CONDUCTIVE STRUCTURAL ADHESIVE WITH LOW THERMAL EXPANSION COEFFCIENT FOR AEROSPACE APPLICATIONS

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Abstract

We have developed conductive structural adhesives with low coefficient of thermal expansion (CTE) based on Epon 862 resin, nickel nanostrands and single wall carbon nanotubes as electrically conductive fillers and zirconium tungstate a ceramic material with negative CTE. The adhesives containing only conductive fillers displayed very low bond resistance and shear strength similar to the reference structural adhesive Hysol EA 9392. The adhesives containing both conductive fillers and zirconium tungstate displayed low bond resistance and 50 % lower CTE than the base resin, but the shear strength showed an important decrease attributed to the high volume fraction of zirconium tungstate.

1 Introduction

Conductive structural adhesives are needed to ensure electrical continuity of adhesively bonded parts and to eliminate supplemental time-consuming operations like inter-panel jumper cabling or silver brazing. Especially for satellite antennas made of CFRP composites, besides good electrical conductivity structural adhesive should have low coefficient of thermal expansion (CTE) in order to minimize the thermal stresses in extreme space environments.

Recently we have reported highly conductive epoxy composites based on carbon nanotubes (CNTs) [1, 2]. According to Hansen [3] nickel nanostrands (NiNSs) are a very promising filler to produce highly conductive structural adhesives.

Zirconium tungstate (ZT) exhibits isotropic negative thermal expansion over a wide range of temperatures that makes this ceramic material attractive filler that could significantly reduce the CTE of polymeric materials [4, 5].

In the present study we investigate the combined effects of zirconium tungstate and conductive nanofillers on the adhesive mechanical, electrical and thermal performances.

2 Materials and testing methods

2.1 Materials

Epoxy resin Epon 862 was purchased from Miller Stepheneson, zirconium tungstate of 99.7% purity from Alfa Aesar and nickel nanostrands from Conductive Composites. Single wall carbon nanotubes (SWCNTs) were provided by Nikkiso Co. All materials were used as received. Hysol EA 9392 adhesive system from Henkel was used as reference.

2.2. Filler dispersion

SWCNTs were dispersed by an optimized three-roll milling (EXAKT 80E, EXAKT Technologies, Inc.) in Epon 862 [1]. NiNSs and the resin were hand mixed then screened though a wire-mesh with 55x80 mesh size. A masterbatch of zirconium tungstate (95 wt %) in Epon 862 was prepared by three-roll milling.

2.3. Sample preparation

Single lap-joints with dimensions shown in Fig. 1 were prepared using aluminum 2024 T3 adherents. The aluminum coupons, prior bonding, were cleaned with acetone in an ultrasonic bath then etched in chromic acid for 30 min at 65 °C. Bond-line of 0.2 mm was obtained by glass beads.

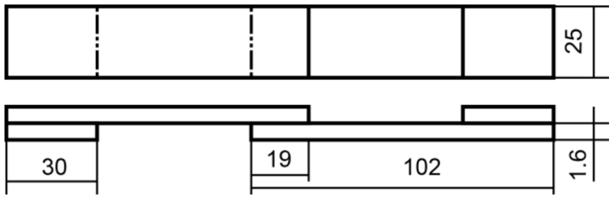

Figure 1 Single lap-joint; dimensions in mm.

Plates of 40x40x1.6 mm were obtained by loading the adhesive between two aluminum plates separated by a silicon rubber spacer. All samples were cured at room temperature for 7 days.

2.4. Testing methods

The coefficient of thermal expansion from -60 to +160°C was measured on a thermo-mechanical analyzer (TMA) TA Q400 at a heating/cooling rate of 10°C/min in pure nitrogen.

The resistance of the lap-joint was measured using a four wire method. For the electrical measurements a Keithley 6220 DC current source and a Keithley 218A nanovoltmeter were used.

The apparent shear strength was determined according to ASTM D1002-01 on a MTS 100 kN testing machine at 1.3 mm/min strain rate.

The dispersion of the fillers in the fractured samples was observed on a Hitachi S4700 SEM.

