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Antiwear Performance Evaluation of Halloysite Nanotube (HNT) Filled Polymer Nanocomposites

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Abstract*: Polymer nanocomposites containing various types of reinforcements and fillers are oftenly used in applications such as sliding elements in the machine and automotive parts, gear assemblies etc., in which tribological performance parameters viz. friction and wear are the major issues. In this work, the specific wear rate of HNT filler loading (0-4wt %) in Glass-Epoxy nanocomposites fabricated by vacuum bagging technique are evaluated experimentally. For this purpose, the specimens are prepared and tests are conducted as per the ASTM G-99 standard for a number of trials with the assistance of a pin-on-disc machine by varying load and speed values, keeping time and track diameter constant. The results obtained from experiments reveals that reduction in specific wear rate and the amount of material loss is quite significant for HNT loaded specimens when compared with neat sample even at higher operating conditions. This indicates that HNT comprises of hard ceramic elements viz. SiO_2 and Al_2O_3 which eventually enhances the antiwear behaviour of prepared nanocomposites. Finally, a study on wear mechanisms and morphologies are carried out by analyzing the worn surfaces through SEM micrographs.

***Keywords:** Halloysite Nanotube (HNT), Glass-Epoxy, Nanocomposites, Vacuum bagging, Specific Wear Rate.*

I. INTRODUCTION

There is an increasing demand for polymer based nanocomposites which are used in automotive, marine, electrical, structural and recreational applications, the researchers and scientists are putting their efforts to develop the new class of polymeric materials by combining various types of fillers and reinforcements in order to enhance their properties [1-2]. The experimental investigations are carried out through the pin on disc apparatus to evaluate the tribological characteristics for different proportions of Titanium Oxide (TiO_2) nano particles in the epoxy base composites. The test results reveals that the incorporation of nano-TiO_2 significantly reduces the contact temperature, wear loss and friction coefficient in the short carbon fiber reinforced epoxy composites even at higher operating conditions [3-4]. Thomas O. Larsen et al. considered the different concentrations of nano-CuO particles and added them to both epoxy and epoxy-PTFE micro particles matrix system, further they examined the state of dispersion and wear behaviour with the assistance of scanning electron microscopy (SEM) and custom-made pin-on-disc type tribotester respectively. The investigation proves that the addition of nano-CuO doesn't cause any effect to reduce material loss due to wear of epoxy base composites at all loading conditions, wherein other system namely PTFE micro particles added epoxy composites exhibit improved antiwear performance [5]. The effect of addition of silica and carbon black at nano scale on hardness and antiwear performance of the woven E-glass fabric reinforced epoxy composites has been studied. The conclusions drawn from the study, under all applied load conditions improved the wear resistance property significantly with the addition of nano-silica and nano-carbon black reinforcements [6]. Furthermore, Rashmi et al carried out a study towards mechanical and tribological characteristics of polymer nanocomposites in which epoxy is used as a matrix phase and Organo-modified montmorillonite (OMMT) nano clay is used as a filler with different proportions. The study concludes that addition of nano clay is a major aspect in the improvement of the tribological and mechanical performances of nanocomposites [7]. From the literature reviews, it is herewith understood that the most effective way to increase the antiwear performance of any class of polymer matrix composites is by the addition of a small quantity of nanoparticles in the matrix phase. The inclusions of these reinforcements may lead to an enhancement in the wear performance of the nanocomposites due to development of the larger contact surface area of the nanoparticles and also more interactions with the polymers due to their high aspect ratio [8-12]., Halloysite nanotube (HNT) is a potential filler which has tubular morphology and belonging to kaolin group with their features similar to single wall carbon nanotube (SWCNT) and having several advantages namely cost effectiveness, easy processing, high aspect ratio, better compatibility with polymers, better resistance against organic solvents and ease of disposal or reusability has been reported, it oftenly improves the mechanical performance [13-16].

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Further, HNT reinforcements comprises of the two hard ceramic elements viz. SiO_2 and Al_2O_3 which may possess the antiwear behaviour of glass-epoxy composites. Hence this work is taken up to measure the antiwear performance parameters namely specific wear rate and wear loss of material for the woven fabric E-glass reinforced epoxy composites with different proportions of HNT loading under combined operating conditions. Further, a study has been carried out to understand the microstructure and various wear mechanisms by analyzing the worn surfaces through Scanning Electron Microscopy (SEM).

