

SCRATCH TEST OF EPOXY COMPOSITES REINFORCED BY ALLIGNED CARBON NANOTUBES BY MAGNETIC FIELD

Ali A. S.¹ and Ali W. Y.²

¹Mechanical Engineering Department, Faculty of Engineering, Suez Canal University, EGYPT.

²Department of Production engineering and Mechanical Design, Faculty of Engineering, Minia University, El-Minia, EGYPT.

ABSTRACT

Based on the observation obtained from the tested composites with and without the application of magnetic field, it can be concluded that both the measured friction coefficient and wear observed for the composites prepared under magnetic field are lower than that of an ordinary epoxy resin. As a consequence, it can be recommended that oriented MWCNTs reinforced epoxy composites can be successfully produced by application of permanent magnet.

However, reduced friction coefficient in aligned composites can be explained in terms of the lubricating action offered by MWCNTs. During scratch, the large interfacial area offered by MWCNTs of relatively lower friction contributed in the significant friction decrease. Scratch in the normal direction, where the orientation of MWCNTs is perpendicular to the radial direction had higher friction due to the weak strength of MWCNTs in that direction.

The enhanced wear resistance observed for aligned MWCNTs reinforcing epoxy may be attributed to the strengthening mechanism and the strong interfacial bonding offered by MWCNTs. Besides, as the magnetic intensity increased, wear significantly decreased. At relatively higher values of MWCNTs, wear recorded further decrease due to the better dispersion of MWCNTs offered by the magnetic field. Besides, MWCNTs can bind the epoxy chains together to decrease their slippage and improve the wear resistance. Alignment of MWCNTs increases the effective number of loaded MWCNTs in the load direction compared to that in aligned direction. As a consequence, the wear resistance of tested composites prepared at no magnetic field is low.

KEYWORDS

Scratch, friction, wear, epoxy matrix, multi-wall carbon nanotubes, magnetic field.

INTRODUCTION

Epoxy matrix reinforced by carbon nanotubes (CNTs) are widely used in many applications, [1]. It was found that significant decrease in friction coefficient was observed for composites filled by CNTs which was attributed to their self-lubrication performance.

Besides, wear resistance of epoxy/CNTs composites could be significantly improved. That behaviour was attributed to the strengthening effect and self-lubricating property of CNTs. The wear rate of those composites decreased with increasing CNTs content up to 1.0 wt. %. Epoxy/CNTs composites containing 0.6 wt. % CNTs exhibited both the lowest wear rate and friction coefficient. CNTs are difficult to disperse during preparation, but they can be oriented by the application of electric and magnetic fields. It is aimed to improve the mechanical properties by controlling the CNTs orientation direction to withstand the parallel or perpendicular loading.

Alignment of Multi-walled carbon nanotubes (MWCNTs) in epoxy matrix can be done by DC electric fields applied during composite curing, [2 - 11]. This process can improve electrical conductivity and mechanical properties compared to those with random orientation. Alignment of MWCNTs in polyimide matrix was achieved by simultaneous application of DC electric and magnetic fields, [12]. Simultaneous application of electrical or magnetic fields to the polyimide composite enhanced the level of alignment. The alignment of MWNTs has been achieved through deposition of magnetite/maghemite nanoparticles of 6 - 10 nm diameter and use of an external magnetic field. The coating of CNTs with magnetic nanoparticles was performed by combining the polymer wrapping and layer-by-layer techniques. The improvement of addition of MWCNTs was discussed, [13 - 16], where their dispersion could limit interfacial interaction with polymer matrix [17 - 21]. Application of electric and magnetic field results in orientation of the MWCNTs in the field direction, forming network of tubes in chain like structure and representing a path of the electric current and reorient the magnetic MWCNTs to form chains in line and they touch each other in a head-to-tail order. The drawbacks of epoxy composites can be diminished by reinforcing by MWCNTs, where the fracture toughness and stiffness can be increased, [22 - 28]. The mechanism of action included crack-bridging and deflection.

The alignment of MWCNTs can be developed by using metallic and magnetic particles, [29 - 32], such as Fe and Ni. It was reported that increase in tensile strength and elastic modulus was observed with the increase of MWCNTs content in polymer composite [34 - 36]. Besides, composites reinforced with MWCNTs have large interfacial shear strengths, due to better bonding between MWCNTs reinforcement and matrix material. Based on experimental results, [37, 38], it is expected that increasing polymer chain and MWCNTs alignment should result in an increase in the modulus of the material.

In the present work, it is aimed to study the effect of alignment of MWCNTs on tribological properties of epoxy matrix. Experiments were carried under the effect of permanent magnetic field of 0.2, 0.4 and 0.6 mG intensity.

EXPERIMENTAL

In the present work, the multi-walled carbon nanotubes (MWCNTs) were used as reinforcement in epoxy matrix. Their contents were 0, 0.2, 0.4, 0.6, 0.8 and 1.0 wt. % relative to the epoxy matrix. The diameter and length ranged between 8 - 15 nm and 10 - 15 nm, respectively. Alignment was carried out by permanent magnet of three intensities, 0.2, 0.4 and 0.6 milli Gauss (mG). The use of magnetic field aimed to enhance the dispersion of MWCNTs agglomerates and develop the adherence into epoxy. The MWCNTs were added into the epoxy resin (Kimapoxy 150). MWCNTs were aligned in the epoxy matrix by applying a permanent magnet. In this work, MWCNTs were used as

reinforcement in epoxy matrix in order to determine the role of fibers alignment on the tribological properties of the tested composites.

