

Aligned HNT for Abrasion Resistance in Solar Cell Coatings

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ABSTRACT

Halloysite nanotubes (HNT), a kind of naturally formed ceramics, encompass high aspect ratio, stiffness and low cost while remain understudied about their coating usage. Theoretical and experimental results have shown a modulus as high as 400 GPa. In this study HNT was included in polymer based thin films fabricated using coating method on glass substrate. Mechanical tests have shown a consistent increase in stiffness, hardness in our previous work and here composite scratch resistance as compared to polymer materials without HNT were conducted. Composite mechanics based calculations showed as high as 300 GPa in HNT modulus, which is close to theoretical predictions and top in literature. The high reinforcement as well as wear resistance was attributed to high tube orientations, as revealed from electron microscopy from the same team. This study aims at development of environmentally friendly and cost effective coating, which is highly potential to be commercialized in solar cell industries.

Keywords: HNT, composite, mechanics, indentation

1 INTRODUCTION

Polymer composites have been used for structural applications. One method to reinforce the soft polymer matrix is to include stiff and strong nano-sized segments, such as carbon fillers of carbon nanotubes and graphene¹, inorganic particles of clay and metal oxides² and bio-fillers of cellulose and wood³. These fillers can also be categorized as one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) materials based on their dimensional and geometric features⁴. Among them, 1D nano-particles have been attractive mainly due to their anisotropic properties⁵ and effective unidirectional reinforcement in polymers.

To utilize nanotube's anisotropic properties along the axis, studies have been focusing on fabricating both in-plane and out-of-plane oriented assemblies. These research involve dispersion of nanotubes in appropriate solvent and using (i) exterior field forces of electric field⁶ and magnetic field⁷, or (ii) shear forces induced by extrusion/injection flow⁸, in liquid or melt polymer matrix. In the former case, attachment of either conductive or super-paramagnetic carriers to nanofillers is the key technique; and in the latter case, localized in-plane control of particle alignment has been found to be effective. Other researchers focus on composite fabrication directly from the aligned forest or array synthesized by chemical vapor deposition method (CVD)⁹ or electrochemical deposition¹⁰. Carbon nanotubes are popular in these methods due to their flexibility, and drawability from the growth substrate¹¹. Naturally-generated mineral clays such as montmorillonite, mica, talc, kaolinite and halloysite, however, are mechanically stiff and hard to synthesize in an economic deposition method due to natural abundance¹². Under this circumstance, the *in-situ* drawing^{11, 13}, infiltration/impregnation¹⁴, or compression molding¹⁵ method utilized based on CVD growth may not be plausible to achieve unidirectional out-of-plane reinforcement. For this reason, this paper aims to develop practical processing means to tailor particle alignments.

Halloysite nanotubes (HNTs), a naturally occurred clay mineral with one-dimensional hollow cylindrical structure, are exceptionally stiff and hard for their ceramic chemical composition¹⁶. The presence of hollow lumens in HNTs have also been extensively studied regarding their drug carrier/release properties¹⁷ and nanoreactor potential¹⁸. Besides, HNTs has low surface charge and easily get dispersed in solvents and polymers of medium to high polarity. Significant mechanical and thermal improvements have been demonstrated in starch, chitosan, gelatin, cellulose, pectin, and polyvinyl alcohol¹⁹. However, to achieve their maxim potential the main challenge is to eliminate the random distribution of tube orientations. The misalignment of particles will cause inefficiency in stress

transfer, and lead the properties of HNT filled nanocomposites to be far below theoretical predictions²⁰. For this reason, management of particle orientations to achieve desired macroscopic assembly of HNTs would be the focus of this contribution.

2 EXPERIMENTATION

Dragonite HNT clay was obtained from Applied Minerals (density $2.54 \pm 0.03 \text{ g}\cdot\text{cm}^{-3}$, inner diameter 10-20 nm, outer diameter 40-60 nm, and aspect ratio ranges between 20 and 200. BET pore volume 20%, surface area up to $100 \text{ m}^2\cdot\text{g}^{-1}$, refractive index 1.534). Epoxy 142-112 (purchased from Epoxy Technology, Inc., density $1.18 \text{ g}\cdot\text{cm}^{-3}$) and acetone (purchased from VWR, density $0.79 \text{ g}\cdot\text{cm}^{-3}$) were used as obtained. All the composite films were coated on glass slides with different viscosity levels.

