

High conductivity with low friction dry film based coating containing carbon nano-tube for aerospace fasteners applications

Liang Zeng

Alcoa New Product Development, Alcoa Fastening System,
900 Watson Center Road, Carson, CA 90745, USA
Liang.zeng@alcoa.com

Luke Haylock

Alcoa New Product Development, Alcoa Fastening System,
3000 W. Lomita Blvd., Torrance, CA 90505, USA
Luke.haylock@alcoa.com

Abstract

Carbon fiber reinforced composite aircraft components such as wing skins are commonly mechanically fastened metallic components such as reinforcing ribs which are significantly more conductive. When an aircraft is struck by lightning, typically the charge disperses as current flowing from the composite skin through metallic component such as a rib. Typically the fasteners are the current pathway of current between the wing skins and other structures. Aircraft fastener ideally should have a combination of near metal like conductivity and low friction coefficient to manage the large currents associated with lightning strike. This is especially relevant for composite aircraft structures. Since aircraft fasteners are usually coated, there is a need for fastener coating with high conductive coatings and low friction coefficient over the last decade, coinciding with increased use of composite structures.

Currently, there are three possible methods to design conductive coatings: utilize conductive polymers as the continuous matrix, incorporate metal particles or flakes at sufficient concentration, or a combination of both methods. Increasing conductivity by incorporating conductive metal powders or flakes into a polymeric matrix requires a high amount of metallic particles, resulting in unwanted high friction coefficient and low oxidation resistances. Recently, Alcoa Fastening Systems (AFS) has successfully developed high conductivity low friction coatings by adding a small concentration of carbon nano-tubes (CNTs).

Electrically conductive coatings were prepared from aqueous dispersion of CNT and polymers based particles. With the additional carbon nanotube, the coating surface resistivity dropped significantly. The inclusion of nanotube at concentration of only 1% produced a reduction in surface resistivity from $>10^{12}\Omega/\text{square}$ to a value of $\sim 10^5\Omega/\text{square}$, and higher concentrations produced further reductions to around $500\Omega/\text{square}$. Thus, high conductivity can be achieved for aerospace fastener coatings with minimum or zero metal particles. The detailed relationship between surface resistivity and carbon nanotube concentration was evaluated. In addition, the effects of CNT on coating thermal conductivity and frictional coefficient were investigated. These coatings can be used to protect the aircraft from the consequences of lightning strike, by improving the electrical conductivity between fasteners and composite structure.

I. Introduction

Electrically conductive coatings are required for a variety of applications such as charge dissipation and radio frequency interference shielding [1]. In recent years, the development of composite aircrafts has led to a greater demand for coatings with tailored high electrical conductivity properties and functions since continuous fiber reinforced composites are more susceptible to lightning damage compared to metallic structures. This provides additional

challenges for aerospace fastener coatings. Aerospace fastener coating is designed to satisfy a wide variety of functions, such as friction modification and corrosion protection. Coating is also commonly used as a method of identification or decorative appearance. Additionally, high electrical conductivity is preferred for fastener is in the path of large currents, such as those experienced in lightning strikes on airplane composite structures. There has been a steady increase in the need for high

conductive coatings over the last two decades and the trend is expected to continue.

Theoretically, to impart electrical conductivity of coating, the quantity of conductive particles must be high enough for the particles to form an interconnected network [1-2]. The magnitude of the conductivity of coating strongly depends on the properties of the conductive particles themselves and the connections between the particles. High conductivity can be obtained through the use of very high aspect ratio conductive elements. Garboczi et al. [3] indicated that percolation occurs at 28.5% for the aspect ratio of spherical conductive particles. However, when the particle geometry is changed to an aspect ratio of 10 and 100, the percolation drops to 10.6% and 1.2%, respectively. Thus, a significant reduction in conductivity threshold can be obtained through the use of very high aspect ratio conductive pigments.

Currently, in the aerospace industry, most conductivity coatings are produced by incorporating conductive metal powders or flakes into a polymeric matrix that has desirable physical/chemical properties. Unfortunately, the typical randomly oriented metal sphere or ellipsoids have very low aspect ratio, leading to low electrical conductivity. Further increment of metal particle concentrations would improve electrical conductivity. However, this could add considerable weight for aerospace fastener coatings due to high density of metal particles. Often times, the conductive metal concentration required for a desired conductivity is very near, or above, the critical value in which a significant reduction in mechanical properties is usually observed. Furthermore, many metal particles can provide environmental effects upon outdoor exposure. Aluminum, often used as particles or flakes to improve electrical conductivity, could oxidize or even become an insulator, resulting in significantly increased electrical resistance over time. In the current aerospace fastener coating industry, there are no organic coatings conductive enough to provide complete lightning strike protection.