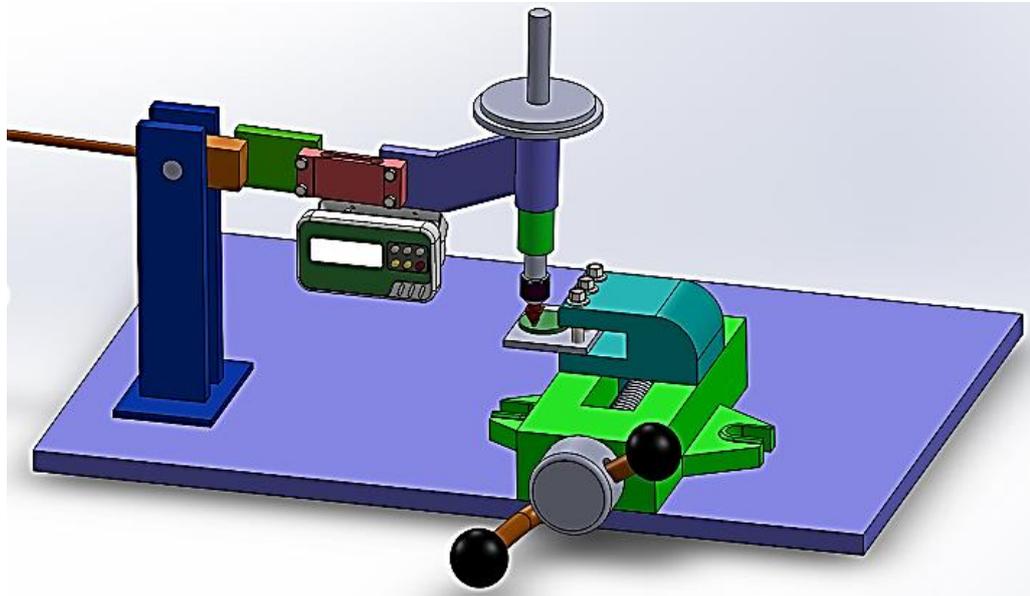


Fig. 1 Arrangement of scratch test rig.

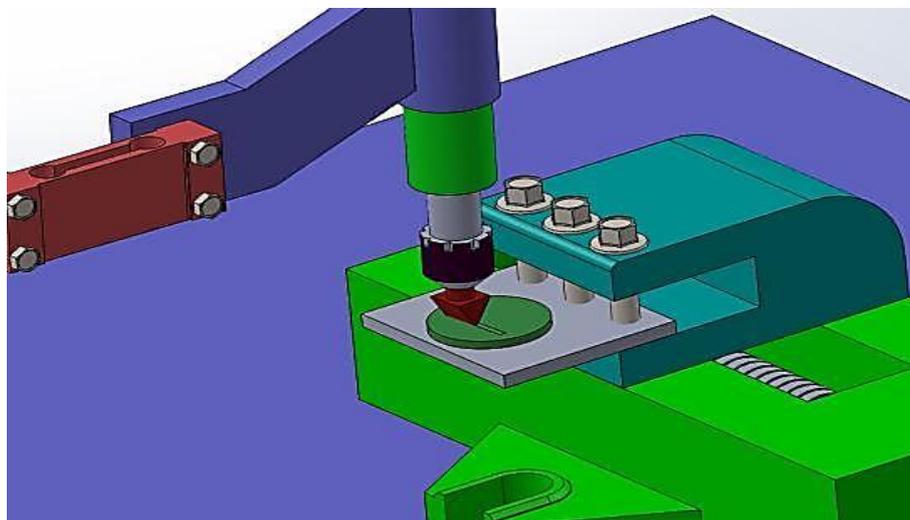


Fig. 2 Details of the scratch test.

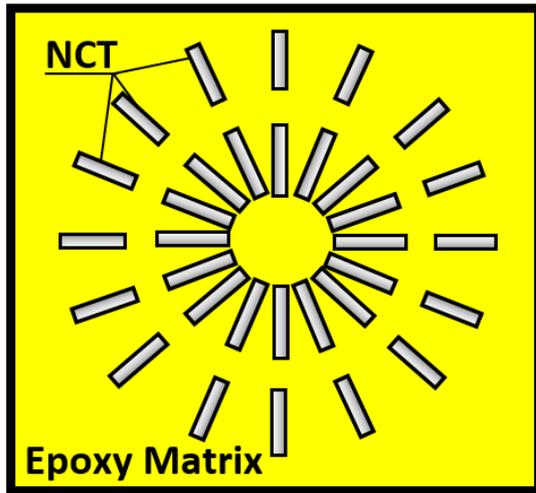


Fig. 3 Distribution of the MWCNTs by the action of the magnet.

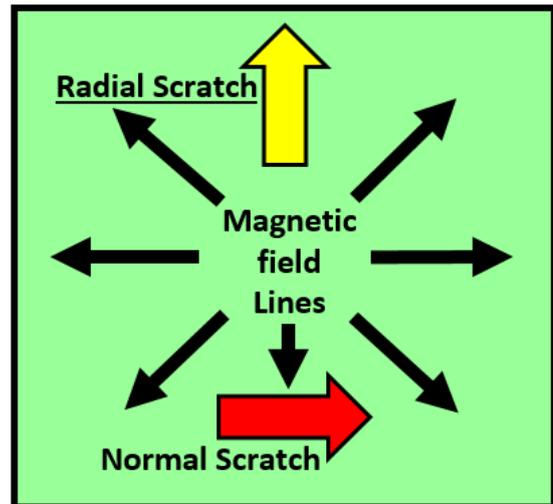


Fig. 4 The direction of the scratch relative to magnetic field lines.

The test rig used in the experiments was top scratch tester. It is consisted of a rigid stylus mount to produce a scratch on a flat surface with a single pass, a diamond stylus of apex angle 90° and hemispherical tip as shown in Figs. 1 and 2. The loading lever mounted to the stylus through three-jaw chuck. A counter weight is used to balance the loading lever before process of loading. Weights of 2, 4, 6, 8 and 10 N are vertically applied. Scratch resistance force was measured using a load cell mounted to the loading lever and connected to display digital monitor. The test specimen was held in the specimen holder mounted in a horizontal base with a manual driving mechanism to move specimen in a straight direction. The test was conducted under dry conditions at room temperature. An optical microscope was used to measure scratch width with an accuracy of $\pm 1.0 \mu\text{m}$. Magnetic field was applied by a coil assembled under the steel base where the epoxy composites were fixed. The flux intensities of the magnetic field were 0.2, 0.4 and 0.6 mG.