II. EXPERIMENTAL WORK

A. Materials used and their specifications

The materials used for fabrication of nanocomposites in this work includes woven fabric of E-glass mat purchased from SunTech Fabrics Pvt. Ltd, Bengaluru, India having 210 grams per square meter used as a primary reinforcing material and the Epoxy as a matrix material of "commercial code name - Lapox L-12" having a density of 1120 kg/m^3, along with the hardener K6 (956 kg/m^3) and N, N- dimethyl benzyl amine (BDMA) accelerator, which are procured from ATUL India Ltd, Gujrat, India. The secondary reinforcing material namely Halloysite nanotubes (HNT) having a chemical composition as well as physical properties as listed in Table-I are obtained from Sigma Aldrich Company, Bengaluru, India.

Table- I: The elemental composition and physical properties of HNT.

Composition		Physical properties		
Element	Weight fraction (%)	Parameter	Typical Values	Unit
SiO_2	47.95			
Al_2O_3	16.37	Molecular weight	294.19	g/mol
Fe_2O_3	14.58			
CaO	6.89	Average diameter	30 to 70	Nm
K_2O	6.73			
Na_2O	2.03	Average length	1 to 3	µm
TiO_2	1.67	Surface Area	64	m^2/g
ZnO	0.85	Density	2.53	g/cc
MgO	0.82			
ZrO_2	0.38	Refractive Index	n20/ D 1.54	
SO_3	0.38	Pore Size	1.26 to 1.34	mL/g

B. Fabrication method of nanocomposites

The nanocomposites are prepared with a standard procedure after the intensive study of literature. The HNT nanoparticles are initially mixed with Epoxy matrix using ultra-sonicator to obtain uniform dispersion and also develop an intermolecular connections. Further, the hardener (K6) in proportion of 1:10 of epoxy resin is added to mixture. The accelerator is also added to increase the rate of curing. After the addition of hardener and accelerator, the resultant mixture is stirred again for 15 minutes at 1000 rpm using a mechanical stirrer for effective dissolution of nanoparticles. Thereafter, ultrasonication is done for a brief interval of 15 minutes, followed by the process of removal of the air bubbles present in the mixture by effective degassing during the stirring and ultrasonication with assistance of vacuum oven at 80^0 C for 30 minutes. Finally, the laminates consisting of 12 layers of woven E-glass mat and resultant mixture are prepared by Vacuum bag moulding technique by laying layers subsequently one over the other. At the end, the uncured laminates are kept for 24 to 48 hours at room temperature until final curing is completed. A schematic representation of nanocomposite laminates fabrication procedure is as shown in the Fig. 1.

C. Testing procedure

The pin on disc machine of Ducom make 'TR-20LE-PHM-600' model, as shown in the Fig. 2 is used for performing wear tests as per ASTM G-99 standard.
The machine includes wear monitoring test rig with computer interface which is used to estimate the performance of prepared nanocomposites (as shown in Table- II) under dry sliding operating conditions as tabulated in Table- III. The pin attached with specimen of dimension 12 mm ×12 mm× 3 mm is held stationary against the rotating disc made up of hardened ground steel with surface roughness of 5µm and hardness of 72 HRC. Further pin is subjected to loading by lever attached with load carriers. The speed and time of wear testing machine are adjusted manually. The test trials are conducted in ambient conditions by considering three specimens and averaging the values recorded. The specifications of wear testing machine are enlisted in the Table-IV.

A precision electronic weight balance with an accuracy of ±0.0001g is used to measure the weight loss of the nanocomposite during dry sliding test. Finally, the specific wear rate is calculated on the basis of wear volume using equation 1 .

$$K_S = \frac{\Delta w}{\rho \times t \times V_s \times F_n} \quad \ldots\ldots (1)$$

Where

K_S = Specific wear rate in mm^3/N.m.

$\Delta w = w_1 - w_2$ = weight loss in g.

W_1= Initial weight in g.

W_2= Final weight in g.

ρ = Density of the composite in g/cc.

t = Time in seconds.

$V_S = \frac{\pi DN}{60000}$ = Sliding velocity in m/sec.

D= Diameter of track in mm.

N= Speed in RPM.

F_n = Average normal load in Newton.

