Multifunctional nanocomposite coating for wind turbine blades

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In this study, multifunctional carbon nanofiber (CNF) paper-based nanocomposite coating was developed for wind turbine blades. The importance of vibration damping in relation to structural stability, dynamic response, position control, and durability of wind turbine blades cannot be underestimated. The vibration damping properties of the nanocomposite blades were significantly improved and the damping ratio of the nanocomposite increased by 300% compared to the baseline composite. In addition, the CNF paper-based composite exhibited good impact-friction resistance, with a wear rate as low as $1.78 \times 10^{-4}$ mm$^3$/Nm. The nanocomposite also shows the potential to improve the blockage of water from entering the nanocomposite, being a superhydrophobic material, with a contact angle higher than 160.0$^\circ$, which could improve the longevity of a wind turbine blade. Overall, multifunctional nanocomposite coating material shows great promise for usage with wind turbine blades, owing to its excellent damping properties, great friction resistance, and superhydrophobicity.

Keywords: multifunctionality; nanocomposite; surface coating; wind turbine blade

1. Introduction

Wind energy is a renewable energy source that produces no atmospheric pollution in the process of energy production. The fastest growing sustainable energy source, worldwide capacity of wind energy has reached 159,213 MW, out of which 38,312 MW were added in 2009, according to the World Wind Energy Association. Between 2008 and 2009 wind power showed a growth rate of 31.7%, the highest rate since 2001, with a doubling of wind capacity every three years. The maintenance of the ever increasing number of wind turbines become a significant issue, calling for research into the environmental risks associated with the operation of large-scale commercial wind ventures. The structural and aerodynamic properties of the blades are fundamental to efficiently deriving power from
wind. Ideal wind turbine blades are a combination of smooth surface for aerodynamic efficiency and optimal mass distribution. With regards to the weight consideration, glass fiber-reinforced or carbon fiber-reinforced polymer composites are commonly used for the fabrication of wind turbine blades. Although a strong database of documentation exists for industry standards, there are still several issues associated with the use of these materials.

The smooth surface of wind turbine blades disappears as a result of the wind that the turbine is designed to use, due to the large amounts of sand and water droplets it carries, which significantly degrade the aerodynamic performance and reduces power output. The potential for erosion depends on the force with which the particulate matter impacts the airfoil, which itself is related to geometric shapes and relative velocities of both the airfoil and impacting particles; the wind speed and rotational speed of the blade determine the impact velocity. According to the research of van Rooij and Timmer [1], the effect of roughness on a blade’s aerodynamic performance depends on the geometric design of the blade. Whereas a blade may be initially designed to produce minimal energy loss, surface roughness changes during operation due to erosion, and will inevitably lead to unpredicted energy loss. The resistance to friction wear of the blade’s surface is the key to the erosion. A great deal of research has been done to increase the friction resistance of the polymer composites by adding different kinds of fillers including short aramid, glass, or carbon fibers [2–6], alumina, titanium dioxide (TiO₂), zirconium dioxide (ZrO₂), silicon carbide (SiC), polyetheretherketone (PEEK) [7], polyamide (PA) [8–11], polyphenylene sulfide (PPS) [12–15], polyoxymethylene (POM) [16], and polytetrafluoroethylene (PTFE). However, all of the previous research focused on the results from directly mixing the particles with resin. In this study, a carbon nanofiber (CNF)-based hybrid paper was developed to be used as surface coating material and integrated with composite panels as a surface protective layer. In addition to erosion, the wind loading of the blades of a wind turbine introduces a considerable amount of vibration, with resonance posing a great concern by both decreasing production efficiency and potentially damaging the structure itself. As such, the vibrational damping properties of wind turbine blades should also be taken into consideration, with blade materials possessing a high damping ratio being highly desirable. In this study, CNF paper-based coatings were investigated for use on wind turbine blades to promote impact-friction resistance, superhydrophobicity, and high damping ratio. Such a multifunctional coating made from carbon nanofiber paper was applied to composite laminate using standard resin transfer molding process.

