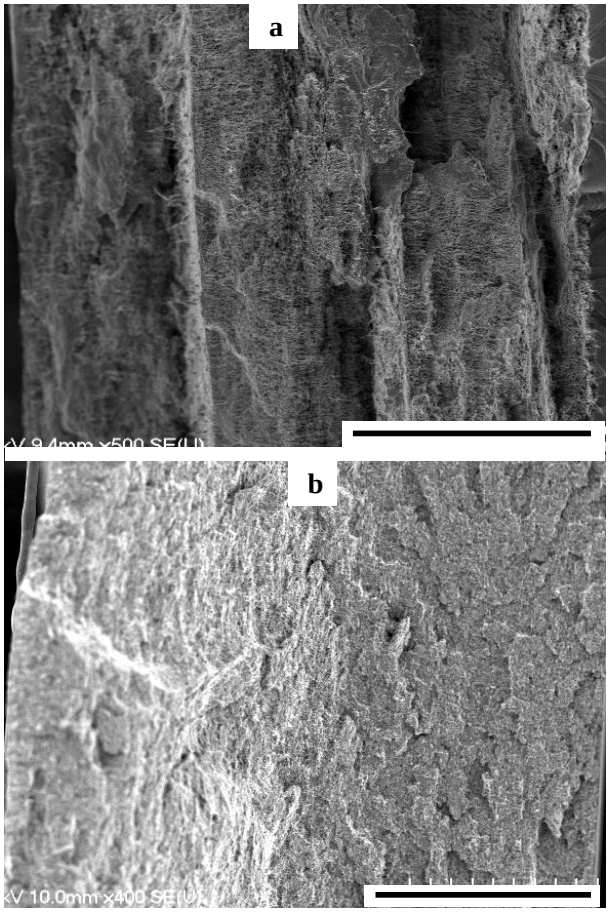

Fig. 4 SEM images of sBP (a) and hBP (b) cross sections produced by SI; scale bar 50 μm

Furthermore, fractured lap joint presented in Fig. 7a evidences the stratified morphology of the sBP (layer edges highlighted by the dashed lines), while in the case of hBP the fracture surface evidences the 3D entanglement (Fig 7b)

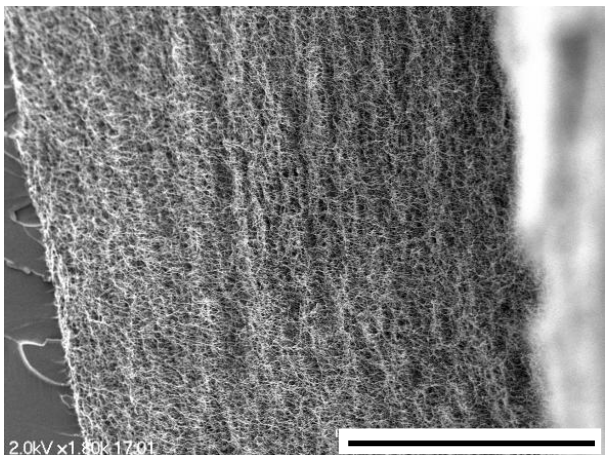

Fig. 5 SEM micrograph of a sBP cross section produced by OSI; scale bar 30 μm

It is well known that for lap joints the shear and peel stresses are maximum at the joint ends, hence the presence of a medium with low normal strength at the joint ends will clearly affect the shear strength.

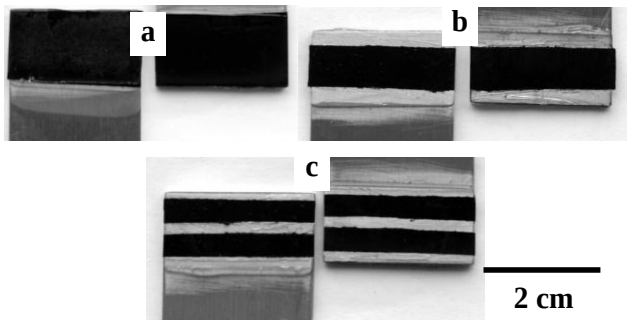

Fig. 6 Fractured lap joints with different BP patterns

The solution for this problem is to cover partially the overlap area with BP as shown in Fig 6b and c, therefore the middle part of the bonded area will be the functional part of the bond, and the resin-only strips at the end of overlap area will provide strength. The apparent shear strength of lap joints made with BP-strips that cover only 50% of the overlap area is very close to that of the neat resin while the bond

resistance is close to that obtained at 100 % surface coverage (Table 2).