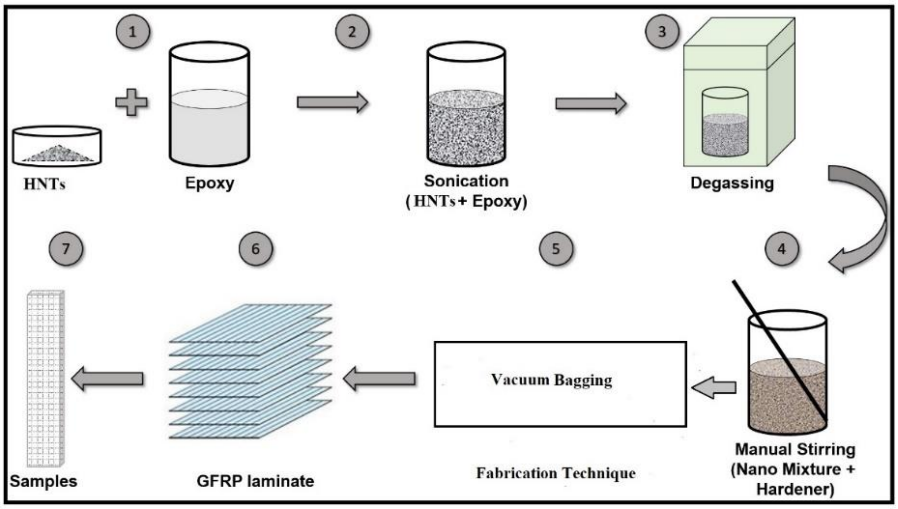

Fig. 1: A schematic diagram of nanocomposite laminates fabrication procedure.

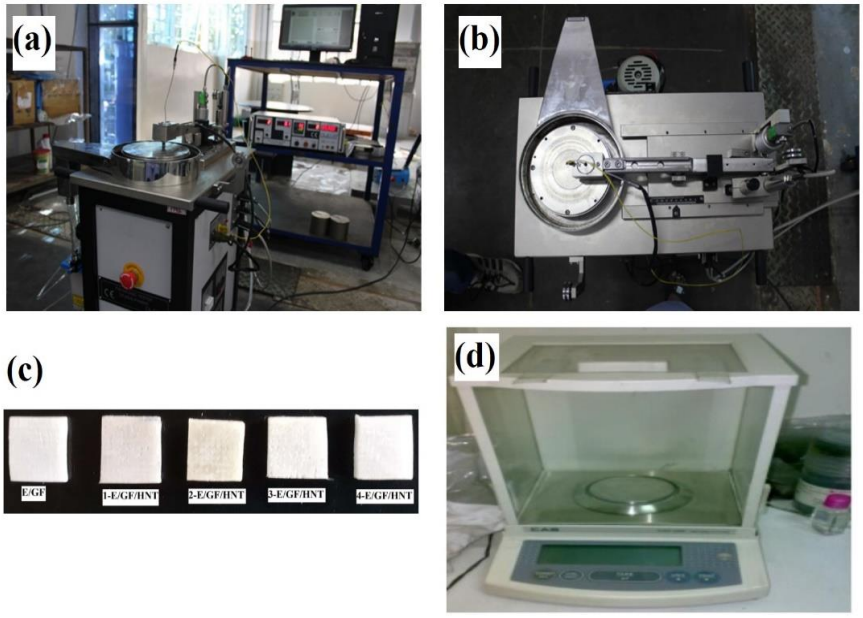

Fig. 2: (a). Computer interface Pin on disc test rig. (b). Specimen attached pin loading on disc. (c). Worn-out specimens. (d). Electronic weighing balance.

Table- II: The composition and designation of nanocomposite.

Sl. No.	Designation	Composition (in wt. %)			Fabrication method
		Epoxy	HNT	Glass Fiber	
1	E/GF	40	-	60	Vacuum bag Moulding
2	1-E/GF/HNT	39	1	60	
3	2-E/GF/HNT	38	2	60	
4	3-E/GF/HNT	37	3	60	

5	4-E/GF/HNT	36	4	60	

Table- III: The operating conditions for dry sliding test.

Sl. No.	Track diameter D (mm)	Time t (sec)	Load F_n (N)	Speed N (rpm)	Sliding Velocity V_s (m/sec)
1	100	3600	40	400	2.09
2				800	4.19
3				1200	6.28
4	100	3600	80	400	2.09
5				800	4.19
6				1200	6.28
7	100	3600	120	400	2.09
8				800	4.19
9				1200	6.28

Table- IV: The specifications of pin on disc machine.

Sl. No	Parameter	Unit	Min	Max	Remarks
1	Pin diameter	mm	3	12	Diagonal/Diameter
2	Disc (diameter x thickness)	mm	165 x 8		
3	Wear track diameter	mm	50	100	
4	Sliding velocity	m/sec	0.5	10	
5	Disc speed	rpm	200	2000	LC – 1 rpm
6	Normal load	N	5	200	In steps of 5 N
7	Frictional Force	N	0	200	LC – 0.1 N
8	Wear	µm	0	2000	LC = 1 micron
9	Pin Heating	0 C	Ambient	600	
10	Chamber Heating	0 C	Ambient	600	

D.Surface topography

The worn out surfaces of specimens are examined by using a TESCAN - VEGA 3 model Scanning Electron Microscope (SEM) having underneath 25 kV accelerating voltage. A thin layer of gold coating by sputtering is done effectively on the specimens in vacuum chamber to create conducting surface layers before taking micrographs.