2. Experimental

2.1. Materials

Pyrograf-III™ carbon nanofibers (PR-PS-25) were obtained from Applied Sciences Inc. The nanofibers have diameter and length ranges of 50–100 nm and 30–100 μm, respectively. Nanoalumina particles (Kronos 2310), short carbon fiber (Kureha M-2007s), and graphite flakes were incorporated into the carbon nanofiber paper. Unidirectional carbon fiber mats, woven glass fiber, woven carbon fiber, and woven basalt fiber were used as fiber reinforcements, each of which could potentially be used for manufacturing wind turbine blades. Unsaturated polyester resin from Eastman Chemical Company was used as the matrix, with a mixture weight ratio of the polyester resin to a methyl ethylketone peroxide (MEKP) hardener of 100:1.

2.2. Grating Polyhedral Oligomeric Silsesquioxane (POSS) onto carbon nanofibers

Figure 1 illustrates the preparation of POSS covalently functionalized CNFs. The pristine CNFs were oxidized with a mixture of nitric acid and sulfuric acid (1/3 by volume) in
an ultrasonic bath at 40°C for 2 h and then refluxed for 2 h. After cooling to room temperature, the mixture was diluted with a large amount of deionized water, then vacuum filtered through a polycarbonate film. The acid-modified CNFs were washed with deionized water until the pH value of the mixture was close to 7. The modified CNFs were dried at 60°C in vacuum oven for 2 h and then grounded to a powder with a mortar and pestle. A mixture of acid-modified CNFs (0.6 g), thionyl chloride (SOCl₂ with large amount), and N,N-dimethylformamide was dispersed in an ultrasonic bath for approximately 2 h and refluxed at 70°C for 24 h. The residual SOCl₂ was removed by reduced pressure distillation to yield acyl chloride-functionalized CNFs (CNFs-COCl). The CNF-COCl (0.5 g), POSS-NH₂ (3 g), and 1 ml triethylamine (Et₃N) – used as a catalyst – were added in a glass flask and dispersed in an hydrous chloroform (CHCl₃). The mixture was suspended in an ultrasonic bath at 40°C for 2 h, and stirred by magnetic stirrer for 72 h in an oil bath under highly purified nitrogen gas atmosphere. The product obtained was then vacuum-filtered and washed five times with excess CHCl₃ to remove the residual POSS molecules, and then dried to yield the POSS-g-CNF.

2.3. Preparation of carbon nanofiber papers incorporated with other nanoparticles
The nanofibers were divided into several parts evenly, and then were transferred to three 1000 ml beakers and 400 ml deionized water was added to each. The solution was sonicated using a sonicator for 30 min, and then cooled to room temperature and 10 drops of Triton-X 100 surfactant were added. The preparations were then sonicated twice more at 30 min intervals and cooled to room temperature. Finally, the as-prepared suspensions were sonicated for 2 min and then transferred to a filtration system. The CNF paper was made by filtering the suspension through 0.4μm hydrophilic polycarbonate membrane using a pressure filtration system. Once the paper has finished filtration, the filter with CNF paper was carefully removed and placed onto a piece of paper where the filter was detached. The finished piece of the nanofiber paper, which was approximately 12.5 cm in diameter, was then dried in an oven at 120°C for 2 h to prepare it for usage in the nanocomposite.

For the tribological study of the coating, six different types of paper were fabricated from the aforementioned paper-making process, and are listed in Table 1. The fabrication procedures of the various types of hybrid CNF paper can be found in previous research [17].