The bulk rheological response of epoxy/acetone solutions was measured at $25 \text{ }^\circ\text{C}$ using a cone-and-plate (CP) geometry (2° cone, 60 mm, and truncation gam $58 \mu\text{m}$, part #513606905) on the AR-G2. The steady shear viscosity of the solutions was measured at shear rates between 10 to 1000 s^{-1} .

The scratch test is a simple and rapid means to assess the abrasion resistance and interfacial adhesion of coatings with the substrate. Scratch tests include three procedures: pre-scan under a small load, scratch, post-scan. A standard scratch test device measures both the tangential and normal loads generated during scratching and hence offers a good estimate of abrasion resistance of the material under study. The advantages of the scratch testing are (a) it induces the same stress field and deformation as does the abradant, (b) the results are reproducible, and (c) the critical load (L_c), which means the load required to lift a coating off the substrate can be easily calculated from friction force. Here in this study, the tests were performed with a Rockwell-shaped diamond indenter tip (radius of $10 \mu\text{m}$) continuously loaded with a normal force of 200 uN . The transverse velocity of the sample to the diamond was $10 \text{ mm}\cdot\text{min}^{-1}$, and the loading rate, $dF_N/dx=10 \text{ N}\cdot\text{mm}^{-1}$. The scratches were $10 \mu\text{m}$ long. To ensure the homogeneity of HNT in composites, 5 scratches with spacing of $2 \mu\text{m}$ were performed.

During the scratch procedure, the tangential force, F_T , is also continuously measured and the friction coefficient is defined,

$$\mu^* = \frac{F_T}{F_N} \quad (1)$$

A plot of the coefficient against the sliding distance should approach an equilibrium value (after a short scratching-in period) as long as no drastic changes in the scratch mechanisms during the course of the scratch occur. If, on the other hand, a transition from one scratch feature (e.g. microcracking) to another (e.g. plowing associated with material removal) takes place, this should also be associated with a change in μ^* .

An estimation of the specific scratch wear rate, w_r , can also be determined from the final parts of the scratches when considering the loss in volume of the material over an average short distance of the scratch lave, under an average normal load $F_{N_{ave}}$, that acted over this distance,

$$w_r = \Delta V / (F_{N_{ave}} l_{ave}) = C_r l_{ave} / (F_{N_{ave}} l_{ave}) = C_r / F_{N_{ave}} \quad (2)$$

where C_r refers to the cross-section of the scratch shortly before its end. The cross section can be assumed to have the shape of a segment of a circle, with a chord length equal to w (residual width) and height equal to the scratch depth h ,

$$C_r = h(3h^2 + 4w^2) / (6w) \quad (3)$$

Assuming further that $F_{N_{ave}}$ is nearly equal to F_N at the end of the scratch, the specific scratch wear rate reduces to,

$$w_r = C_r / F_N \quad (4)$$

3 RESULTS AND DISCUSSIONS

Viscosity plays a significant role in aligning HNT particles and therefore has been studied and plotted in Figure 1. As observed, the addition of acetone drastically decreased the viscosity. In contrast, the addition of HNT did not viscously change the suspensions. And in our contribution it is believed that the higher viscosity induced higher level of alignment. And this effect has also been proven from our previous work.

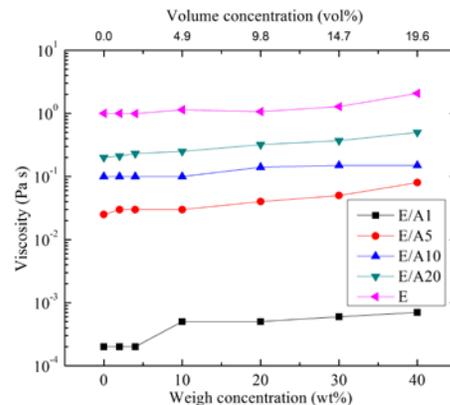


Figure 1 Viscosity of various epoxy/acetone/HNT solutions examined at shear rates between 10 to 1000 s^{-1} . The addition of acetone to epoxy greatly lowered the viscosity; as a comparison, the increase of HNT loadings did not change the viscosity much.