III. RESULTS AND DISCUSSION

The data depicting the amount of material loss and calculated value of specific wear rate under different loading conditions and different speeds are reported in the Table-V and the results are plotted graphically in Fig. 3, 4 and 5 respectively for different load conditions.

Table- V: Wear Loss (Δw) and Specific wear rate (Ks) of nanocomposites.

Speed N (RPM) →	400		800		1200		Material
Parameter → / Load F_n (Newton) ↓	Δw (g) × 10^{-3}	K_s (mm^3 / N.m) × 10^{-5}	Δw (g) × 10^{-3}	K_s (mm^3 / N.m) × 10^{-5}	Δw (g) × 10^{-3}	K_s (mm^3 / N.m) × 10^{-5}	
40	5	60.12	5.8	34.8	14.8	59.2	E/GF
80	8.6	51.59	12	35.99	27.8	55.59	
120	16.8	67.16	18	35.98	53.6	71.43	
40	1.2	13.9	1.8	10.4	2.3	8.89	1-E/GF/HNT
80	2.1	12.16	2.5	7.24	7.4	14.28	
120	3.5	13.51	4.2	8.11	11.7	15.07	
40	1.3	14.73	2	11.31	4.2	15.84	2-E/GF/HNT
80	2	11.32	2.6	7.36	6.3	11.89	

120	3.3	12.45	4.2	7.92	10.5	9.21	
40	1.8	19.4	2.2	11.85	6.2	22.29	3-E/GF/HNT
80	2.4	12.93	3.8	10.24	7.6	13.66	
120	6	21.58	6.5	11.68	18.6	22.29	
40	2	20.79	2.5	12.99	6.3	21.83	4-E/GF/HNT
80	2.6	13.52	4.1	10.66	8.5	14.73	
120	6.6	22.88	7.7	13.35	22.4	25.88	

A. Weight loss and Specific wear rate

Fig. 3, 4 and 5 shows the weight loss due to wear and specific wear rate of neat and the HNTs filled Glass-epoxy nanocomposites w.r.t. varying speed and loading conditions. The incorporation of HNTs could cause a dramatic improvement in the wear resistance as compared to neat composites even under increased load and speed conditions.

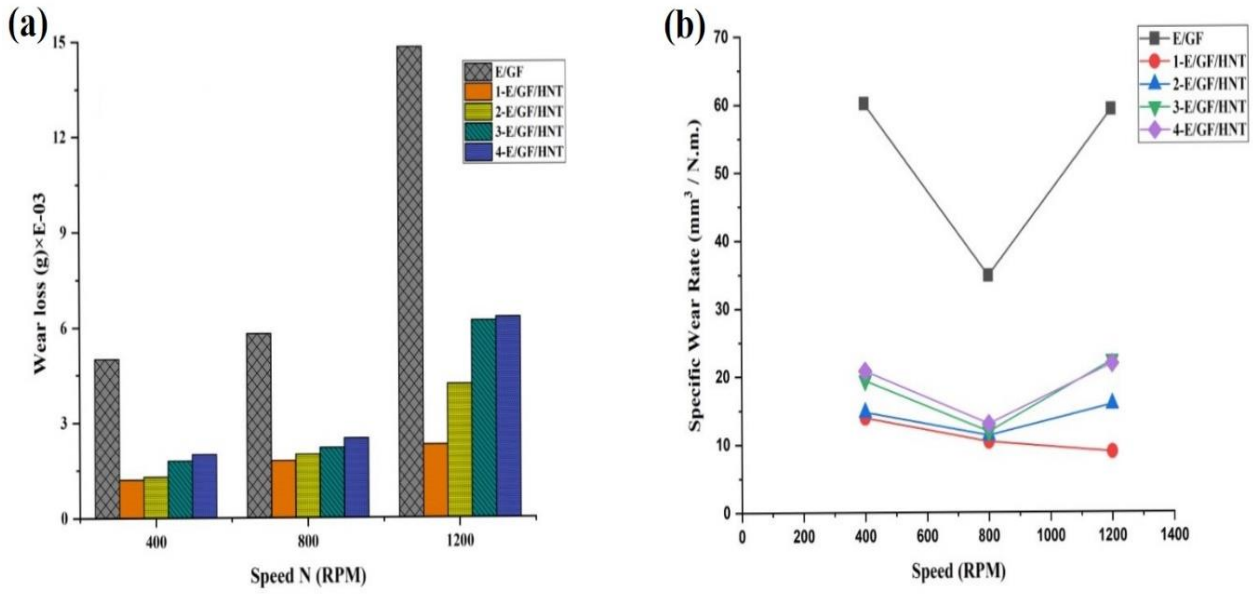

Fig. 3: (a).Wear loss and (b). Specific wear rate of nanocomposites at 40 N Loading.