RESULTS AND DISCUSSION

Friction coefficient displayed by the tested composites prepared at no magnetic field decreased down to minimum at 0.6 wt. % MWCNTs content then slightly increased with further increase of MWCNTs, Fig. 5. The decrease may be from the lubrication action of the MWCNTs, while the increase can be from the agglomeration of the MWCNTs. It is shown that the enhancement in friction coefficient was limited by the good dispersion of the reinforcement inside epoxy matrix.

The aligned MWCNTs reinforced epoxy composites prepared under the effect of 0.2 mG magnetic field showed 12 % and 8 % decrease in friction coefficient for radial and normal scratch direction respectively, Fig. 6. Friction coefficient showed decreasing trend with increasing MWCNTs content indicating that agglomeration of the MWCNTs diminished. Further friction decrease was observed for the tested composites prepared under the effect of the magnetic field of 0.4 and 0.6 mG intensities, Figs. 6 and 7 respectively, where the effect of magnetic intensity on the alignment is clearly shown. The change in magnetic intensity from 0.2 to 0.6 mG led to the decrease of friction coefficient.

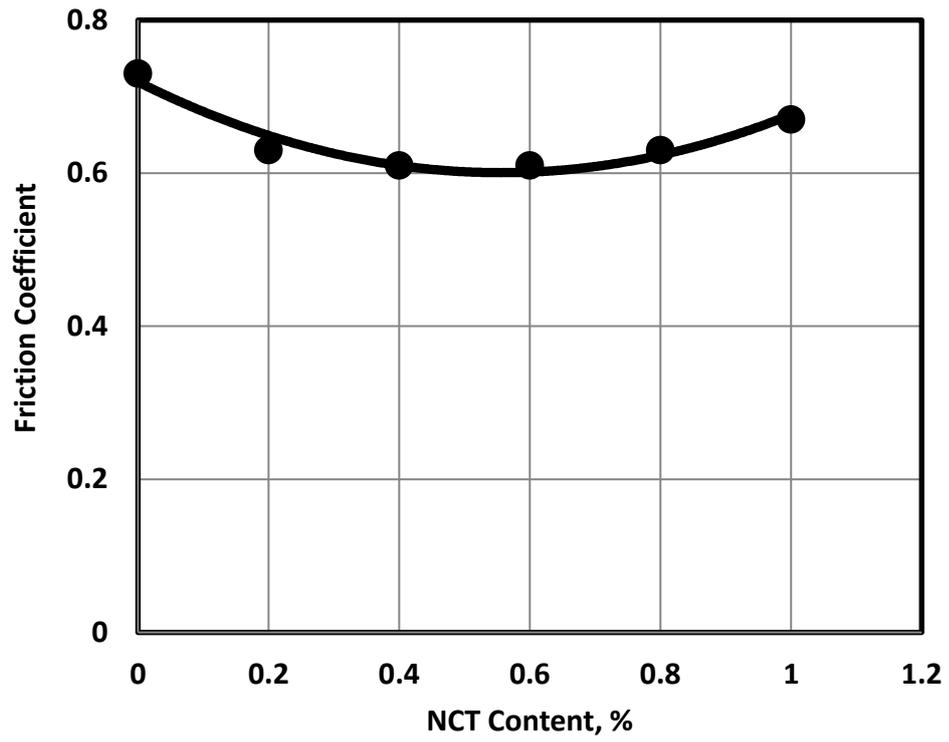


Fig. 5 Friction coefficient displayed by the tested composites prepared at no magnetic filed.

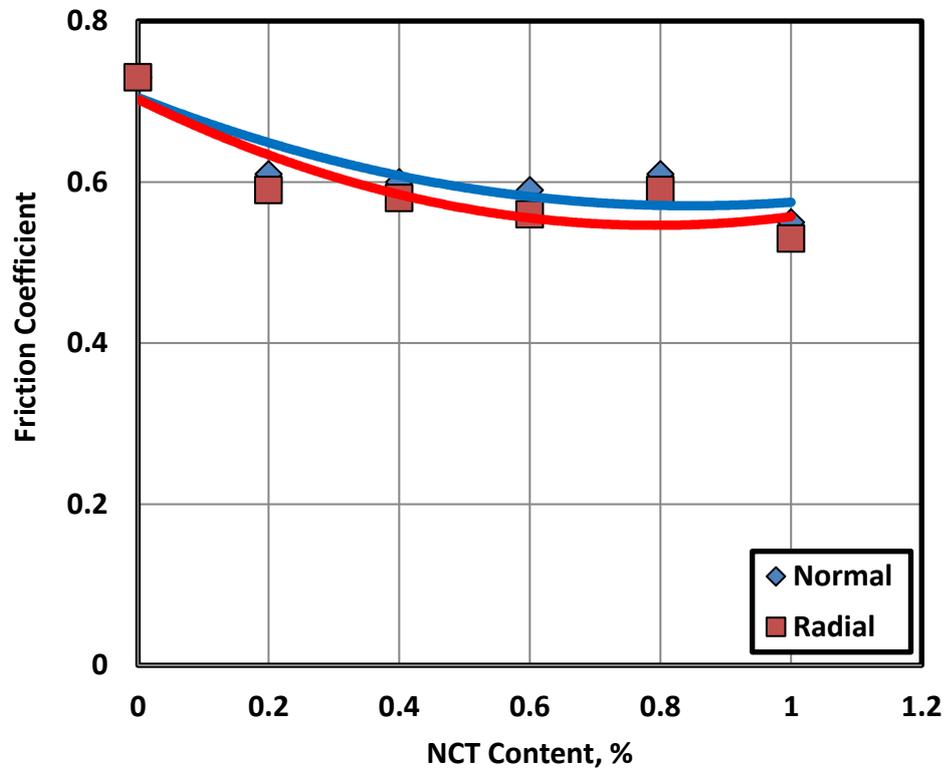


Fig. 6 Friction coefficient displayed by the tested composites prepared at magnetic filed of 0.2 mG intensity.