With excellent electrical and chemical stability, mechanical and thermal properties, Carbon nanotubes (CNTs) have enjoyed immense attention over the last several years, ranging from candidate material for use in cold cathodes for field emission display technology [4] to hydrogen storage material [5]. Another unique application of the CNTs is as electrical conductive filler in coatings, because the CNTs

have a high electrical conductivity which is higher than that of copper. Johnson et al. developed conductive coatings using very low volume concentrations multi-walled carbon nanotubes [1]. Moreover, Show et al. evaluated electrically conductive material made from CNT and PTFE [6]. The interconnection of the CNTs with one another facilitated electrical conduction. However, the amount of CNTs reached 90% that could significantly negatively affect other properties.

In this paper, CNTs were used to develop organic aerospace fastener coatings. CNTs were mixed with a few typical aerospace non-conductive coatings in an aqueous dispersion. The CNTs added aerospace coatings demonstrated sufficiently high electrical conductivity to provide enough partial or complete lightning strike protection for aerospace fasteners using extremely minimum amount of CNTs. The relationship between electrical conductivity and the amount of CNTs was evaluated. In addition, microstructural development of the CNTs added coatings were characterized. Furthermore, the effects of CNTs on fastener coatings properties such as thermal conductivity and friction coefficient were evaluated.

2. Experimental procedures

2.1. Carbon nanotube

The CNTs used in this investigation were commercial available, industrial grade multiwall nanotube (IGMWNT). They are characterized by an average diameter of 10-30 nm, a length of 2–4 μ m, a carbon purity of 90%. The CNTs were dissolved in IPA. To decrease CNTs aggregative tendency, a surfactant such as sodium dodecylbenzene sulfonate (SDDBS) was used [7].

Coating formulations were created by adding a specified amount of CNTs dispersion and typical aerospace fastener coating solution together followed by thorough shear mixing. For CNTs, due to their large surface energy, they cannot be dispersed uniformly by only mechanical mixing [8-9]. In this study, we utilized ultrasonication to disperse CNTs to avoid their agglomeration, and fabricated CNTs added fastener coating. The CNTs concentration in this coating was varied from 0 to 10% and the relationship between the electrical property and the structure of the new coating was discussed.

2.2. Coatings

In this evaluation, two typical aerospace coatings were used, APL-3 and Incotec 8G. APL-3 is phenolic resin and lubrication based coating which provides protection from damage during relative movement and to reduce friction and galling for aerospace fasteners. While Incotec 8G is an aluminum particles added phenolic resin based pigment coating that provides corrosion protection for aerospace titanium fasteners. All coating tests were conducted at Incotec Corporation. APL-3 and Incotec 8G are registered trademarks of Incotec Corporation.

2.3. Panels and measurements

To measure coating surface electrical conductivity, the CNTs added PTFE dispersion was applied to a fiberglass substrate. The sample was dried and baked at elevated temperature for an extended time. The extent of CNTs distribution within the coating was evaluated using Scanning Electron Microscopy (SEM) at an accelerating voltage of 30KV. Due to increased electrical conductivity via CNTs, no additional carbon coating was applied during SEM evaluation. The surface electrical conductivity was measured using Surface Resistivity Meter with model Monroe 272A per ASTM D-257 at low electrical conductivity, and DELCOM Conductance Monitor at high electrical conductivity up to $0.1 \Omega^2$. The friction coefficient, one of the most important reasons for applying coating on fasteners, was measured using a Friction test and wear machine with model number F-1500C Falex pin and vee block test machine per testing specification ASTM D2625. The Falex Pin & Vee Block machine utilize a 1/4 inch diameter rotating test pin against two 1/2 inch diameter vee blocks to evaluate friction and wear properties of coatings at prescribed load or pressures. In addition, thermal conductivity measurements were recorded using a TPS 2500S thermal constants analyzer, based on the theory of the hot disk transient plane source technique.