TriboIndenter was used to measure the abrasion resistance, and the images were taken *in-situ* as shown in Figure 2. An extraction of the profilometry information in pure epoxy was conducted using Gwyddion and plotted in

Figure 3, including scratch volume and wear rate. It can be observed that the scratch volume showed a quasi-linear increase with higher scratching force. A calculation of the wear rate, which is the normalized volume to applied loading, was almost constant. This also suggests an even curing quality along film thickness. Therefore the same measurement procedure was applied in all composites for comparison for consistence.

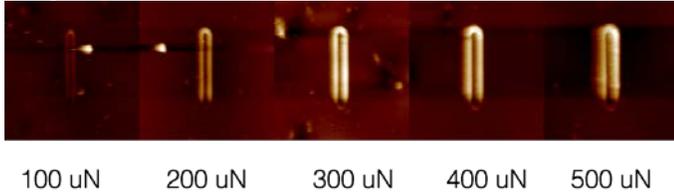


Figure 2 Optical images from in-situ TriboIndenter in scratching tests in pure epoxy samples under 100, 200, 300, 400 and 500 μN scratching force.

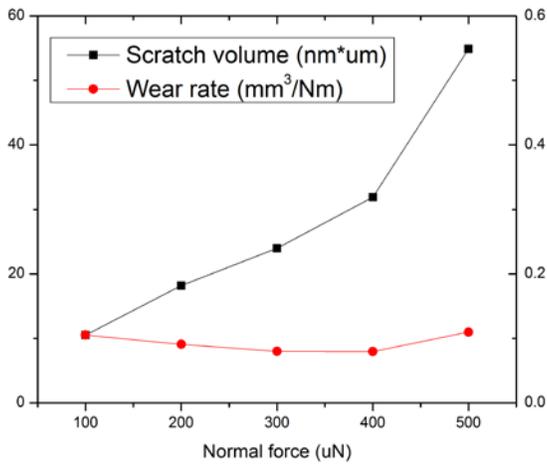


Figure 3 Scratch volume per unit scratching length ($\text{nm} \cdot \mu\text{m}$) and wear rate in pure epoxy at scratching force of 100, 200, 300, 400, 500 μN .

To improve the measurement precision, AFM was used to measure the profile in all samples and as shown in Figure 4. It can be observed that (i) with the increase of loading levels the depth and scratched volumes are getting larger; (ii) with the inclusion of HNT, the resistance to scratching is becoming better and better. The calculated wear rates were plotted in Figure 5. Very distinguishably, with the increase of HNT concentrations, the composites showed lower wear rates; in other words, the inclusion of HTN in all composites retards the abrasion procedure and improved the wearing resistance. On the other hand, with higher HNT alignment facilitated by higher viscosity, the abrasion was also improved. However the degree of orientation needs to be further studied before the hypothesis of varied HNT alignment, which requires more work and is going-on now.

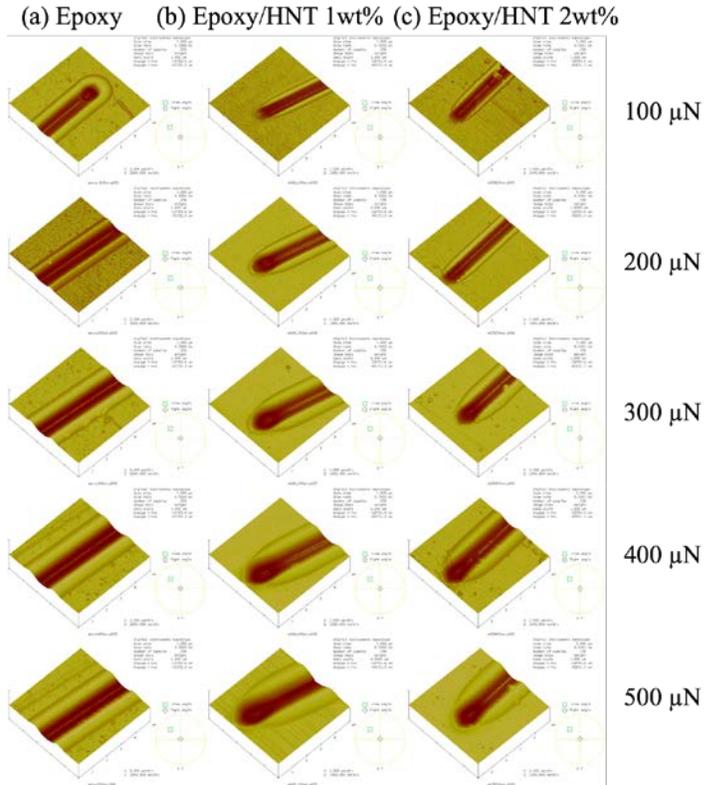


Figure 4 Profilometry for (a) Epoxy, (b) Epoxy/HNT 1wt% and (c) Epoxy/HNT 2wt% under scratching force of 100, 200, 300, 400 and 500 μN .