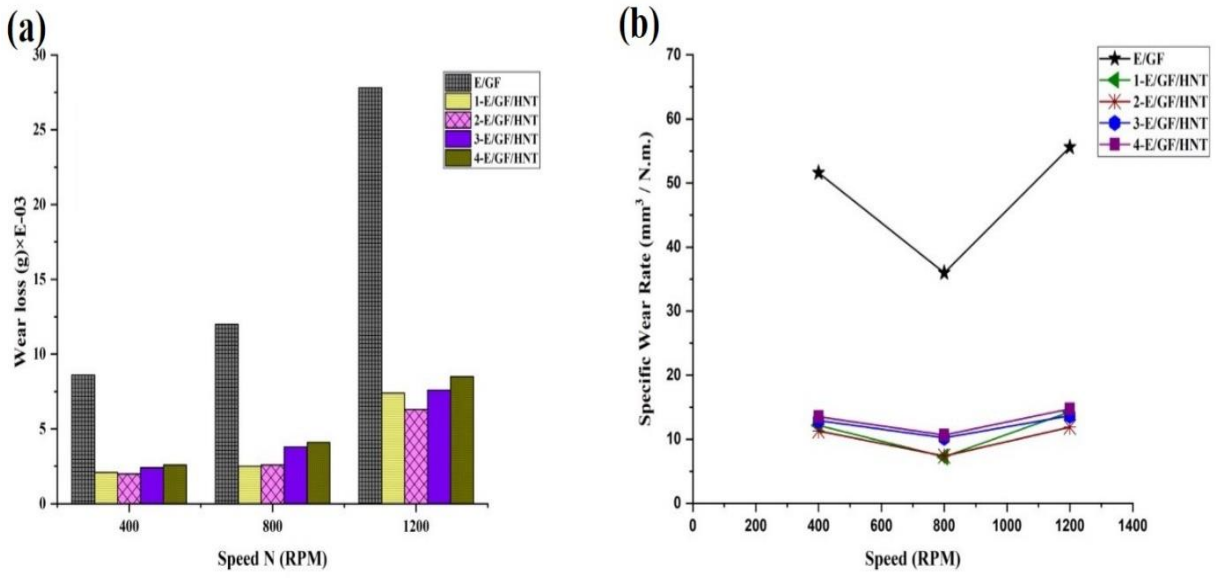

Fig. 4: (a). Wear loss and (b). Specific wear rate of nanocomposites at 80 N Loading.

The enhancement in wear resistance properties are measured precisely by two attributes viz., amount of weight loss and specific wear rate in this study. The amount of weight loss reduction in percentages are 78.17 %, 80.41 %, 65.29 % and 58.21 %, similarly specific wear rate reduces to 78.9 %, 87.11 %, 68.79 % and 63.76 % for the addition of 1 wt %, 2 wt %, 3 wt % and 4 wt % of HNT respectively at extreme operating conditions viz., 120N and 1200 RPM respectively. This may be due to the presence of hard ceramic elements viz. SiO_2 and Al_2O_3 in HNT, which may cause an increase in surface hardness of matrix phase and also avoid the increase in temperature due to frictional forces, Also another reason for the improvement in the wear properties is due to uniform dispersion of HNT particles which enhances the bonding between fiber and matrix interface. It means that HNT is treated as an effective filler for improving the tribological performance of glass fiber reinforced epoxy composites.

The lowest value of weight loss and specific wear rate are registered in case of 2 wt % inclusion of HNT in nanocomposites as shown in Fig. 5. However, these improvements are not observed at higher HNT loading conditions due to the probability of agglomeration and more dislodging of wear debris. Furthermore, in order to understand the effect of HNTs on the wear properties, the SEM micrographs of the worn surface of nanocomposites are captured to study in detail about morphology and wear mechanisms.