2.4. Processing of carbon nanofiber paper based composites
Vacuum-assisted resin transfer molding (VARTM) process has been widely used to produce low-cost, high quality, and geometrically complicated composite parts. In this study,
Table 1. Particle composition of tested CNF papers.

| Sample ID | PR-PS-25 CNF (g) | Graphite flakes (g) | Short carbon fiber (g) | Nano-TiO$_2$ particles (g) | Nano-Al$_2$O$_3$ particles (g) |
|-----------|------------------|---------------------|-----------------------|---------------------------|-----------------------------|
| G1        | 2.4              | –                   | –                     | –                         | –                           |
| G2        | 1.6              | 0.8                 | –                     | –                         | –                           |
| G3        | 1.6              | –                   | 0.8                   | –                         | –                           |
| G4        | 1.6              | 0.4                 | 0.4                   | –                         | –                           |
| G5        | 1.6              | 0                   | 0                     | 0.4                       | 0.4                         |
| G6        | 1.6              | 0.4                 | 0.4                   | 0.4                       | 0.4                         |

The VARTM process was used to fabricate the CNF paper-based composites, which was carried out in three steps. In the first step, glass fiber mats and CNF paper were placed on the bottom half of a mold. After the lay-up operation was completed, a peel ply, resin distribution media, and vacuum bag film were placed on the top of fiber mats. The vacuum film bag was then sealed around the perimeter of the mold and a vacuum pump was used to create a vacuum within the mold cavity, which then utilized atmospheric pressure to push the resin from a reservoir into the cavity and infuse the part. In the VARTM process, the distribution media provided a high permeability region in the mold cavity, allowing the resin to quickly flow across the surface of the laminate and then wet the thickness of the laminate, with the dominant impregnation mechanism in the VARTM process being the through-thickness flow of resin. Following the completion of the infusion process, the composite part was cured at the room temperature of 177°C for 24 h, and finally post-cured in the oven for an additional 2 h at 100°C. For the damping study, composite laminates consisted of eight plies of fiber glass with a single layer of carbon nanofiber on the surface.

2.5. Tribological test of composites coated with carbon nanofiber paper

The pin-on-plate testing was performed with a tribometer manufactured by Microphotonics. In a typical pin-on-plate tribology test, the pin (or ball) is loaded with dead weight and pressed against the plate (coated laminate) that is then spun at a given speed. During the test, the instrument gives real-time outputs of frictional force, coefficient of friction (COF), temperature of the pin/ball, wear depth, and wear factor for the sample being tested.

2.6. Damping test of carbon nanofiber paper based nanocomposites

The composite beam without the CNF paper and the nanocomposite beam with CNF paper were used as the specimens for the damping test. For each beam, a 20 mm square lead zirconate titanate (PZT) patch was attached to one end as an actuator to excite the beam and a smaller PZT patch (10 mm × 8 mm) was attached on the other side of the beam as a sensor to detect the beam’s vibration, as shown in Figure 2. In this study, three kinds of fiber reinforcement were used including glass fabric, carbon fabric, and basalt fabric. To study the effects of the CNF paper on the damping properties of the nanocomposite, 0.5 mm, 1.0 mm, and 1.5 mm thick pieces of CNF paper were applied to the surface of the composite.
2.7. Contact angle measurement

The static contact angle was acquired by a ‘DropImage’ contact angle measurement system at room temperature. The deionized water (15 μl) was introduced using a micro-syringe and images were captured to measure the angle of the liquid–solid interface. Five measurements were taken and averaged.

3. Results and discussion

3.1. Tribological properties of nanocomposites coated with carbon nanofiber paper

Scanning electron microscopy (SEM) images of carbon nanofiber paper with varied types of nanoparticles are shown in Figures 3–7. In Figure 3a, CNFs were well dispersed, demonstrated by the lack of large CNF clusters, indicating that the coating layers are homogenous. Owing to its strength and toughness, carbon nanofibers can act as micro-crack reducer. In Figure 3b, the two-dimensional structure of the graphite flakes was observed to be evenly distributed into CNFs. Graphite flakes have self-lubricant ability which can act as friction reducer, and is intended to complement the properties of CNF.

In Figure 4a, micron-sized short carbon fibers were incorporated with CNFs. Short carbon fibers have good compressive strength and creep resistance, additionally acting as a frame of the whole matrix system and improving the stress transfer of the composites. In Figure 5, nano-alumina and nano-titanium dioxide were dispersed on the surface of CNFs. The surface hardness can be significantly increased by adding ceramic nanoparticles. They also act as a spacer, both protecting the matrix and creating a rolling
Figure 4. SEM images of CNF paper with SCFs (a) and CNF paper with graphite flakes and SCF (b).