2 Results and discussion

Figure 2 presents the SEM images of NiNSs – highly conductive metallic filler but with high density, and SWCNTs – a highly conductive carbon material with low density and high aspect ratio.

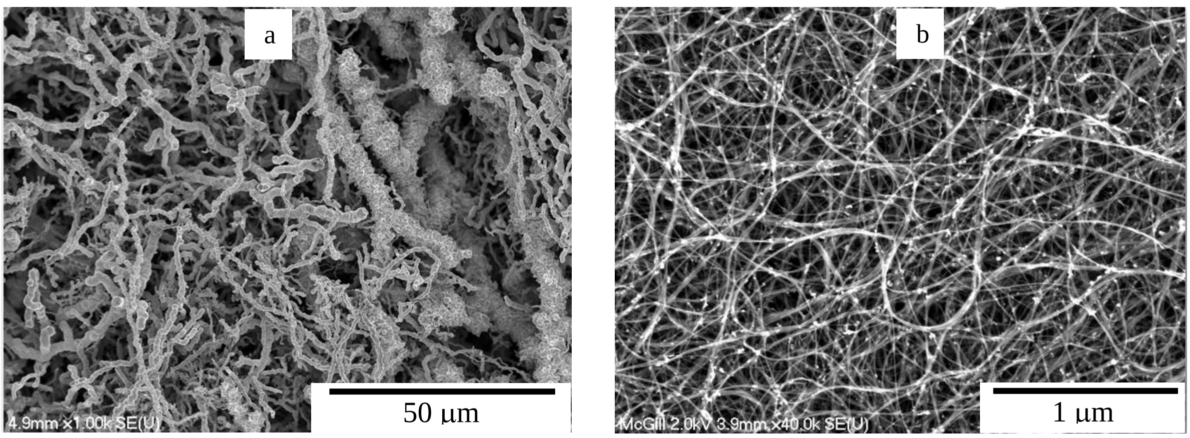

Figure 2 SEM micrographs of NiNSs (a) and SWCNTs (b)

Observing entries 3 and 4 in Table 1 the bond resistance was decreased by 11 and 8 orders of magnitude compared to reference resin when incorporating 5 vol% of NiNSs and 0.5 vol% of SWCNTs respectively into Epon 862, while the shear strength of the corresponding lap-joints was similar to that of the reference resin.

Table 1 Mechanical and electrical properties of aluminum lap-joints made with different adhesives

No	*Adhesive*	*Shear Strength MPa (SD)*	*Resistance Ω (SD)*	*Failure mode*
1	Hysol EA 9392	28.4 (0.3)	$>10^{10}$	Cohesive
2	Epon 862	29.8 (0.3)	$>10^{10}$	Cohesive
3	Epon 862 + NiNSs	28.3 (0.5)	0.08 (0.03)	Cohesive
4	Epon 862 + SWCNTs	30.1 (1.3)	83 (14)	Cohesive
5	Epon 862 + ZT	19.2 (0.3)	$>10^{10}$	Adhesive/Cohesive 50/50
6	Epon 862 + ZT + NiNSs	16.4 (0.3)	0.35 (0.14)	Adhesive/Cohesive 50/50
7	Epon 862 + ZT + SWCNTs	21.3 (0.4)	95 (16)	Adhesive/Cohesive 50/50

