CARBON NANOFIBER FILLED MATERIALS FOR CHARGE DISSIPATION

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Abstract

This work explores the possibility of using carbon nanofibers to create improved versions of antistatic and conductive polyimide (e.g. Kapton™) for use in satellite charge control and dissipation. Carbon nanofibers have superior properties making them a candidate for this application, including very small diameter (to fit within a thin film), high aspect ratio (to form a network), moderate electrical conductivity, and excellent dimensional stability. Nanofibers in the diameter range from 60 – 200 nm (as distinct from smaller nanotubes) are now available relatively cheaply and in quantity. The primary challenge in making polyimide films is achieving adequate dispersion of nanofibers. This is complicated both by the fact that the nanofibers are entangled as produced, and that they are not naturally well wet by the polymer, causing them to agglomerate during processing prior to polyimide film casting. This paper describes methods for surface modification of nanofibers, as well as size separation of nanofiber agglomerates, to promote adequate dispersion in polyimide. Conductivity data on cast nanofiber filled polyimide films are also presented.

Introduction

In order to help mitigate differential charging on spacecraft and satellites, improved polymer materials are needed with electrical conductivity that is both sufficient to bleed charge and stable under temperature excursions typical to the orbital environment. The conductivity must be added without degradation of mechanical properties or increase in the material weight. Conductive versions of polyimide or teflon would be particularly useful.

Polyimide filled with carbon black is currently available. However, because carbon black is characterized by low aspect ratio particles, relatively high loadings are required to obtain a given level of conductivity, potentially compromising mechanical properties of the host polymer. Also, the materials are subject to electrical conductivity reduction or failure during relatively mild temperature excursions as thermal expansion of the matrix polymer pulls the conductive particles out of contact. Such failure may also occur under non thermally induced strains.

The work reported on here seeks to employ low cost carbon nanofibers to create improved forms of carbon filled polyimide. The high aspect ratio of the nanofibers is conducive to formation of a conductive network that both achieves a given level of conductivity at lower loading than is possible for low aspect ratio particles, and is less susceptible to disruption during thermal or mechanical expansion of the matrix. The primary challenges in crafting such a material include achievement of good dispersion of the nanofibers, and creation compatibility between the nanofiber surface chemistry and the polymer processing chemistry.

Carbon Nanofibers

The carbon nanofibers used in this work were Pyrograf®-III. The diameter of this nanofiber is typically in the range from 60 – 200 nm, with a length of 10 – 100 microns, and thus an aspect ratio in the range of 150 – 1500. The morphology of this nanofiber is that of stacked graphitic cones (as opposed to concentric graphitic cylinders, characteristic of multiwall nanotubes), as shown in Figure 1. Note that the graphitic planes do not run parallel to the fiber axis (indicated by a long white arrow), but are tilted at an angle. It is possible for the nanofiber to have a chemical vapor deposition (CVD) of carbon on the surface (as indicated in the figure). However the nanofibers used in the current effort typically do not. While the face of a graphitic plane can be a very inert surface that is difficult modify without damage to a nanofiber/nanotube, the exposed edges of these planes typical of Pyrograf®-III can allow more freedom for chemical modification to tailor the nanofiber for compatibility with specific polymers and polymer chemistries.

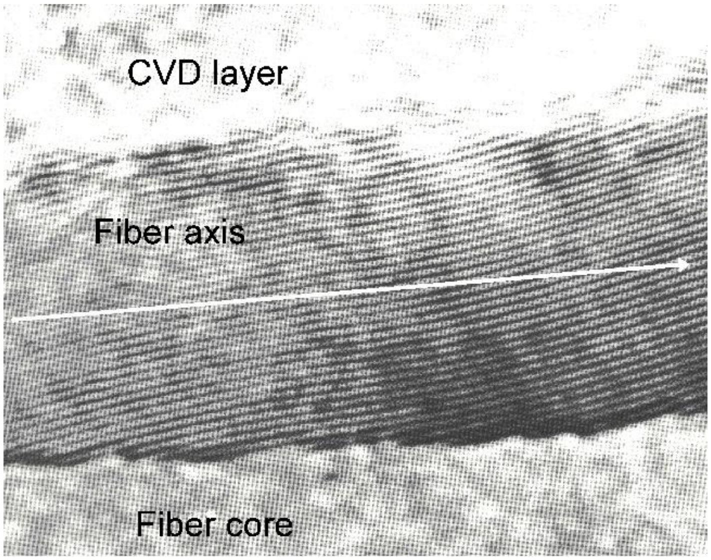

Figure 1. Morphology of Pyrograf®-III carbon nanofibers.

Nanofiber Dispersion

A key to achieving the best performing materials is to obtain the best possible dispersion of carbon nanofibers. This is a particular challenge for carbon nanofibers because they form entangled bundles during their growth process, and because the same property that allows them to form a conductive network at low volume, their high aspect ratio, also makes it difficult for them to move past one another to become disentangled. (Indeed, some aggressive methods to achieve dispersion do so by reducing the aspect ratio, which is detrimental to the desired goal.) Truly monodisperse nanofibers may be extremely difficult to achieve, and often the best one can strive for is to minimize the size of entangled groups of nanofibers. Such minimization of bundle diameter is especially important for polyimide films, which are typically less than 4 mils (100 microns) thick. In these materials, a large nanofiber bundle is not just inefficiently dispersed, but actually represents a visible flaw in film, compromising its mechanical integrity.

Three methods have been used to minimize nanofiber bundle diameter and achieve better dispersion: ultrasonic agitation, a chemical method for sorting nanofiber bundles by size, and chemical modification of the nanofiber surface to promote solvent compatibility.