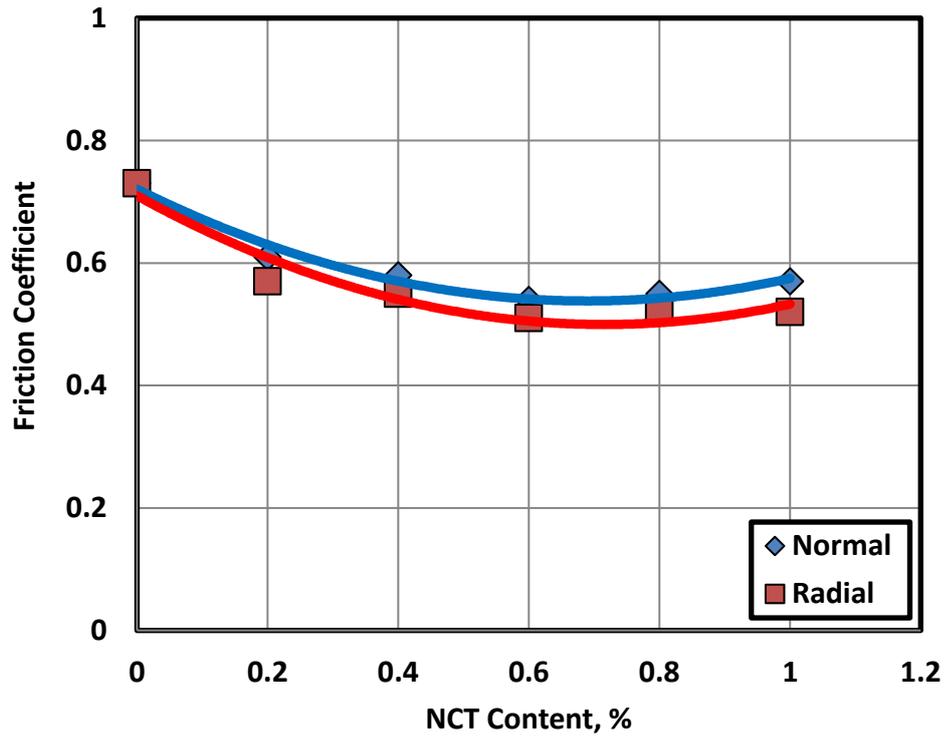


Fig. 7 Friction coefficient displayed by the tested composites prepared at magnetic field of 0.4 mG intensity.

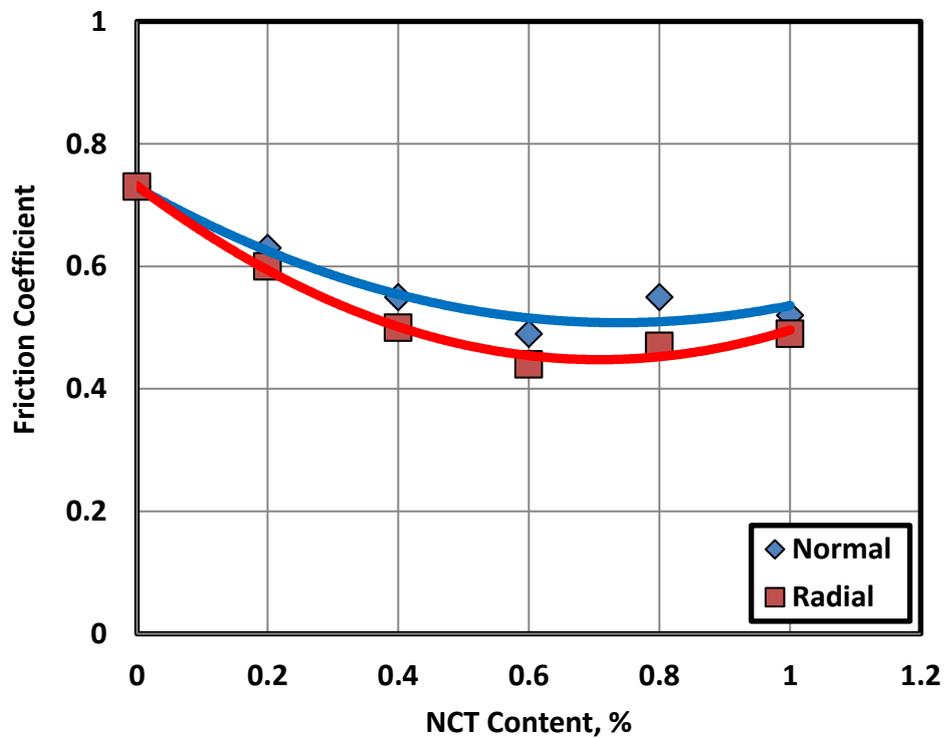


Fig. 8 Friction coefficient displayed by the tested composites prepared at magnetic field of 0.6 mG intensity.