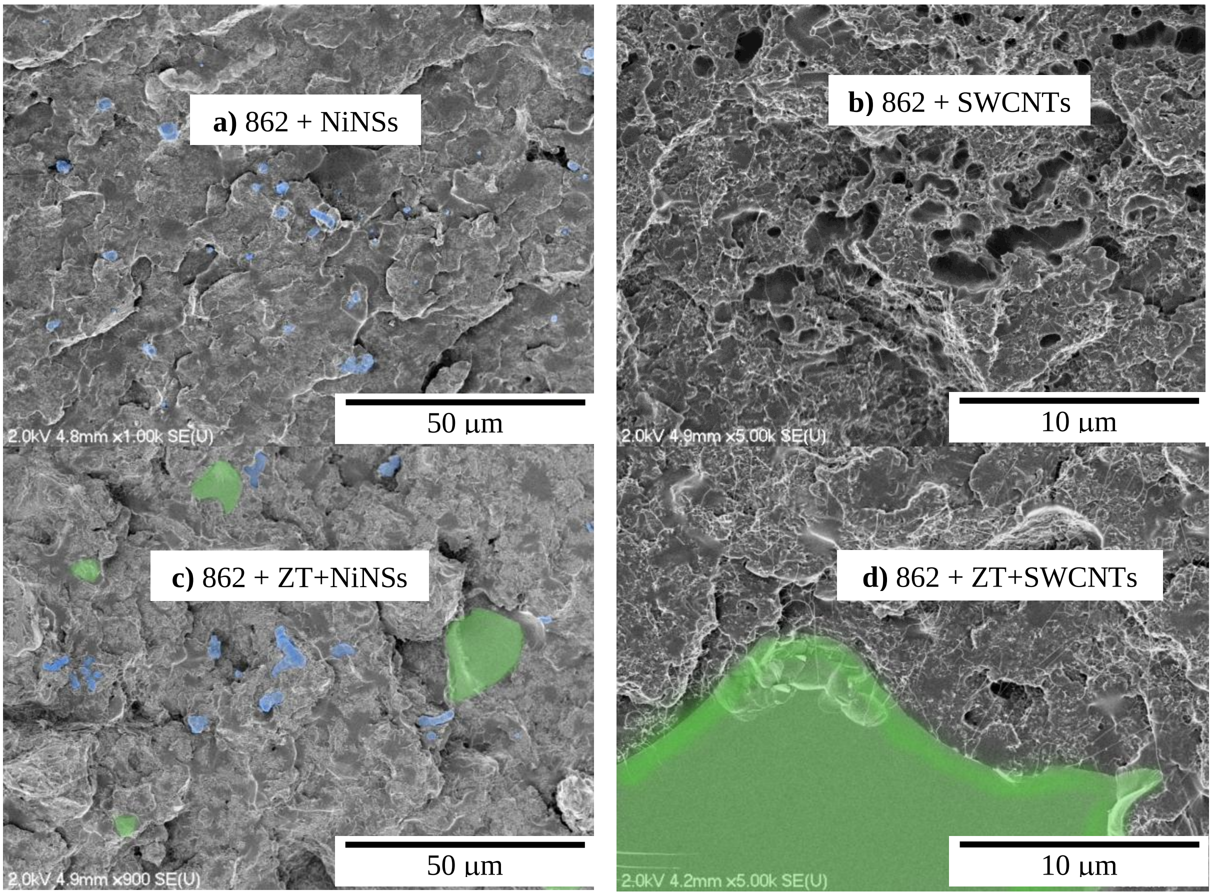

Figure 3 Low magnification SEM images of fractured adhesives with different nanofillers.
Blue – NiNSs; Green- ZT