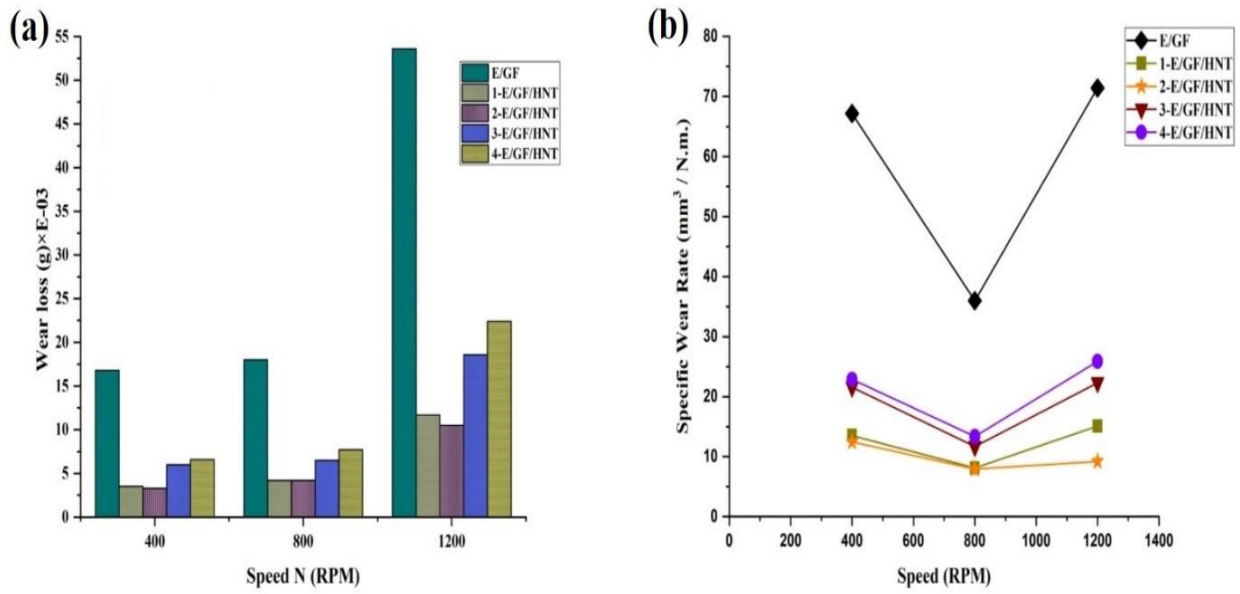

Fig. 5: (a). Wear loss and (b). Specific wear rate of nanocomposites at 120 N Loading.

B. Worn surface morphology

The worn surface analysis is carried out by capturing the SEM images of all the nanocomposites as shown in Fig. 6. It is clearly observed from the Fig. 6 (a), that there is more amount of matrix debris, fiber breakages and fiber-matrix debonding in neat composites due to increase in normal load which will eventually cause more amount of contact stresses acting at specimen and disc interface, leading to the removal of epoxy from the surface of the specimen at faster rate leaving the top layer of fibers exposed to the environment which further causes the brittle failure of glass fibers on the surface of the specimen.

The addition of HNT upto 2 wt % gives a better fiber–matrix bonding at the worn surface due to wear test at high normal load of 120 N. This leads to high wear resistance characteristics due to a strong cohesive bonding between HNT particles and epoxy matrix with glass fibers, thus higher amount of stress is required to separate the particles from the matrix, hence increasing the wear resistance. Furthermore, HNT comprises of ceramic elements in larger proportions, which resists the wear and act as a barrier between the surfaces. Thus the addition of nanoparticles has a positive effect on wear resistance in terms of lesser amount of matrix debris, relatively lesser exposure of fibers to environment as shown in Fig. 6 (b) and (c) respectively.

Beyond 2 wt % of HNT loading conditions, the fiber surfaces do not adhere properly with matrix material, which results in weak bonding at fiber–matrix interface due to more agglomeration of nanoparticles in one particular localized region which further constitutes the development of the voids in other regions. Thus the specimens are not strong enough to resist the higher contact stresses during wear test which initiates the formation of crack, and its initiation, further the crack growth and lack of coalescence at sublayer of the worn surface and also the weak bonds results in severe damage by micro ploughing between the nanoparticles and adjacent surfaces. This may be the reason for drawing the parlance for increased weight loss and wear rate as shown in the Fig. 6 (d) and (e) respectively. Thus HNT particles at higher loading gives poor wear resistance which is not even close to neat composites at higher loads.