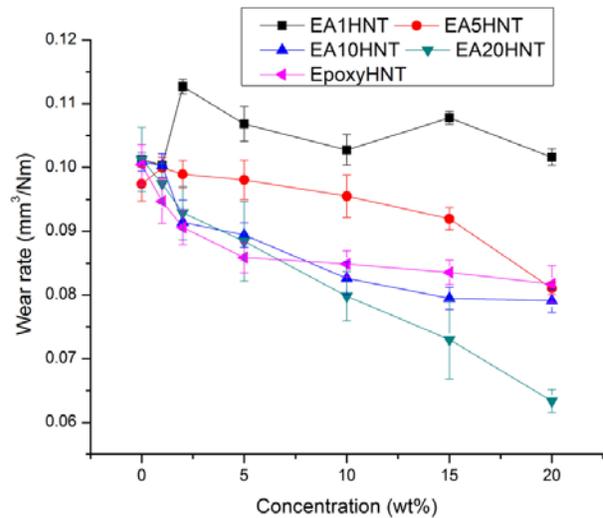


Figure 5 Wear rate vs. concentration relationship in all epoxy composites; epoxy/acetone ratios ranges to show the HNT alignment effects on wear resistance.

4 CONCLUSION

The epoxy/HNT composites were prepared using coating method. This procedure takes advantage of

hydrodynamic flow to align the particles; while the presence of viscosity retains the HNT orientations. The measurement of viscosity was found to have a corresponding relationship to particle alignment. The measurement from scratching tests showed consistent trend. In summary, this study has focused on the HNT alignment effects on abrasion resistance and provides a new perspective for optimal coating design, simple processing and feasible characterizations.