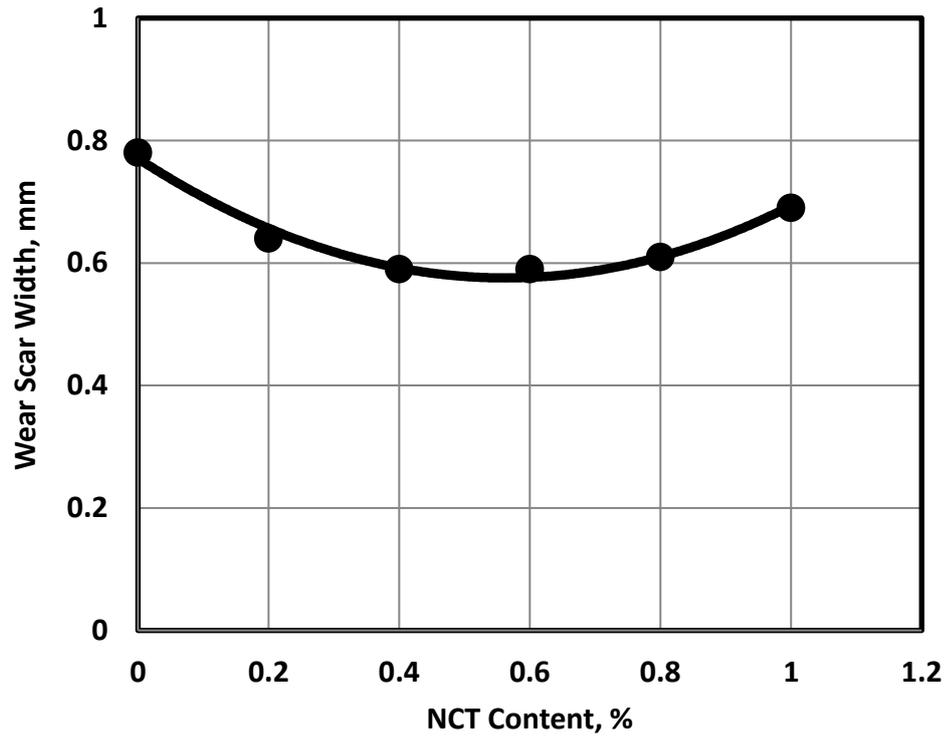


Fig. 9 Wear displayed by the tested composites prepared at no magnetic filed.

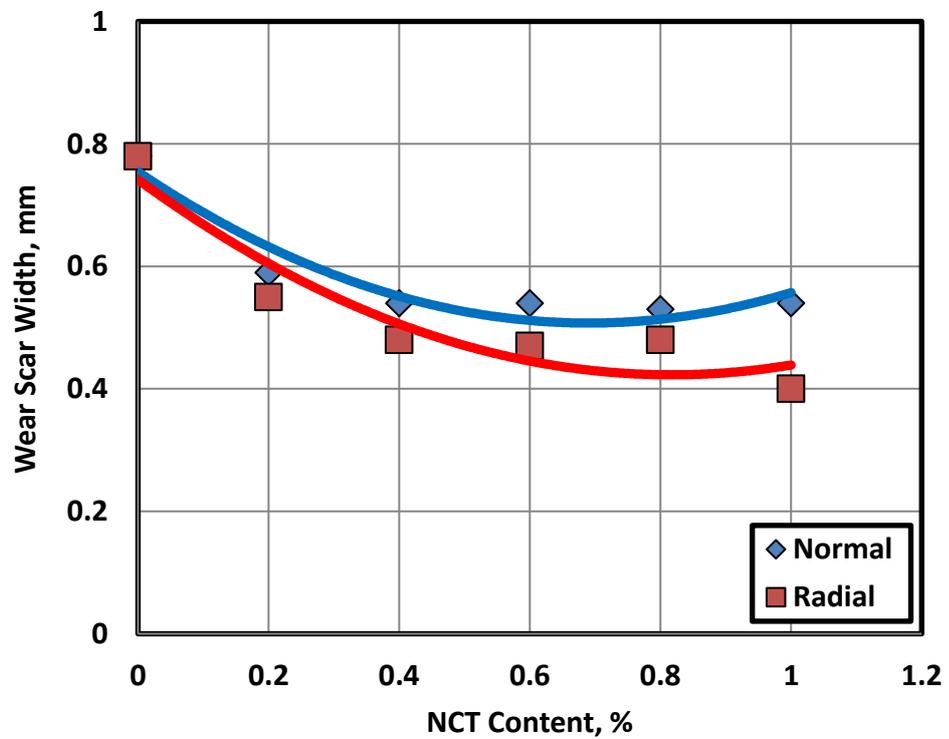


Fig. 10 Wear displayed by the tested composites prepared at magnetic filed of 0.2 mG intensity.

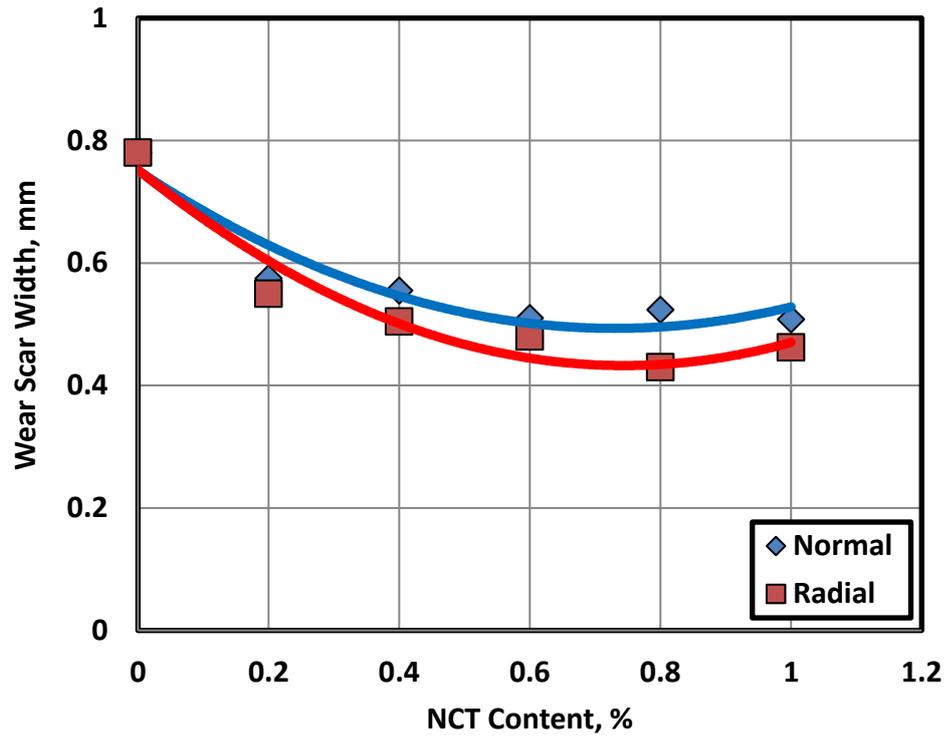


Fig. 11 Wear displayed by the tested composites prepared at magnetic filed of 0.2 mG intensity.