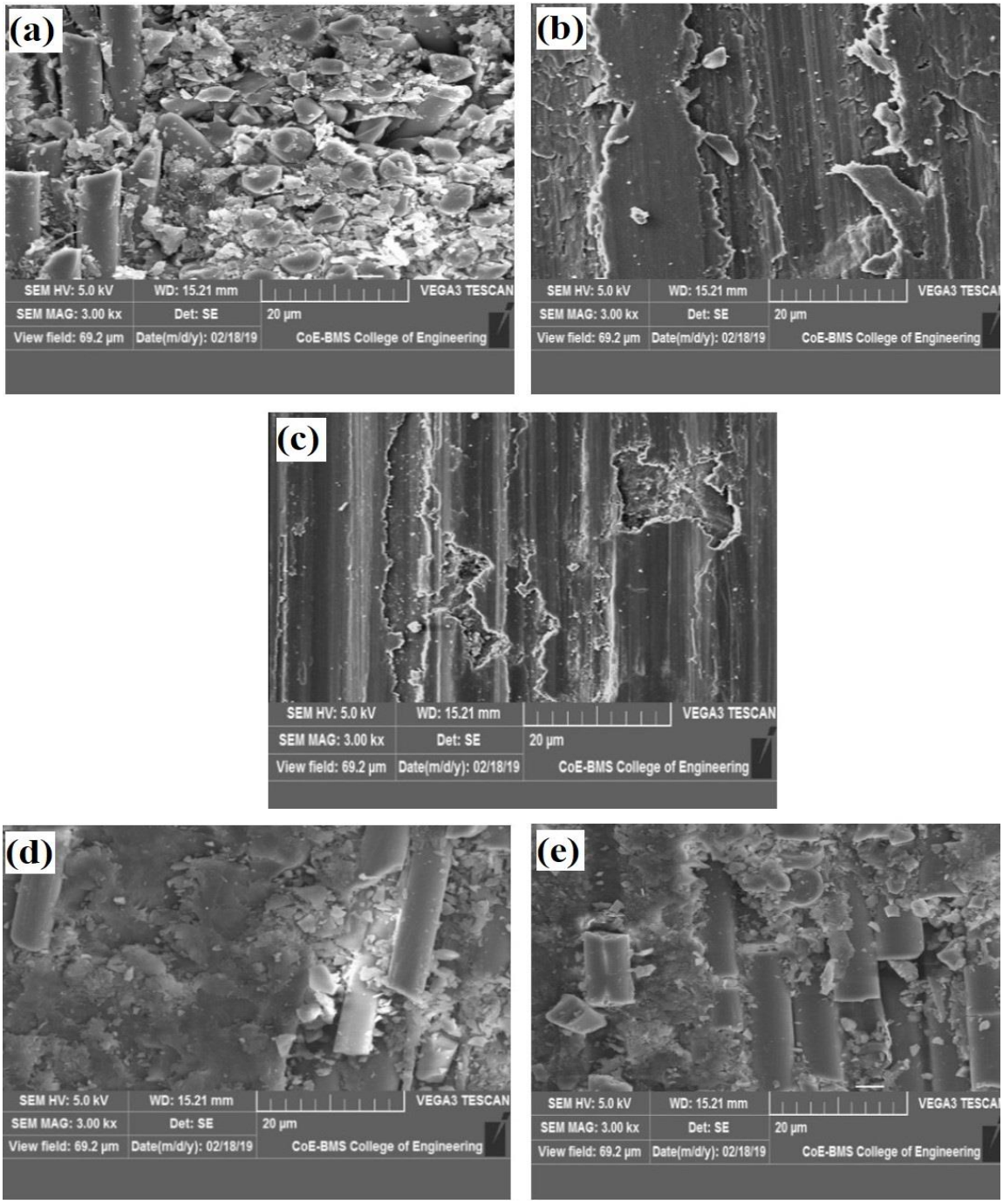

Fig. 6: Worn surface micrographs of (a). E/GF. (b). 1-E/GF/HNT. (c). 2-E/GF/HNT. (d). 3-E/GF/HNT. (e). 4-E/GF/HNT nanocomposites under 120 N load and 1200 RPM Speed.

IV. CONCLUSIONS

After the thorough evaluation of obtained results, certain critical observations are made which are as presented below:

- The antiwear performance of the HNT filled glass-epoxy nanocomposites prepared by vacuum bagging technique is significantly improved as compared to neat composites at all loading conditions and sliding velocities due to the presence of ceramic elements viz. SiO_2 and Al_2O_3 in HNT, which leads to an increase in hardness of nanocomposites and also develops a strong cohesive bond with epoxy matrix and glass fibers.
- The least specific wear rate and weight loss are noticed in the 2 wt. % HNT loaded nanocomposites, hence it is treated as optimum concentration for wear applications of prepared nanocomposites. The addition of HNT upto 2 wt % improves the wear resistance properties in terms of weight loss and specific wear rate i.e., by about 80.41 % and 87.11% respectively as compared to the neat composites which is attributed to the uniform dispersion of HNT in the matrix that eventually act as a barrier between the internal surfaces, hence it resists transfer of load on fiber surfaces.