Figure 5. SEM images of CNF paper with Al₂O₃ and TiO₂ (a), and CNF paper with all above nanoparticles (b).

Figure 6. SEM images of pure resin (a) and CNF paper infused with resin (b).

effect, therefore reducing the coefficient of friction (COF). To study the synergistic effects of these nanoparticles, all the mentioned particles were mixed together with selected composition ratios.

Figures 6 and 7, which show the SEM images of CNF papers after resin infusion, reveal the good adhesion between the resin and nanoparticles.
Figure 7. SEM images of CNF and graphite flakes with resin (a), and CNF, SCF with resin (b).

The coefficient of friction (COF) and wear results from the tribometer tests of the samples listed in Table 1 are shown in Figure 8. The wear rate of the specimens ($W_s$), shown in Figure 8b, was calculated by

$$W_s = \frac{\Delta m}{\rho F_n L} \text{ (mm}^3/\text{Nm)},$$

(1)

Figure 8. Summary of COF (a) and wear rate (b) measurements. G1 is Pure CNFs, G2 is CNFs/graphite, G3 is CNFs/SCF, G4 is CNFs/graphite/SCF. G5 is CNFs/Nano TiO$_2$/Nano-Al$_2$O$_3$, G6 is CNFs/graphite/SCF/Nano-TiO$_2$/Nano-Al$_2$O$_3$. 
where $\Delta m$ is the specimen’s mass loss, $\rho$ is the density of the specimen, $F_n$ is the normal load applied on the specimen during sliding, and $L$ is the total sliding distance. The control sample is carbon nanofiber paper without any additives, labeled as G1 in Table 1. G6 sample exhibits the lowest COF, which is likely due to the synergistic effect among the various particles in the sample. The COF is one of the important performance parameters for friction and wear, and has been shown to be a very good indicator of the wear of a material in part-on-part wear applications. Although not always the case, a lower COF is often related to better performance. This is related to the method that the instrument uses to calculate the COF value. The torque of the arm is used in this calculation. Since the COF is a material-dependent property, it can vary based on the measurement method used to determine it. Sample G2 was found to exhibit the lowest wear rate, due to the self-lubricating effect of the graphite particles. Separately, the addition of graphite and short carbon fibers to the CNF paper led to a low COF and wear rate. Sample G4, however, shows the highest wear rate, which is likely due to a poor quality of the sample.

Figure 9 shows the surface morphology of the G2 and G4 samples. It can be seen that the surface of sample G2 is different from the significantly damaged surface of sample G4. The hybrid paper showed better tribological properties than the control sample due to the synergistic effect of nanoparticles.

### 3.2. Damping properties of nanocomposites coated with carbon nanofiber paper

The vibration damping test was conducted on the composite laminates with the CNF paper as surface layer. During the damping test, a sinusoidal sweep was used as the excitation source for the PZT actuator to obtain the frequency response of the system. A sine sweep range was 100 Hz to 10,000 Hz over a 20 s as used to excite the consequent modes. The beam’s response was measured through the smaller PZT patch at a sampling frequency of 40 kHz. The frequency-domain responses of various nanocomposite beams tested for each sine sweep are shown in Figures 10–12. The peak value in the sweep sine response represents resonance at a certain natural frequency. From the sweep responses, it can be clearly seen that the peak of first mode, second mode and third mode are significantly reduced for the nanocomposite beam, which indicates that the nanocomposite beam has improved the damping property.