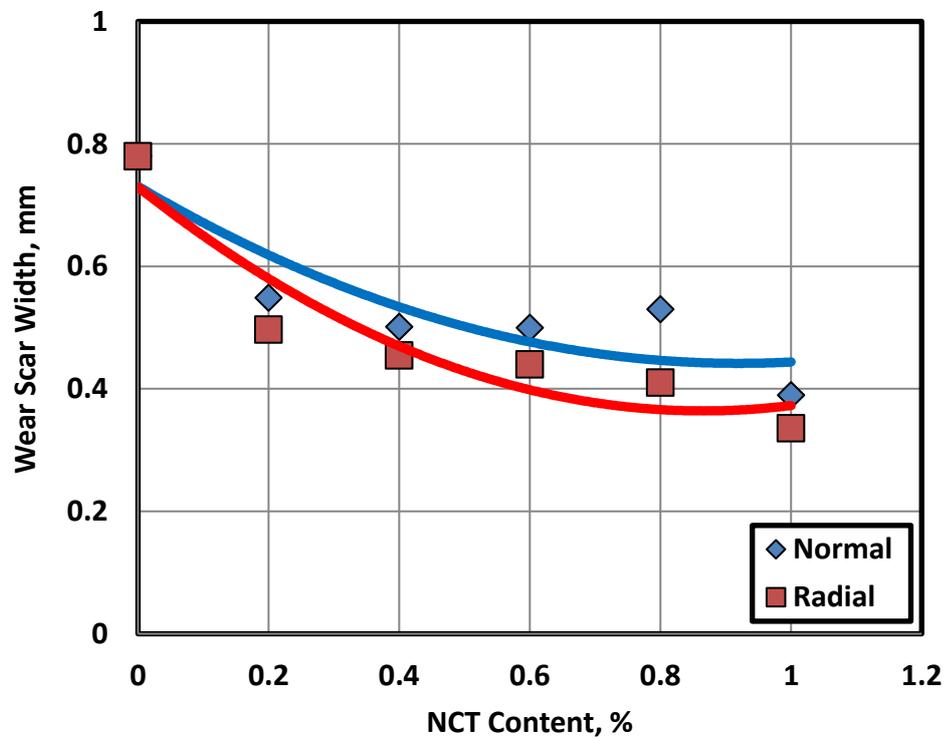


Fig. 12 Wear displayed by the tested composites prepared at magnetic filed of 0.6 mG intensity.

However, reduced friction coefficient in aligned composites can be explained in terms of the lubricating action offered by MWCNTs. During scratch, the large interfacial area offered by MWCNTs of relatively lower friction contributed in the significant friction decrease. Scratch in the normal direction, where the orientation of MWCNTs is perpendicular to the radial direction had higher friction due to the weak strength of MWCNTs in that direction. The scratch in the direction of the aligned MWCNTs gave 8 % friction decrease relative to normal direction.

Wear displayed by the tested composites prepared at no magnetic field decreased down to minimum then increased with increasing MWCNTs content, Fig. 9. The enhanced wear resistance can be explained in terms of the strengthening mechanism and the strong interfacial bonding offered by MWCNTs. It seems that epoxy may have the tendency to align its molecular chains along the pull direction during scratch. Along the radial direction (alignment direction), MWCNTs and epoxy chains aligned themselves in the same direction. During scratch, the shear force transferred from epoxy matrix to large interfacial area offered by MWCNTs of relatively high strength could not abrade the surface effectively. The effect of the alignment of MWCNTs offered by the magnetic field during specimen preparation is shown in Figs. 10, 11 and 12 for magnetic intensity of 0.2, 0.4 and 0.6 mG respectively. Scratch in the normal direction, where the orientation of MWCNTs is perpendicular to the radial direction had lower resistance due to the weak strength of MWCNTs in that direction. Wear is dependent on material removed from the sliding surfaces and material transferred into the surface. Material removed from the surface depends on the cohesion between MWCNTs and epoxy matrix and better cohesion means enhanced wear resistance. This behavior can be achieved by good dispersion of MWCNTs in epoxy matrix to give high interfacial bonding between epoxy and MWCNTs. Alignment of MWCNTs can lead to that result. The scratch in the direction of the aligned MWCNTs gave 23 % wear decrease. Besides, as the magnetic intensity increased, wear significantly decreased. At relatively higher values of MWCNTs, wear recorded further decrease due to the better dispersion of MWCNTs offered by the magnetic field. The wear resistance in the radial direction was relatively higher than that measured in the normal direction.

It was observed that increasing the magnetic field intensity increased the degree of orientation and alignment of both the epoxy chains and MWCNTs alignment. It seems that the MWCNTs in the epoxy matrix aligned and attracted toward each other to form bundles along the radial direction upon the application of magnetic field. The effect of magnetic field on the change in polymer chain may cause chain orientation and alignment as well as the formation of crystalline regions.

The toughening mechanism observed for the composites containing aligned MWCNTs depends on their ability to provide a restraining force withstanding crack propagation inside the matrix, [39]. It seems that alignment of MWCNTs and epoxy matrix chains increases matrix packing density upon chain alignment, and hence increases matrix toughness, [40 - 44]. Besides, MWCNTs can bind the epoxy chains together to decrease their slippage and improve the toughness. The random distribution of MWCNTs is oriented in all directions inside epoxy. Therefore, the effective number of loaded MWCNTs in the load direction is lower than that in aligned direction. As a consequence, the toughness of testes composites prepared at no magnetic field is lower than that of aligned composites.