REFERENCES

- (a) Qian, H.; Greenhalgh, E. S.; Shaffer, M. S. P.; Bismarck, A., Carbon nanotube-based hierarchical composites: a review. *Journal of Material Chemistry* **2010**, *20* (23), 4751-4762; (b) Cai, D. Y.; Song, M., Recent advance in functionalized graphene/polymer nanocomposites. *Journal of Materials Chemistry* **2010**, *20* (37), 7906-7915.
- Azeez, A. A.; Rhee, K. Y.; Park, S. J.; Hui, D., Epoxy clay nanocomposites' processing, properties and applications: A review. *Composites Part B: Engineering* **2012**, (0).
- Khalil, H. A.; Bhat, A.; Yusra, A. I., Green composites from sustainable cellulose nanofibrils: a review. *Carbohydr. Polym.* **2012**, *87* (2), 963-979.
- Dresselhaus, M. S., Fifty years in studying carbon-based materials. *Physica Scripta* **2012**, *2012* (T146), 014002.
- Sajanlal, P. R.; Sreepasad, T. S.; Samal, A. K.; Pradeep, T., Anisotropic nanomaterials: structure, growth, assembly, and functions. *Nano Reviews* **2011**, *2* (5883), 4.
- (a) Martin, C.; Sandler, J.; Windle, A.; Schwarz, M.-K.; Bauhofer, W.; Schulte, K.; Shaffer, M., Electric field-induced aligned multi-wall carbon nanotube networks in epoxy composites. *Polymer* **2005**, *46* (3), 877-886; (b) Kaida, S.; Matsui, J.; Sagae, T.; Hoshikawa, Y.; Kyotani, T.; Miyashita, T., The production of large scale ultrathin aligned CNT films by combining AC electric field with liquid flow. *Carbon* **2013**, *59*, 503-511.
- (a) Camponeschi, E.; Vance, R.; Al-Haik, M.; Garmestani, H.; Tannenbaum, R., Properties of carbon nanotube-polymer composites aligned in a magnetic field. *Carbon* **2007**, *45* (10), 2037-2046; (b) Kimura, T.; Ago, H.; Tobita, M.; Ohshima, S.; Kyotani, M.; Yumura, M., Polymer Composites of Carbon Nanotubes Aligned by a Magnetic Field. *Advanced Materials* **2002**, *14* (19), 1380-1383.
- Sulong, A. B.; Park, J., Alignment of multi-walled carbon nanotubes in a polyethylene matrix by extrusion shear flow: mechanical properties enhancement. *J. Compos Mater.* **2011**, *45* (8), 931-941.
- Zhang, M.; Fang, S.; Zakhidov, A. A.; Lee, S. B.; Aliev, A. E.; Williams, C. D.; Atkinson, K. R.; Baughman, R. H., Strong, transparent, multifunctional, carbon nanotube sheets. *Science* **2005**, *309* (5738), 1215-1219.
- Chen, T.; Cai, Z.; Qiu, L.; Li, H.; Ren, J.; Lin, H.; Yang, Z.; Sun, X.; Peng, H., Synthesis of aligned carbon nanotube composite fibers with high performances by electrochemical deposition. *Journal of Materials Chemistry A* **2013**, *1* (6), 2211-2216.
- Jiang, K.; Li, Q.; Fan, S., Nanotechnology: spinning continuous carbon nanotube yarns. *Nature* **2002**, *419* (6909), 801-801.
- Sivamohan, R., The problem of recovering very fine particles in mineral processing—a review. *International Journal of Mineral Processing* **1990**, *28* (3), 247-288.
- Li, Y.-L.; Kinloch, I. A.; Windle, A. H., Direct spinning of carbon nanotube fibers from chemical vapor deposition synthesis. *Science* **2004**, *304* (5668), 276-278.
- Marconnet, A. M.; Yamamoto, N.; Panzer, M. A.; Wardle, B. L.; Goodson, K. E., Thermal conduction in aligned carbon nanotube-polymer nanocomposites with high packing density. *ACS nano* **2011**, *5* (6), 4818-4825.
- Raravikar, N. R.; Schadler, L. S.; Vijayaraghavan, A.; Zhao, Y.; Wei, B.; Ajayan, P. M., Synthesis and characterization of thickness-aligned carbon nanotube-polymer composite films. *Chemistry of materials* **2005**, *17* (5), 974-983.
- Guimaraes, L.; Enyashin, A. N.; Seifert, G.; Duarte, H. A., Structural, electronic, and mechanical properties of single-walled halloysite nanotube models. *The Journal of Physical Chemistry C* **2010**, *114* (26), 11358-11363.
- (a) Lvov, Y. M.; Shchukin, D. G.; Mohwald, H.; Price, R. R., Halloysite clay nanotubes for controlled release of protective agents. *Acs Nano* **2008**, *2* (5), 814-820; (b) Levis, S.; Deasy, P., Characterisation of halloysite for use as a microtubular drug delivery system. *International Journal of Pharmaceutics* **2002**, *243* (1), 125-134.
- Shchukin, D. G.; Sukhorukov, G. B.; Price, R. R.; Lvov, Y. M., Halloysite nanotubes as biomimetic nanoreactors. *Small* **2005**, *1* (5), 510-513.
- (a) Gaaz, T. S.; Sulong, A. B.; Akhtar, M. N.; Kadhum, A. A. H.; Mohamad, A. B.; Al-Amiery, A. A., Properties and Applications of Polyvinyl Alcohol, Halloysite Nanotubes and Their Nanocomposites. *Molecules* **2015**, *20* (12), 22833-22847; (b) Rawtani, D.; Agrawal, Y., Multifarious applications of halloysite nanotubes: a review. *Rev. Adv. Mater. Sci* **2012**, *30*, 282-295.
- (a) Song, K.; Zhang, Y.; Meng, J.; Green, E. C.; Tajaddod, N.; Li, H.; Minus, M. L., Structural polymer-based carbon nanotube composite fibers: understanding the processing-structure-performance relationship. *Materials* **2013**, *6* (6), 2543-2577; (b) Xie, X. L.; Mai, Y. W.; Zhou, X. P., Dispersion and alignment of carbon nanotubes in polymer matrix: A review. *Materials Science & Engineering R-Reports* **2005**, *49* (4), 89-112.