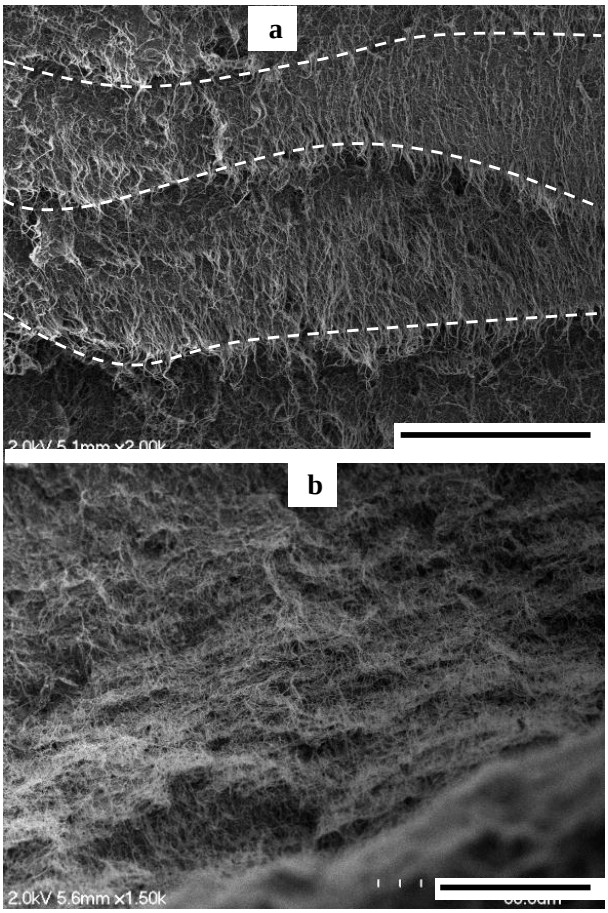

Fig. 7 SEM micrographs of the fractured lap joint made of sBP (a) and hBP (b); scale bar 20 μm

Beside the shear strength, fatigue resistance is equally important for bonded joints. Fatigue test revealed that joints made with sBP have 5 times shorter fatigue life than those made with hBP (Table 2). With high probability the low normal strength of the sBP could be held responsible for this effect.

In conclusion hybrid buckypaper that covers a fraction of the overlap area constitutes the best candidate for high strength and highly conductive adhesive with an extended fatigue life.

4. Conclusions

A new method, based on buckypapers, was developed for obtaining highly conductive bonded joints. Buckypapers made solely of SWCNTs and buckypapers made of a mixture of SWCNTs (25 %) and MWCNTs (75%) were investigated. Direct, solvent and one step impregnation were used to obtain impregnated buckypapers. While direct impregnation is the most economical it results in inhomogeneous impregnation. However, the results showed that impregnation homogeneity have no effect on the shear strength. The results strongly suggest that the BP morphology is the key parameter that determines the shear strength. Because of the stratified nature of the sBP the normal strength is much lower than in the case of hBP were CNTs form a highly entangled 3D structure. The shear strength of the lap joints made BP that covers 100 % of the overlap area was significantly lower that of the neat resin. By optimizing the surface-fraction covered by the BP it is possible to minimize the bond resistance and restore the mechanical performance. HBps that covers a fraction of the overlap area was identified as the best candidate for high strength and highly conductive adhesive with an extended fatigue life. Furthermore, using BPs it is possible to develop adhesive tapes in which the BP act as conductive and reinforcing medium as well as a spacer that allows maintaining a constant bond-line thickness.

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