

CARBON NANOMATERIAL SHEET GOODS FOR MULTI-FUNCTIONAL STRUCTURAL COMPOSITES

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Introduction

Carbon nanofibers (CNF) have been shown to be useful additives for improving the performance of polymer matrix composites (PMC) [1-9], but performance has frequently been hindered by limits encountered in composite processing. Historically, incorporating nanofibers and other nanomaterials into structural composites has required pre-dispersion steps using specialty dispersion techniques. Filtration of CNF by larger reinforcements is often a problem when incorporating nanomaterials into PMCs through RTM and VARTM. The use of a sheet form composed of CNF eliminates issues of pre-dispersion, re-agglomeration during storage or composite processing, and allows insertion into pre-preg in the same manner as traditional reinforcement materials. Composites fabricated with CNF sheets can demonstrate multi-functional property enhancements without altering traditional composite manufacturing processes. The approach investigated involves combining off-the-shelf carbon fiber veil with carbon nanomaterials, both of which are available from domestic producers in large volumes at low-cost. The role of the carbon fiber veil is to provide a low density, sufficiently strong support for the carbon nanofiber. The role of the carbon nanofiber is to boost transport properties such as electrical and thermal conductivity, shielding performance, vibration and acoustic damping, without dramatically increasing the areal weight or thickness. This approach combines traditional composite manufacturing with nano-materials technology to synergistically synthesize reliable, structural multi-functional materials without the need for costly, time consuming secondary operations. CNF typically has an average diameter variable from 60 to 200 nanometers and lengths from 100 to 200 micrometers, resulting in aspect (length/diameter) ratios of 500-1000, or higher, and a very high surface area. CNF, as a discontinuous nanoscale additive, offers a choice of aspect ratio and a high surface area, enabling physical contact and chemical bonding of a much higher percentage of the polymer matrix compared to conventional PAN-derived carbon fiber, essentially providing reinforcement of the matrix at the molecular level. Such molecular level reinforcement has been shown to boost mechanical properties, improve vibration damping, reduce micro-cracking induced by thermal cycling, and reduce permeability.

Experimental

Carbon nanofibers (PR-25-XT-PS and PR-25-XT-HHT, Pyrograf Products, Inc., Cedarville, OH) were dispersed in an organic solvent using a MISONIX sonic probe. The dispersed CNFs were then sprayed onto a PAN carbon non-woven veil material. This method applies a uniform webbing of dispersed

nanomaterial to form a continuous network between the nanofiber and carbon fiber veil for maximum conductivity at the lowest possible loading. An elastomeric binder was applied following CNF spray-deposition to prevent CNF slough-off. CNF mat samples were then consolidated using compression rollers. CNF mat samples that exhibited good flexibility and handle-ability were characterized for thickness, areal weight, and electrical sheet resistivity. Thickness of CNF mat samples was determined using digital micrometers. CNF mat materials were characterized for electrical performance by measuring the DC resistivity of each sample made. This was accomplished by a four-probe sheet resistance measurement system in accordance with ASTM D257. Optical micrographs of the product produced are shown in Fig. 1.



Fig. 1 Optical images of nanofiber mat produced via spraying. The spray process generates a well-developed network of nanofiber supported by the carbon fiber veil.

Over thirty formulations of CNF blends composed of differing aspect ratio fibers and total CNF loading were produced and evaluated for D.C. surface resistivity, density, and thickness. An optimum formulation was used to generate over 250 ft of nanomat for use in prepegging trials. High strength to provide handling ease and straightforward production of pre-preg rolls using conventional methods has been observed from the nanofiber mat.

It is known in the literature that bromine intercalation increases the electrical conductivity of graphitic materials to be near the electrical conductivity of metals [10]. To explore

the prospect of increasing the electrical conductivity of the CNF mat through intercalation additives, selected samples of CNF mat was exposed to saturated bromine vapor at -5 C for five days, and then allowed to de-gas in an open hood for 8 days. The intercalated CNF mat showed an approximate 7 % gain in mass over the pristine CNF mat.

Results and Discussion

Small hand-sheets were fabricated from several types and grades of carbon nanofiber to determine which carbon nanofiber variant and formulations provide the best electrical resistivity. At the same areal weight, nanomats produced with a blend of PR-25 heat treated to 700°C and 1500°C had significantly higher surface resistivity when compared to a nanomat produced with only PR-25 that has been heat treated to 3000°C. The results of these experiments are shown in Table 1.

Table 1. Effect of CNF type and grade on surface electrical properties.

Sample ID	Areal Weight (gsm)	Thickness (mils)	Sheet Resistivity (ohm/square)
A (Blend of CNF types)	41	12	4.51
B (PR-25 XT HHT)	41	12	2.85

It was also found that blends of milled and non-milled PR-25-XT-HHT provided the best shielding performance at a reduced thickness. Comparison of nanomats produced with various compositions of carbon nanofiber and at various areal weights reveals that the fiber type and aspect ratio of the nanofiber plays a crucial role in the shielding performance.

Bromine intercalation proved an effective way of reducing the electrical sheet resistivity of the CNF mat. Figure 2 shows electrical sheet resistivity of CNF mat before and after intercalation as a function of areal weight.

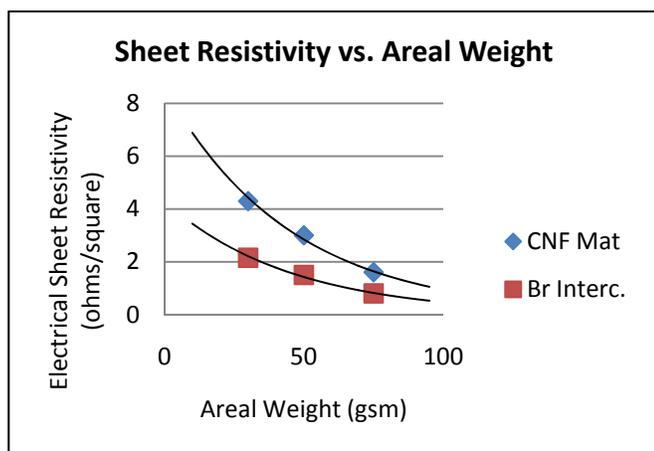


Fig. 2. Sheet Resistivity of CNF mat as a function of areal weight for pristine and bromine-intercalated CNF mat.

Conclusions

A method of producing a nanofiber mat composed of highly graphitic carbon nanofibers (PR-25-XT-HHT) in an isotropic array embedded in carbon fiber veil has been developed. Over thirty formulations of CNF blends were produced and evaluated for D.C. surface resistivity, density, and thickness. Areal weight can be tailored using combinations of CNF having different aspect ratio and degree of graphitization. The surface resistivity of the resulting mats was dependent on the areal weight. Bromine intercalation of heat-treated CNF mat was observed to result in a weight gain (bromine retention) of about 7%, with a corresponding decrease in sheet resistivity by a factor of 2. An optimum formulation was used to generate over 250 ft of nanomat for use in prepregging trials. Sufficient strength to provide handling ease and straightforward production of pre-preg rolls using conventional methods has been observed from the nanofiber mat. Carbon nanofiber mat having properties useful for imparting electrical conductivity to structural composites can be produced with conventional commercial materials.

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