However, further increase in HNT up to 4 wt% leads to agglomeration in a localized region on one side and formation of voids on the other side that eventually initiates crack formation and its growth and lack of coalescence between the sublayers leading to the significant reduction in wear resistance capabilities.

- The study on worn surfaces of all the nanocomposites reveals that there is a severe brittle fracture of glass fibers and more amount of matrix debris in neat composites as compared to HNT filled nanocomposites due to the failure of material notwithstanding the higher contact stresses.

Conflict of Interest

The authors declare that they have no conflict of interest in the subject matter or materials discussed in this manuscript.

REFERENCES

1. Yiu-Wing Mai, Zhong-Zhen Yu (2006). Polymer nanocomposites. Woodhead Publishing, Cambridge, UK. ISBN: 9781855739697.
2. K. Friedrich (2018). Polymer composites for tribological applications. Advanced Industrial and Engineering 1 (1): 3-39.
3. L. Chang, Z. Zhang, C. Breidt, K. Friedrich (2005). Tribological properties of epoxy nanocomposites: I. Enhancement of the wear resistance by nano-TiO_2 particles. Wear 258 (1-4): 141-148.
4. L. Chang, Z. Zhang, C. Breidt, K. Friedrich (2005). Tribological properties of epoxy nanocomposites: I. Enhancement of the wear resistance by nano-TiO_2 particles. Wear 258 (1-4): 141-148.
5. Thomas O. Larsen, Tom L. Andersen, Bent Thorning, Andy Horsewell, Martin E. Vigild (2008). Changes in the tribological behaviour of an epoxy resin by incorporating CuO nanoparticles and PTFE microparticles. Wear 265 (1-2): 203-213.
6. A. A. Megahed, M. A. Agwa, M. Megahed (2017). Improvement of Hardness and Wear Resistance of Glass Fiber-Reinforced Epoxy Composites by the Incorporation of Silica/Carbon Hybrid Nanofillers. J. Polymer-Plastics Technology and Engineering 57 (4): 251-259.
7. Rashmi, N.M. Renukappa, B. Suresha, R.M. Devarajaiah, K.N. Shivakumar (2011). Dry sliding wear behaviour of Organo-modified montmorillonite filled epoxy nanocomposites using Taguchi's techniques. Materials and Design 32 (8-9): 4528–4536.
8. Chang B., Md Akil H., Affendy M., Khan A., Nasir R (2014). Comparative study of wear performance of particulate and fiber-reinforced nano-ZnO/ultra-high molecular weight polyethylene hybrid composites using response surface methodology. Materials and Design 63: 805–819.
9. Li H., Yin Z., Jiang D., Huo Y., Cui Y (2014). Tribological behavior of hybrid PTFE/Kevlar fabric composites with nano-Si_3N_4 and submicron size WS_2 fillers. Tribology International 80: 172-178.
10. José Donato Ambrósio, Caio Vinicius Morisco Balarim, Gustavo Baldi de Carvalho (2016). Preparation, characterization, and mechanical/tribological properties of polyamide 11/Titanium dioxide nanocomposites. Polymer Composites 37 (5): 1415-1424.
11. Lin G. M., Xie G. Y., Sui G. X., Yang R. (2012). Hybrid effect of nanoparticles with carbon fibers on the mechanical and wear properties of polymer composites. Composites Part B: Engineering 43 (1): 44-49.
12. N.M. Barkoula, A. Papadopoulos, G. Gkikas, A.S. Paipetis (2016). Effect of CNTs addition on the erosive wear response of epoxy resin and carbon fiber composites. Composites Part A 84: 299–307.
13. Du, M.L., Guo, B.C., Jia, D.M. (2010). Newly emerging applications of halloysite nanotubes: a review. Polymer International 59 (5): 574-582.
14. Ravindra Kamble, Manasi Ghag, Sheetal Gaikawad, Bijoy Kumar Panda (2012). Halloysite Nanotubes and Applications: A Review. Journal of Advanced Scientific Research 3(2): 25-29.
15. Ravichandran G, Rathnakar G, Santhosh N (2019). Effect of heat treated HNT on physico-mechanical properties of epoxy nanocomposites. Composites Communications 13(4): 42-46.
16. Ravichandran G, Rathnakar G, Santhosh N, Chennakeshava R, Mosharib Ahmad Hashmi (2019). Enhancement of mechanical properties of epoxy/halloysite nanotube (HNT) nanocomposites. SN Applied Sciences 1(4): 296-303.

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