CONCLUSIONS

1. Friction coefficient displayed by the tested composites prepared at no magnetic field decreased down to minimum at 0.6 wt. % MWCNTs content then slightly increased with further increase of MWCNTs.
2. The aligned MWCNTs reinforced epoxy composites showed decreasing friction trend with increasing MWCNTs content indicating that agglomeration of the MWCNTs diminished.
3. Further friction decrease was observed as the magnetic field intensity increased.
4. The scratch in the direction of the aligned MWCNTs gave 8 % friction decrease relative to normal direction.
5. Wear in the normal direction, where the orientation of MWCNTs is perpendicular to the radial direction had lower values due to the weak strength of MWCNTs in that direction. Alignment of MWCNTs offered good dispersion of MWCNTs in epoxy matrix and gave high interfacial bonding between epoxy and MWCNTs.
6. As the magnetic intensity increased, wear significantly decreased. At relatively higher values of MWCNTs, wear recorded further decrease indicating better dispersion of MWCNTs offered by the magnetic field.
7. MWCNTs can bind the epoxy chains together to decrease their slippage and improve the toughness. Therefore, the effective number of loaded MWCNTs in the load direction is lower than that in aligned direction. As a consequence, the wear resistance of tested composites prepared at no magnetic field is low.

REFERENCES

1. Badran A. H., Hasan M. K., Ali W. Y., "Tribological Behavior of Epoxy Reinforced with Carbon Nanotubes and Filled by Vegetables Oils", *EGTRIB Journal*, Vol. 14, No. 1, January 2017, pp. 51 – 61, (2017), *KGK*, 11-12, 2017, pp. 38 – 42, (2017).
2. Khan S. U., Pothnis J. R., Kim J. K., "Effects of carbon nanotube alignment on electrical and mechanical properties of epoxy nanocomposites", *Composites: Part A*, 49 pp. 26 - 34, (2013).
3. Camponeschi E., Vance R., Al-Haik M., Garmestani H., Tannenbaum R., "Properties of carbon nanotube–polymer composites aligned in a magnetic field", *Carbon* 45, pp. 2037 - 2046, (2007).
4. Ma C., Zhang W., Zhu Y., Ji L., Zhang R., Koratkar N., Liang J., "Alignment and dispersion of functionalized carbon nanotubes in polymer composites induced by an electric field", *CARBON* 46 pp. 706 – 720, (2008).
5. Monti M., Natali M., Torre L., Kenny J. M., "The alignment of single walled carbon nanotubes in an epoxy resin by applying a DC electric field", *CARBON* 50, pp. 2453 – 2464, (2012).
6. Abdalla M., Dean D., Theodore M., Fielding J., Nyairo E., Price G., "Magnetically processed carbon nanotube/epoxy nanocomposites: Morphology, thermal, and mechanical properties", *Polymer* 51, pp. 1614 - 1620, (2010).
7. Gupta P., Rajput M., Singla N., Kumar V., Lahiri D., "Electric field and current assisted alignment of CNT inside polymer matrix and its effects on electrical and mechanical properties", *Polymer* 89, pp. 119 – 127, (2016).
8. Wang Q., Dai J., Li W., Wei Z., Jiang J., "The effects of CNT alignment on electrical conductivity and mechanical properties of SWNT/epoxy nanocomposites", *Composites Science and Technology* 68, pp. 1644 – 1648, (2008).
9. Ma C., Liu H. Y., Du X., Mach L., Xu F., Mai Y. W., "Fracture resistance, thermal and electrical properties of epoxy composites containing aligned carbon nanotubes by low magnetic field", *Composites Science and Technology* 114, pp. 126 – 135, (2015).

10. Iakoubovskii K., "Techniques of aligning carbon nanotubes", Article in Central European Journal of Physics, December 2009 Cent. Eur. J. Phys., 7(4), pp. 645 - 653, (2009).
11. Duarte M. A. C., Grzelczak M., Maceira V. S., Giersig M., Marzan L. M., Farle M., Sierazdki K., Diaz R., "Alignment of Carbon Nanotubes under Low Magnetic Fields through Attachment of Magnetic Nanoparticles", J. Phys. Chem. B, Vol. 109, No. 41, pp. 19060 – 19063, (2005).
12. Romyen N., Thongyai S., Prasertthdam P., "Alignment of Carbon Nanotubes in Polyimide Under Electric and Magnetic Fields ", Journal of Applied Polymer Science, Vol. 123, pp. 3470 – 3475, (2012).
13. Sham M. L., Kim J. K., "Surface functionalities of multi-wall carbon nanotubes after UV/ozone and TETA treatments", Carbon, 44, pp. 768 - 777, (2006).
14. Ma P. C., Kim J. K., Tang B. Z., "Effects of silane functionalization on the properties of carbon nanotube/epoxy nanocomposites", Compos Sci Technol, 67, pp. 2965 - 2972, (2007).
15. Spitalsky Z., Tasis D., Papagelis K., Galiotis C., "Carbon nanotube polymer composites, chemistry, processing, mechanical and electrical properties", Prog Polym Sci, 35, pp. 357 - 401, (2010).
16. Geng Y., Liu M. Y., Li J., Shi X. M., Kim J. K., "Effects of surfactant treatment on mechanical and electrical properties of CNT/epoxy nanocomposites", Compos Part A 39, 1876 - 1883, (2008).
17. Xie X. L., Mai Y. W., Zhou X. P., "Dispersion and alignment of carbon nanotubes in polymer matrix: a review", Mater Sci Eng, 49, pp. 89 - 112, (2005).
18. Ma P. C., Siddiqui N. A., Maroom G., Kim J. K., "Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: a review", Compos Part A, 41, pp. 1345 – 1367, (2010).
19. Chen X. Q., Saito T., Yamada H., Matsushige K., "Aligning single wall carbon nanotubes with an alternating-current electric field", Appl Phys Lett, 78, (23), pp. 3714 - 3716, (2001).
20. Martin C. A., Sandler J. K. W., Windle A. H., Schwarz M. K., Bauhofer W., Schulte K., "Electric field-induced aligned multi-wall carbon nanotube networks in epoxy composites", Polymer, 46, pp. 877 - 886, (2005).
21. Zhu Y., Ma C., Zhang W., Zhang R., Koratkar N., Liang J., "Alignment of multiwalled carbon nanotubes in bulk epoxy composites via electric field", J Appl Phys;105, 054319, (2009).
22. Tang L. C., Wan Y. J., Peng K., Pei Y. B., Wu L. B., Chen L. M., "Fracture toughness and electrical conductivity of epoxy composites filled with carbon nanotubes and spherical particles. Compos Part A-Appl Sci Manuf, 45, pp. 95 - 101, (2013).
23. Spitalsky Z., Tasis D., Papagelis K., Galiotis C., "Carbon nanotube–polymer composites: chemistry, processing, mechanical and electrical properties", Prog Polym Sci, 35, (3), pp. 357 - 401, (2010).
24. Thostenson E. T., Chou T. W., "Processing-structure-multi-functional property relationship in carbon nanotube/epoxy composites. Carbon, 44 (14), pp. 3022 - 3029, (2006).
25. Hollertz R., Chatterjee S., Gutmann H., Geiger T., Nueesch F. A., Chu B. T., "Improvement of toughness and electrical properties of epoxy composites with carbon nanotubes prepared by industrially relevant processes", Nanotechnology, 22(12), pp. 211 – 219, (2011).