To estimate the damping ratio for each mode, half-power band width method was used. Corresponding to each natural frequency, there is a peak in the magnitude frequency plot.
of the system. 3 dB down from the peak, there are two points corresponding to half-power point. A larger frequency range between these two points means a larger damping ratio value. The damping ratio is calculated by using the following equation:

$$2\zeta = \frac{\omega_2 - \omega_1}{\omega_n},$$  

(2)

where $\omega_1$, $\omega_2$ are the frequencies corresponding to the half-power point, $\omega_n$ is the natural frequency corresponding to the peak value, and $\zeta$ is the damping ratio. Tables 2–4 show the first three modal frequencies and associated damping ratio for the composite beams with their varied types of fiber reinforcement and/or CNF paper coating. Comparing the damping ratios, it is evident that the damping ratio of the nanocomposite beam can be increased.
Figure 12. Frequency response for carbon fiber-reinforced composite beam with different thicknesses of carbon nanofiber paper as surface layer.

Table 2. Damping ratios for glass fiber reinforced composites calculated by half-power band width method.

| Natural frequency (Hz) | Glass fiber | Glass fiber with 0.5 mm CNF paper | Glass fiber with 1 mm CNF paper | Glass fiber with 1.5 mm CNF paper |
|------------------------|-------------|----------------------------------|---------------------------------|----------------------------------|
| 1st mode               | 1.0254e + 003 | 0.0096                           | 0.0044                          | 0.0074                           | 0.0462                           |
| 2nd mode               | 1.9751e + 003 | 0.0062                           | 0.0049                          | 0.0096                           | 0.0088                           |
| 3rd mode               | 3.2129e + 003 | 0.0059                           | 0.0066                          | 0.0137                           | 0.0099                           |
| 4th mode               | 4.6387e + 003 | 0.0037                           | 0.0063                          | 0.0113                           | 0.0092                           |
| 5th mode               | 6.3672e + 003 | 0.0074                           | 0.0104                          |                                   | 0.0107                           |

Table 3. Damping ratios for carbon fiber reinforced composites calculated by half-power band width method.

| Natural frequency (Hz) | Carbon fiber | Carbon with 0.5 mm CNF paper | Carbon with 1 mm CNF paper | Carbon with 1.5 mm CNF paper |
|------------------------|--------------|------------------------------|--------------------------|------------------------------|
| 1st mode               | 1.5112e + 003 | 0.0057                       | 0.0034                   | 0.0055                       | 0.0089                           |
| 2nd mode               | 2.8101e + 003 | 0.0065                       | 0.0025                   | 0.0064                       | 0.0061                           |
| 3rd mode               | 4.5239e + 003 | 0.0076                       | 0.0052                   | 0.0074                       | 0.008                            |
| 4th mode               |              |                              |                          |                              | 0.007                            |

up to 300% at the second and third mode frequencies. The test results in Tables 2–4 clearly show a strong, clear correlation between the thickness of CNF paper and the damping ratio of the nanocomposites. The composites coated with 1 mm CNF paper exhibit the highest damping ratio, which indicates the best combination between the resin penetration of composites and the size of the interface between CNFs and resin. The fiber reinforcements also
Table 4. Damping ratio for basalt fiber reinforced composites calculated by half-power band width method.

| Natural frequency (Hz) | Basalt fiber | Basalt fiber with 0.5 mm CNF paper | Basalt fiber with 1 mm CNF paper | Basalt fiber with 1.5 mm CNF paper |
|------------------------|--------------|----------------------------------|---------------------------------|----------------------------------|
| 1<sup>st</sup> mode    | 1.0522e + 003| 0.0097                           | 0.0078                          | 0.0097                           |
| 2<sup>nd</sup> mode    | 2.0483e + 003| 0.0138                           | 0.0078                          | 0.0081                           | 0.0066                           |
| 3<sup>rd</sup> mode    | 3.2837e + 003| 0.0078                           | 0.0073                          | 0.0081                           | 0.0082                           |
| 4<sup>th</sup> mode    | 4.8022e + 003| 0.0087                           | 0.0038                          | 0.0081                           | 0.0044                           |
| 5<sup>th</sup> mode    | 6.5186e + 003| 0.0088                           | 0.0097                          | 0.0111                           | 0.0096                           |

have a significant influence on the damping ratio due to the unique molecular structure of each type. However, there is little change in modal frequencies, indicating only a slight change in the stiffness of the composites. This demonstrates an advantage of nanocomposite over regular composite with viscoelastic layers, whereas the regular composites with viscoelastic layers will sacrifice stiffness to improve their damping properties.