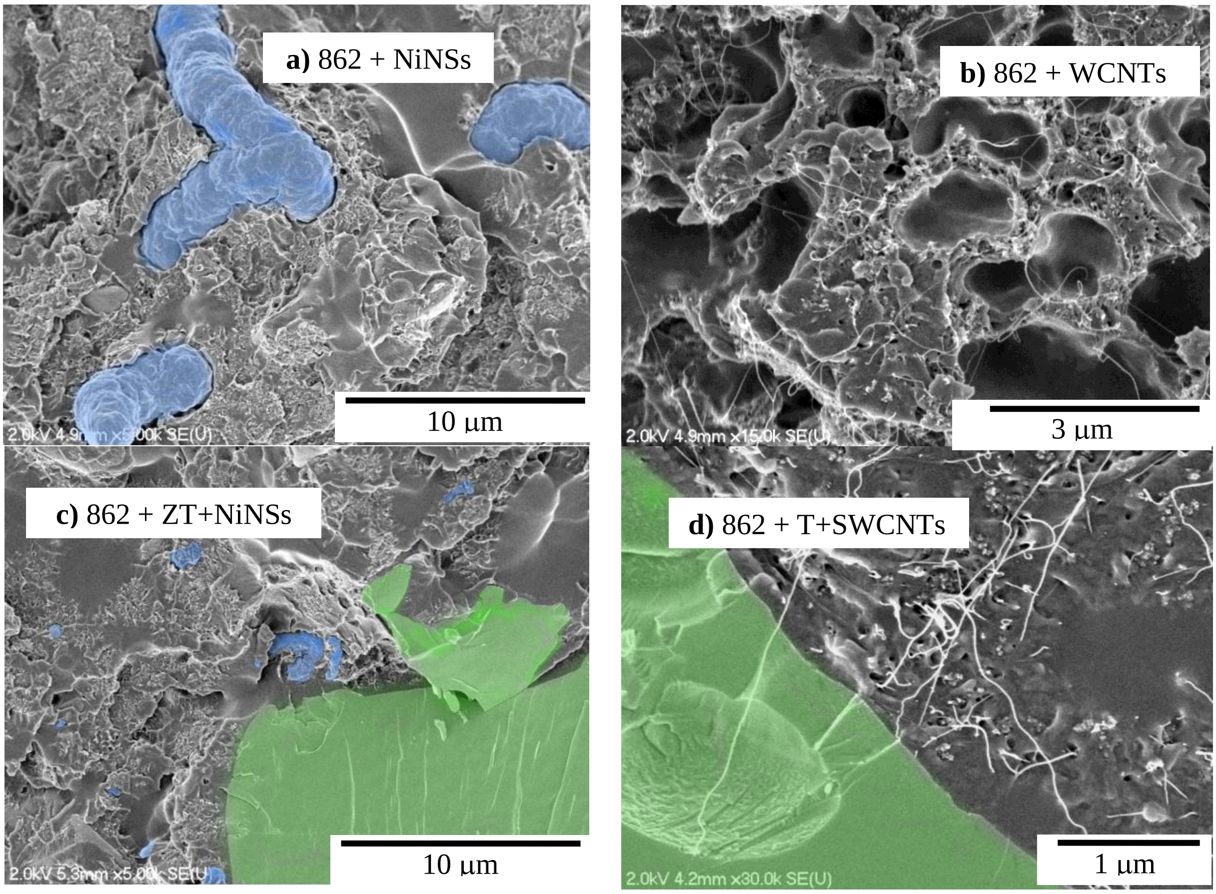

Figure 4 High magnification SEM images of fractured adhesives with different nanofillers.
Blue – NiNSs; Green- ZT