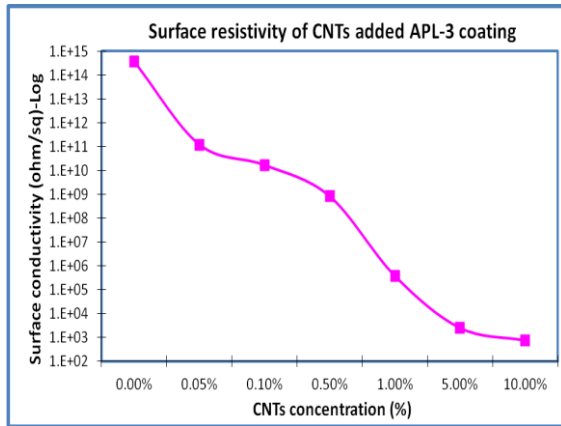
II. Results and discussions

3.1 Electrical conductivity

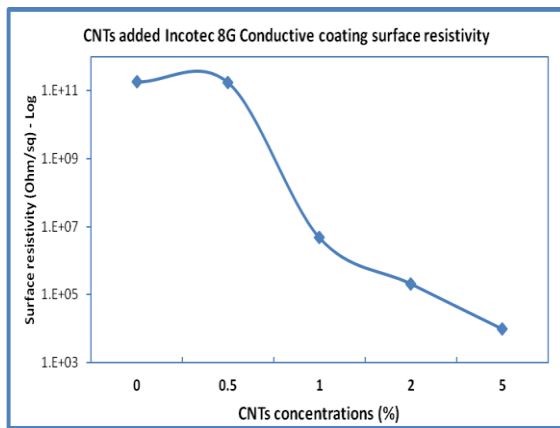
As stated earlier, a fundamental reason behind the development of this novel conductive coating is to permit formulation of electrically conductive aerospace fastener coatings at

sufficiently low volume concentrations of CNTs. Figure 1 shows the electrical resistivity of the CNT-filled APL-3 and Hi-KOTE1 coating at various CNT concentrations. Minimum electrical conductivity was observed for the pure APL-3 film with surface resistivity more than $10^{12} \Omega/\text{square}$. With the additional carbon nanotube, the coating surface resistivity dropped significantly. The inclusion of nanotube at concentration of only 1% produced a reduction in surface resistivity from $>10^{12} \Omega/\text{square}$ to a value of $\sim 10^5 \Omega/\text{square}$ and higher concentrations produced further reductions to around $500 \Omega/\text{square}$.

SEM analysis of CNTs added APL-3 films, at sufficient concentration to allow surface conductivity was also performed. Figure 2 shows the SEM image of the CNTs added APL-3 coating. The CNTs were tube shaped and open-ended. The diameter and the length were approximately 10-30 nm and few millimeters, respectively, resulting in an ultra-high aspect ratio. This is consistent with the vendor's specifications. The CNTs seem uniformly distributed with the absence of large agglomerates. The CNTs were successfully dispersed in the APL-3 coating by using the CNTs dispersion fluid. The CNTs worked as a conductive path throughout the APL-3 coating. A three-dimensional conductive network of CNTs is needed to form a highly-conductive film. From figure 1, a CNTs concentration of 1% seems high enough to form the three dimensionally conductive networks, as evident by the sharp drop of surface resistivity. This drastic drop in resistivity or increase in conductivity is called the percolation threshold. The conductivity of the coating linearly increases with the CNT concentration above the percolation threshold of 1%. Thus, the conventional coating preparation approach could make the conductive CNTs randomly distributed in the coating.

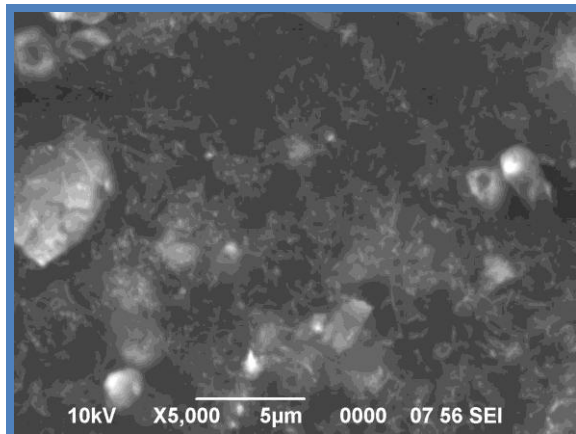


(a)

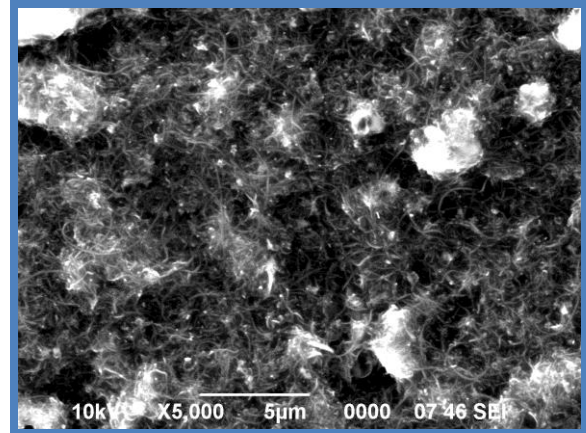


(b)

Figure 1 The relationship between surface resistivity and CNTs concentrations for CNTs added APL-3 (a) and Incotec 8G coatings (b).