26. Gojny F. H., Wichmann M. H. G., Fiedler B., Schulte K., "Influence of different carbon nanotubes on the mechanical properties of epoxy matrix composites – a comparative study", *Compos Sci Technol*, 65, (15–16), pp. 2300 – 2313, (2005).
27. Miyagawa H., Mohanty A. K., Drzal L. T., Misra M., "Nanocomposites from biobased epoxy and single-wall carbon nanotubes: synthesis, and mechanical and thermophysical properties evaluation", *Nanotechnology*, 16 (1), pp. 118 - 24, (2005).
28. Park S. J. Jeong H. J., Nah C., "A study of oxyfluorination of multi-walled carbon nanotubes on mechanical interfacial properties of epoxy matrix nanocomposites", *Mater Sci Eng A-Struct Mater Prop Microstruct Process*, 385 (1 - 2), pp. 13 - 16, (2004).
29. Tyagi P. K., Singh M. K., Misra A., Palnitkar U., Misra D. S., Titus E., et al. Preparation of Ni-filled carbon nanotubes for key potential applications in nanotechnology", *Thin Solid Films*, 469, pp. 127 - 30, (2004).
30. Correa-Duarte M. A., Grzelczak M., Salgueirino-Maceira V., Giersig M., Liz-Marzan L. M., Farle M., "Alignment of carbon nanotubes under low magnetic fields through attachment of magnetic nanoparticles", *J Phys Chem B* 109 (41), 19060 - 10963, (2005).
31. Chiolerio A., Musso S., Sangermano M., Giorcelli M., Bianco S., Coisson M., "Preparation of polymer-based composite with magnetic anisotropy by oriented carbon nanotube dispersion", *Diam Relat Mater*;17(7 - 10), pp. 1590 - 1595, (2008).
32. Ma C. G., Wang Y. R., Yu Y. J., "Electrical and thermal properties of carbon nanotubes/PMMA composites induced by low magnetic fields", *Plast Rubber Compos* , 39 (2), pp. 49 - 53, (2010).
34. Liu T., Phang I.Y., Shen L., Chow S.Y., De Zhang W., "Morphology and mechanical properties of multiwalled carbon nanotubes reinforced nylon-6 composites", *Macromolecules* 37, pp. 7214 - 7222, (2004), <http://dx.doi.org/10.1021/ma049132t>.
35. Qian D., Dickey E., Andrews R., Rantell T., "Load transfer and deformation mechanisms in carbon nanotube-polystyrene composites", *Appl. Phys. Lett.*, 2868, pp. 4 - 7, (2000), <http://dx.doi.org/10.1063/1.126500>.
36. Coleman J. N., Khan U., Blau W. J., Gunko Y. K., "Small but strong: a review of the mechanical properties of carbon nanotube-polymer composites", *Carbon N. Y.* 44, pp. 1624 - 1652, (2006), <http://dx.doi.org/10.1016/j.carbon.2006.02.038>.
37. Al-Haik M. S., Garmestani H., Li D. S., "Mechanical properties of magnetically oriented epoxy", *J Poly Sci B*, 42, pp. 1586 - 600, (2004).
38. Garmestani H., Al-Haik M. S., Dahmen K., Tannenbaum R., Li D. S., Sablin S. S., "Polymer-mediated alignment of carbon nanotubes under high magnetic fields", *Adv Mater*, 15, (22), pp. 1918 - 1921, (2003).
39. Kim J. K., Mai Y. W., "High strength, high fracture toughness fibre composites with interface control – a review", *Compos Sci Technol*, 41, pp. 333 - 78, (1991).
40. Melick H., Dijken A., Toonder J., Govaert L., Meijer H., "Near-surface mechanical properties of amorphous polymers", *Philos Mag B* 2002, 82 (10), pp. 2093 - 2102, (2002).
41. Beranger S., Fortier M. H., Baril D., Armand M. B., "Inducing order in polymer. *Solid State Ionics* 2002;148(3–4):437–41, (2002).
42. Gupta P., Sharan S., Roy P., Lahiri D., "Aligned carbon nanotube reinforced polymeric scaffolds with electrical cues for neural tissue regeneration", *Carbon, N. Y.* 95, pp. 715 - 724, (2015), <http://dx.doi.org/10.1016/j.carbon.2015.08.107>.
43. Kumar R. M., Sharma S. K., Kumar B. V., Lahiri D., "Effects of carbon nanotube aspect ratio on strengthening and tribological behavior of ultra high/molecular weight polyethylene composite", *Compos. Part A Appl. Sci. Manuf.* 76, pp. 62 - 72, (2015). <http://dx.doi.org/10.1016/j.compositesa.2015.05.007>.

44. Arash B., Wang Q., Varadan V. K., "Mechanical properties of carbon nanotube/polymer composites", Nature, pp. 1 - 8, (2014), <http://dx.doi.org/10.1038/srep06479>.