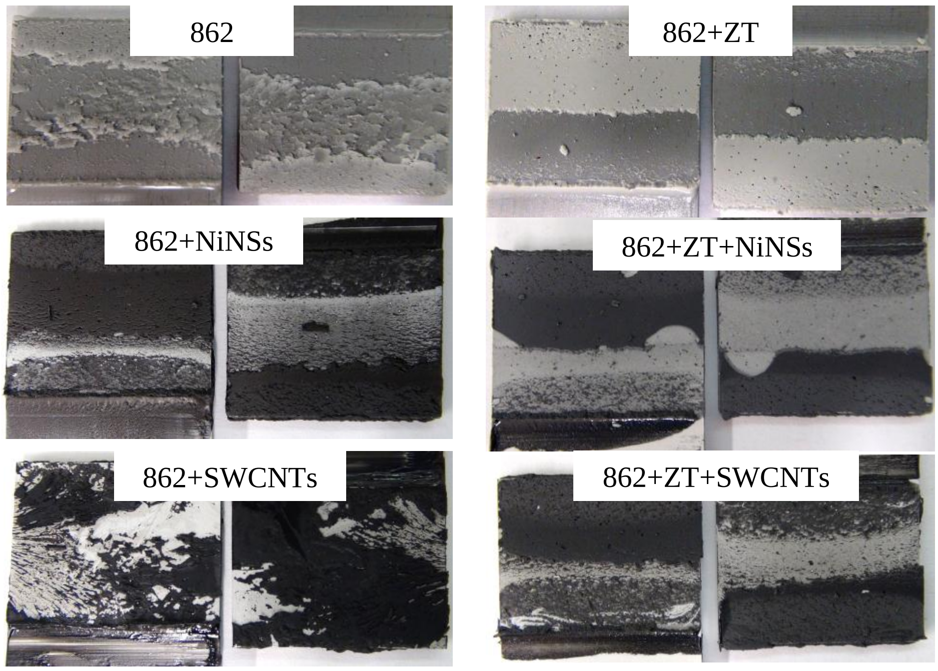

Figure 5 Images of fractured lap-joints made with different adhesives

In order to significantly reduce the CTE of the adhesive, relatively high volume fractions (30%) of zirconium tungstate had to be incorporated that in turn adversely affected the shear strength of the lap-joints (entries 5-7 Table 1). While the shear strength was affected by zirconium tungstate the resistances of the conductive adhesives were almost the same as for the adhesives without zirconium tungstate.

Lap-joints made with the base resin and adhesives containing only conductive fillers displayed cohesive failure (Figure 5 first column of images), while those containing also zirconium tungstate displayed 50% cohesive and 50 % adhesive failure (Figure 5 second column of images).

A uniform distribution of the conductive nanofillers and zirconium tungstate can be observed from the SEM images presented in figures 3 and 4.

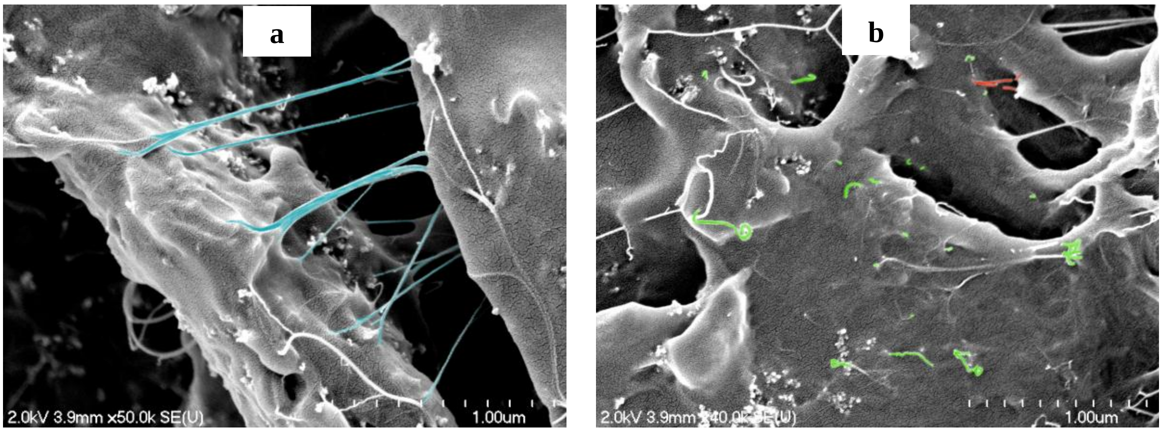

Figure 6 SEM images of the fractured lap-joint evidencing different reinforcing mechanisms of the SWCNTs

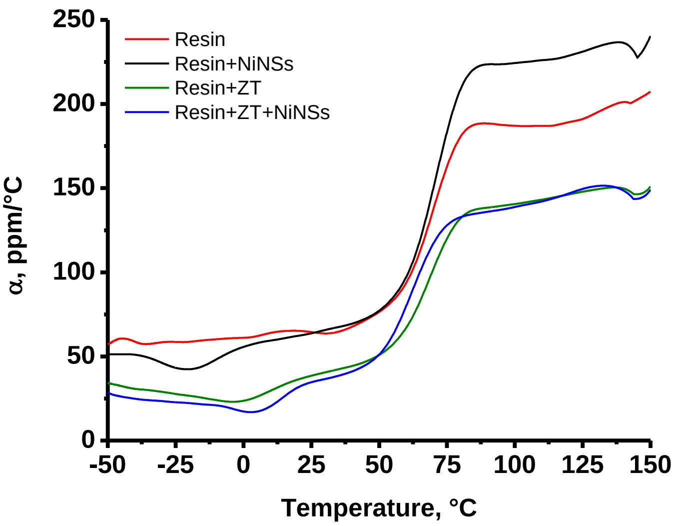

Figure 7 Temperature dependence of the CTE of adhesives made with NiNSs and ZT

Nanotube bridging (Figure 6a), short pull-outs and fractured nanotubes (Figure 6b) observed on fractured lap-joints confirm that SWCNTs are an effective reinforcement for the adhesive.