(a)



(b)

Figure 2 SEM graphs showing APL-3 coating with addition of 1% (a) and 5% CNTs (b). Due to high conductivity, no surface carbon deposition was needed to view in SEM.

As expected, a significant reduction in threshold of high conductivity was achieved through the use of very high aspect ratio CNTs. CNTs have two dimensional networks of conducting nanoscale wires. Such networks show two dimensional percolation features, and evidences of a transport process that proceeds through a thermally activated charge between the various nanotube segments, without the need of heavy metal addition. Therefore, only a small amount of CNTs are needed to form the conductive network, resulting in a very low percolation threshold of 1%.

3.2 Thermal conductivity and friction coefficient

Figure 3 shows the thermal conductivity of the original APL-3 and CNTs added APL-3 coatings at various concentrations. At both testing temperature, all CNTs added APL-3 coatings demonstrated lower thermal conductivity. This is consistent with expectations that CNTs have excellent thermal conductivity along tube direction and very low thermal conductivity along the transverse direction [10-12]. The reason may relate to CNTs growth defects, entanglement of CNTs ropes, high interfacial thermal resistance between CNTs and surrounding matrix, and impact alignments [10-12]. For the current coating spraying technology, most CNTs aligned parallel to the panel direction, leading to measured lower thermal conductivity.

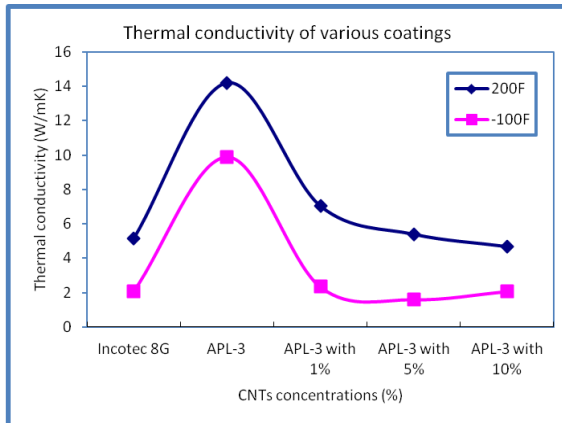
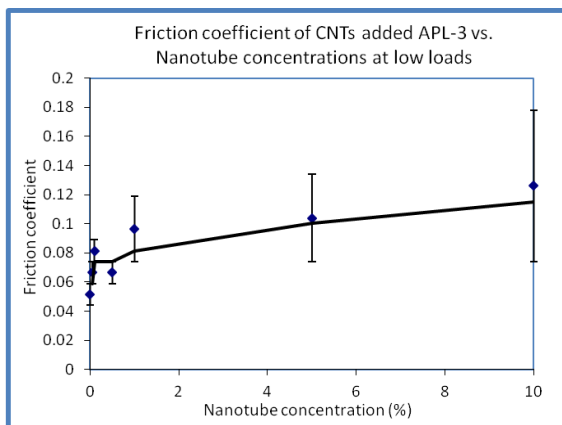


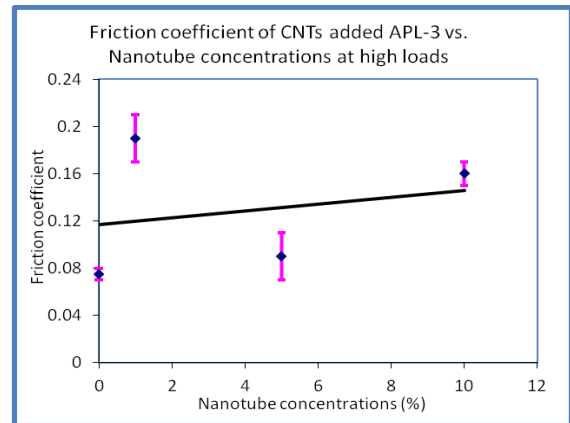
Figure 3 The additional CNTs leading to lower thermal conductivity.