3.3. Superhydrophobicity of POSS-grafted carbon nanofiber paper

The FTIR spectra of pristine CNFs, POSS, and POSS-g-CNFs are shown in Figure 13. Comparing the curves in Figures 13a and 13b, a new peak appeared at around 1110 cm<sup>-1</sup>, which was attributed to the symmetric stretching vibration of Si–O bond, confirming that the POSS particles were grafted onto the CNFs.

Figure 14 shows the images used to measure the water contact angle of the CNF paper. The water contact angle of pristine CNF paper is found to be 140.0 ± 0.5°, which suggests that the surface of CNFs paper is highly hydrophobic. When contact angle was measured for the POSS-g-CNF paper it was significantly increased to 160.0 ± 0.4°. The significant increase in hydrophobicity is partially attributed to the POSS molecules attached covalently to the nanofiber surface, which lowers the surface energy of the nanofibers [18].

![Figure 13. FTIR spectra of: (a) pristine CNFs, (b) POSS-g-CNFs, (c) POSOS.](image-url)
Another possible reason for the superhydrophobicity is surface roughness [18], as shown by the difference in the surface morphologies of the papers observed in Figure 15. The CNF paper shows a relatively smooth surface marked slightly with wrinkles; however, the POSS-g-CNF paper exhibits a honeycomb-like structure with a diameter of the cell ranging from 10 to 60 μm. A high magnification SEM image reveals that the ‘wall’ of the honeycomb is composed of entangled POSS-g-CNFs, as shown in Figure 15c. This honeycomb structure makes a contribution to the superhydrophobicity, by decreasing the contact area between the water droplet and the surface [18,19].

The formation of a honeycomb structure, although not fully understood, may result from the change in the surface tension of the solution and self-assembly of POSS-g-CNF [20,21]. The solution always tends to decrease its Gibbs free energy level, which is proportional to the surface tension. In the case of CNF/CHCl₃ solution, CNF may precipitate because of the low solubility. Due to the good compatibility between the POSS-g-CNF and solvent, the amount of POSS-g-CNF will assembly on the surface of the filter papers and form a thin surface film, which will decrease the surface energy of the system. With the vaporization of the volatile solvent, the capillary forces are exerted on the nanofibers, and result insome nanofibers being reoriented parallel to the direction of the liquid retraction. After the solvent evaporates completely, the honeycomb structure remains. The stability of the superhydrophobic surface is a critical issue that needs to be addressed from a practical point of view. A main drawback of superhydrophobic surfaces made from carbon nanotubes, as reported in the work of Lau et al. [22], is that the superhydrophobicity can only last for several minutes. The superhydrophobicity then decreases or even disappears as the water droplet penetration into the voids of the paper. Unlike the previously mentioned study, the superhydrophobicity of the CNF paper in this study is very stable. After the sample was exposed to a high-humidity environment for three weeks, the water contact angle was 155.0±0.3°, indicating the surface is remained superhydrophobic.
4. Conclusions

In this study, multifunctional carbon nanofiber (CNF) paper was developed and optimized as a platform material. Carbon nanofiber paper was integrated into polymer composites through the VARTM process, which is compatible with the manufacturing process of wind turbine blades. This CNF paper-based nanocomposite has good impact-friction resistance with the wear rate as low as $1.78 \times 10^{-4} \text{mm}^3/\text{Nm}$. Carbon nanofiber paper can be used for sand erosion mitigation of wind turbines by incorporating other nanoparticles, which could provide effective protection for wind turbines installed in desert. Meanwhile, the vibrational test results also demonstrated significant increases in the damping ratios of the nanocomposite laminates, which is critical for the structural stability and dynamic response, position control, and durability of wind turbine blades. The POSS-g-CN paper exhibits a stable superhydrophobicity, with the contact angle higher than 160.0°C, even exposure to a high-humidity environment over a long period, which can provide separation of water droplets from the wind turbine blades installed in offshore area.

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