By adding 30 vol% of zirconium tungstate the CTE of Epon 862 was reduced by 50 % below as well as above the glass transition temperature (Tg) as can be observed from Figure 7. The same tendency was observed for the adhesives containing conductive fillers (Figure 7 and 8). Unexpectedly, the resin containing SWCNTs displayed significantly higher CTE especially above Tg compared to the base resin (Figure 8). We attributed this anomaly to the fact that the structure of the adhesive containing SWCNTs is highly porous (Figures 3b and 4b). In our future work we will change the degassing method to ensure a low level of porosity.

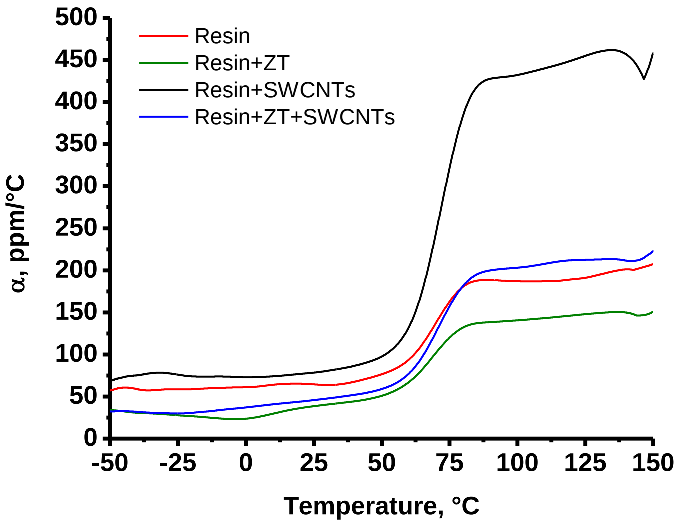

Figure 8 Temperature dependence of the CTE of adhesives made with SWCNTs and ZT

3 Conclusions

We have successfully developed new conductive structural adhesives based on Epon 862, NiNSs and SWCNTs. Bond resistances as low as 80 mΩ were obtained while maintaining the shear strength at a same level as that of the reference adhesive. Adding up to 30 vol% of zirconium tungstate it is possible to reduce by 50 % the CTE of the adhesive while maintaining low bond resistances, but the strength of the lap-joint is decreased by 45 % and 29 % for the adhesives containing NiNSs and SWCNTs respectively.

Acknowledgements

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References

[1] Rosca I.D, Hoa S.V. Highly conductive multiwall carbon nanotube and epoxy composites produced by three-roll milling. *Carbon*, **47**, pp. 1958-68 (2009).

[2] Rosca I.D, Hoa S.V. Conductive nanocomposites based on mass produced carbon nanotubes and epoxy resin, *Proceedings of the American Society for Composites, Technical Conference, 24th*, Newark, Delaware, USA (2009).

[3] Hansen N., Adams O.A., DeVries K.L., Goff A., Hansen G. Investigation of electrically conductive structural adhesives using nickel nanostrands, *J. Adhesion Sci Technol* **25(19)** pp. 2659-70 (2011)

[4] Goertzen W. K., Kessler M. R. Three-phase cyanate ester composites with fumed silica and negative-CTE reinforcements. *Journal of Thermal Analysis and Calorimetry* **93(1)** pp. 87–93 (2008).

[5] Lind C., Coleman M.R., Kozy1 L.C., Sharma G.R. Zirconium tungstate/polymer nanocomposites: Challenges and opportunities. *Phys. Status Solidi B* **248(1)** pp. 123–129 (2011).