Friction is the one of the most important factors for selecting fastener coatings. Measurement was conducted using a Failex testing machine at loads of 200 up to 500 pounds. At both loading conditions (Figure 4), friction coefficients consistently increased with the addition of CNTs. This is different from most reports that CNTs could reduce the friction coefficient of composite considerably under both sliding conditions, due to the effective self-lubricating effects of CNTs on coating matrix [13]. However, most researchers used high friction composites. In this evaluation, the baseline coating APL-3 already has an ultra low friction coefficient. Addition of any other component into APL-3 seems more than likely lead to a higher friction coefficient.

To achieve high electrical conductivity in combination with low friction coefficient, optimal amount of CNTs need to be determined. From figure 5, with the addition of only 0.5-1% of CNTs, low surface resistivity and friction coefficient can be reached.



(a)



(b)

Figure 4 The relationship between friction coefficient and CNTs concentrations at load of 200 (a) and 500 pounds (b).

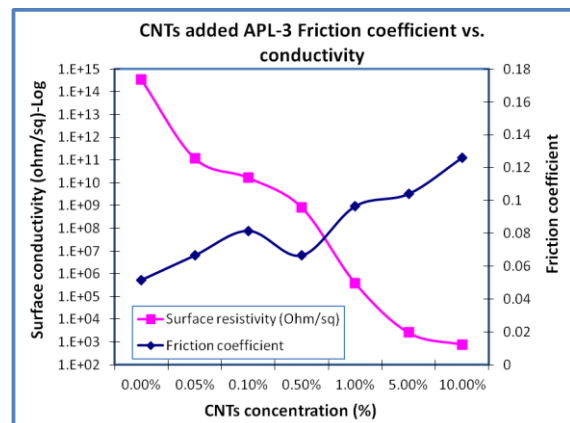


Figure 5 Optimal selection of CNTs concentration to achieve low resistivity and friction coefficient for aerospace fasteners coating applications.

3. Applications and conclusions

The CNTs filled APL-3 coating was formed by using the dispersion fluids of the CNT and the APL-3 via conventional coating approach. This new coating showed properties of electrical conductivity facilitated by the CNTs within the coating. The surface resistivity of the coating dropped significantly with an increase in the CNTs concentration, due to an ultra high aspect ratio. The inclusion of nanotube at concentration of only 1% produced a reduction in surface resistivity from $>10^{12}\Omega/\text{square}$ to a value of $\sim 10^5\Omega/\text{square}$ and higher concentrations produced further reductions to only around $500\Omega/\text{square}$. Thus, high conductivity can be achieved for aerospace fastener coatings with minimum or zero metal particles. Meanwhile, the

new CNTs added APL-3 showed very low friction coefficient.

Therefore, the CNTs added aerospace fastener coating offers lightening strike protection for airplanes due to substantially enhanced electric conductivity, mass reduction, toughness and durability, at very low nanotube concentrations over conventional metal based conductive coating.

4. References

1. J.A. Johnson, M.J. Barbato, S.R. Hopkins, M.J. O'Malley, *Progress in Organic Coatings* 47 (2003) 198.
2. R. Zallen, *The Physics of Amorphous Solids*, Wiley, New York, 1983.
3. E.J. Garboczi, K.A. Snyder, J.F. Douglas, M.F. Thorpe, *Phys. Rev. E* 52 (1995) 819.
4. Q.H. Wang, M. Yan, R.P.H. Chang, *Appl. Phys. Lett.* 78 (2001) 1294.
5. A.C. Dillon, K.M. Jones, T.A. Bekkedahl, C.H. Kiang, D.S. Bethune, M.J. Heben, *Nature* 386 (1997) 377.

6. Y. Show, H. Itabashi, *Diamond & Related Materials*. 17 (2008) 602.
7. S. Cui, R. Canet, A. Derre, M. Couzi, P. Delhaes, *Carbon* 41 (2003) 797.
8. H. Wang, *Current Opinion in Colloid & Interface Science*. 14 (2009) 364.
9. N. Grossiord, J. Loos, L. Laake, M. Maugey, C. Zakri, C.E. Koning, A. J. Hart, *Adv. Funct. Mater.* 18 (2008) 3226.
10. R.S. Ruoff, D.C. Lorents, *Carbon* 33 (1995) 925.
11. T. Borca-Tasciuc, R. Vajtai, B.Q. Wei, P.M. Ajayan, Anisotropic thermal conductivity of aligned carbon nanotube arrays, in *Thermal challenges in next generation electronic system*, Joshi & Garimella (eds), 2002 Millpress, Rotterdam., P. 79.
12. Z. Han, A. Fina, *Progress in polymer science* 36 (2011) 914.
13. H. Meng, G.X. Sui, G.Y. Xie, R. Yang, *Composites Sci. & Tech.* 65 (5) (2009) 606.