Ultrasonic agitation was somewhat effective improving nanofiber dispersion and reducing nanofiber bundle size. Table 1 shows an example of how the distribution of bundle diameters changes for nanofiber suspended in water as a function of sonication time. The "mean" column gives the bundle diameter, in microns, that represents the 50th percentile of those in suspension. The "d10" and "d90" columns given the diameter for the 10th and 90th percentiles, respectively. "d99.9" indicates the maximum observed bundle diameters. One can see that sonication reduces the bundle diameters at all percentiles. One also observes that the accessible surface area of the nanofiber increases as the nanofibers are dispersed. Importantly, the size of the largest bundles is greatly reduced. Ideally, the maximum bundle diameter should be below 20 µm for casting of high quality polyimide films. Sonication alone is not sufficient to achieve this goal.

Table 1. Example of nanofiber bundle diameter distribution vs. sonication time.

Sonication time (min)	d10 (µm)	Mean (µm)	d90 (µm)	d99.9 (µm)	Surface Area (cm^2/cm^3)
0	13.61	48.56	98.67	145.00	2,569
1	5.79	18.58	29.06	45.24	7,397
5	4.44	16.92	24.84	37.47	9,008
10	3.89	16.18	23.68	36.90	10,651
∞ (projected)	~3	~16	~23	~35	~12,000

A second method for reducing bundle diameter in the final material is to sort the larger bundles out of the mix at the start. This can be done by a chemical process in which the nanofiber is treated with starch. The starch attaches to the outside of the nanofiber bundles and facilitates their suspension in water. This sets up a competition between the starch working to hold the fiber bundles in suspension, and gravity. Only smaller bundles, with a higher surface to volume ratio, and therefore a larger proportion of starch, are able to stay in suspension. Large bundles precipitate and can be removed before further processing. The starch can then be easily removed from the nanofiber that is retained in suspension.

Table 2 shows an example of nanofiber bundle diameter distributions after a starch sorting procedure. Here we see that the diameter distribution is improved at all percentiles relative to unsonicated nanofiber, and in particular there the size of particles at and below the 10th percentile is much smaller than even for the most sonicated nanofiber. The accessible surface area is concomitantly increased. There still remain a small percentage of larger diameter bundles, but these seem to be more readily broken up by sonication than those that have not received the starch treatment, as evidenced by the last line of the table. (Presumably, these are bundles of nanofibers that are less densely packed than others. Such bundles would allow starch to penetrate toward their center, giving them a high proportion of starch and better tendency toward suspension. Also, such loosely packed bundles would more easily fall apart during sonication.) The combination of the starch and sonication treatments appears to reduce all bundle diameters below the 20 μm limit for high quality films.

Table 2. Example of nanofiber bundle diameter distribution after starch treatment.

Sample Treatment	d10	mean	d90	d99.9	Surface Area
Starched	0.61	18.3	76.4	86.4	28,558
Starched and Sonicated	0.52	5.5	10.1	14.7	39,135

Finally, dispersion can be enhanced by treating the nanofiber for maximum compatibility with the solvent needed for casting the given polymer system. Polyimides, such as Kapton™, are typically cast from a chemistry that starts with the polymer dissolved in dimethylacetamide (DMAc) or similar solvent. The carbon nanofibers must also be suspended and dispersed in the solvent. As grown, the nanofibers are incompatible with DMAc and tend to precipitate out in larger agglomerates. To overcome this, the surface must be functionalized with carboxylic acid groups (COOH). This can be accomplished by wet treatment with sulfuric and nitric acid, which can put up to 20 atom % of oxygen, primarily in the form of carboxylic acid, on the nanofiber surface. Somewhat lesser, but still sufficient, amounts of oxygen can added by proprietary alkaline wet chemistry or *in situ* modification of the nanofiber growth process. The latter two methods are more amendable to large scale production than the acid based treatment. Nanofibers treated by the above methods were found to suspend readily in DMAc, and to disperse far better than untreated nanofiber.

Polyimide Film Casting and Properties

A 75 micron (3 mil) thick film cast in a Kapton™-like material with 16.7 % carbon nanofibers by weight was adequately strong (as determined by qualitative inspection), and had an electrical conductivity of 70 Ω/square (equivalent to a bulk resistivity of 0.5 Ω-cm). This material was cast from a solution in DMAc.

A similar effort in a polyamic acid derived polyimide resulted in a sample with resistivity of approximately 30 Ω/square. The mechanical properties of this specimen were also acceptable. This material, with a ketone linkage rather than the ether linkage typical of Kapton, was cast from a solution of n-methyl pyrrolidone (NMP).

The electrical performance of these films is superior as compared to Du Pont's current version of conductive polyimide, Kapton 275XC, which has a conductivity of 230 to 290 Ω/sq. It is apparent that there is latitude to work at lower nanofiber volume fraction (which could have mechanical benefits) and still obtain improved electrical performance over the state of the art. (It should be noted that the Kapton film was not cast with the best nanofiber dispersion so far observed, and it is possible that further gains in performance will result when a more uniform film is cast from a suspension containing smaller nanofiber agglomerations.)

Additional casting efforts are underway to study higher and lower loadings of nanofibers, and to extend into other polyimide materials, such as bis analine M, and oxydianaline.

Conclusion

While this remains a work in progress, with much of the parameter space yet to be examined and some improvements in the degree of nanofiber dispersion desirable, it appears that carbon nanofibers can indeed be the basis for an improved family of conductive polyimide materials, giving specific levels of conductivity at lower loading fractions than carbon black based materials.

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References

1. Produced by Pyrograf Products, Inc., Cedarville, OH.