Sains Malaysiana 43(6)(2014): 959–966

Effect of Nano- and Micro- Reinforced Agents on Dry Sliding Wear of Polyester Composites

(Kesan Agen Memperteguh Nano-dan Mikro- terhadap Haus Gelongsor Kering Komposit Poliester)

CHONG MENG MUN*, CHANG SIANG YEE, NORAIHAM MUHAMMAD,
ZULKIFLI BIN MOHD ROSLI & QUMRUL AHSAN

ABSTRACT

Dry sliding wear of polyester hybrid composites containing carboxylic functionalized multi-walled carbon nanotubes (CNT) and microparticles, silica (SiO_2) was studied at different sliding distances. An attempt has been made to produce uniform dispersion of nano- and micro- particles in the test samples by ultrasonication. The tribological properties of the hybrid composites were performed by using pin-on-disc (POD) tester against grey cast iron countersurface. The dry sliding wear tests were carried out under pressure-velocity (pv) condition of 0.4 MPa and 4 m/s for total sliding distance of 28800 m and at an interval of every sliding distance of 3600 m, wear properties and behavior were studied. The samples containing 10 wt.% silica (microparticles) with and without CNT always show increase in coefficient of friction at the expense of wear rate. However, samples containing only CNT have the lowest wear rate with the increase in coefficient of friction. Sliding distance studies also provide the information on wear rates which were ever changing at different sliding distances whereas average coefficient of friction did not vary throughout the tests. SEM observations of wear surfaces showed different wear morphologies when reinforcement (CNT or SiO_2) incorporated into the composites either alone or in combination.

Keywords: Carbon nanotubes; silica; wear behavior

ABSTRAK

Komposit hibrid poliester yang mengandungi fungsi karbosilik pelbagai dinding karbon tiub nano (CNT) dan mikropartikel, silika (SiO_2) telah dikaji tentang kehausan gelongsor kering pada beberapa jarak gelongsor. Percubaan serakan seragam telah dijalankan dengan penggunaan ultrasonikasi untuk menyerakkan nano- dan mikro- partikel dalam komposit. Ciri tribologikal komposit hibrid telah dijalankan dengan menggunakan penguji pin atas cakera (POD) terhadap permukaan kaunter besi tuang kelabu. Ujian haus gelongsor kering telah dijalankan dalam keadaan gelongsor yang mempunyai daya tekanan 0.4 MPa dan halaju 4 m/s bagi jumlah jarak gelongsor sebanyak 28800 m pada jarak gelongsor setiap 3600 m. Sampel yang mengandungi 10 %.bt silika (mikropartikel) dengan atau tanpa CNT sentiasa menunjukkan peningkatan dalam pekali geseran dan kadar haus. Walau bagaimanapun, sampel yang mengandungi CNT sahaja mempunyai ketahanan haus yang terendah dan pekali geseran tertinggi dalam ketiga-tiga komposit. Kajian pada jarak gelongsor juga menunjukkan bahawa kadar haus sentiasa berubah pada jarak gelongsor yang berbeza manakala pekali geseran tidak mempunyai perbezaan yang ketara sepanjang ujian. Cerapan SEM pada permukaan haus menunjukkan morfologi yang berbeza apabila poliester bergabung dengan satu jenis partikel (CNT atau silika) atau kedua-dua jenis partikel (CNT dan silika).

Kata kunci: Haus; karbon tiub nano; silika

INTRODUCTION

Polymer composites have been used extensively for tribological applications such as clutches, brake components and bearings of automotives. The utilization of these materials on automobile sectors is due to their self-lubricity, light weight and near-net shape manufacturing (Feyzullahoglu & Saffak 2008). An addition of fillers in polymer composites are due to the properties improvement that can be obtained by the resulting interfacial zones between polymers and fillers. Thus, interaction or reaction between the polymer chains and fillers can manifest unexpected properties (Bugnicourt et al. 2007). One of the nano-reinforcing agents, carbon nanotube (CNT) has attracted attention around the world by virtue of its outstanding characteristics. The high aspect ratio coupled with low density and high strength as well as stiffness makes CNT a potential reinforcing candidate for polymeric materials (Chauhan et al. 2010; Laurent & Peigney 2004). Besides, nano- fillers are capable to overcome the drawbacks of enhanced stiffness and strength of polymer composites at the expense of toughness. As a matter of fact, neat polymers network are known to have less potential to resist from crack propagation. Several studies on the nano- and micro- reinforcing agents have proven to improve the tribological properties of polymer composites (Xing & Li 2004; Zhang et al. 2007). Silica particles (20-40 µm) added into epoxy resin at 68.5 wt.% had decreased wear loss with increasing sliding speed (Kanchanomai 2011). A significant enhancement in wear resistance of CNT/epoxy composites was also reported by Chen et al. (2007) whereby wear rate was reduced by a factor of 5.5 with the incorporation of 0.1 wt.% of CNT. Though both of nano- and micro- reinforcing agents showed enhancement of tribological properties in polymer matrix composites, the synergistic effects of hybridizing these fillers are not yet studied extensively.

It is known that CNT is difficult to be dispersed homogeneously in polymer matrix due to its chemical inertness and large surface area (Ma et al. 2010). Thus, chemical modification is usually employed to increase the exemption of CNT agglomeration in polymer matrix (Chen et al. 2007; Men et al. 2008). Apart from this, ultrasonication is one of the physical methods of dispersion which is able to mitigate the CNT agglomeration problem effectively (Ahir & Terentjev 2007; Chen et al. 2007).

Wear mechanism is a system response whereby wear properties correlate with operational parameters which are able to be forecasted by simulation of system (Bayer 2004). Thus, it is imperative to understand the possible wear mechanism during specific sliding conditions for the purpose of materials design with optimum wear and frictional characteristics.

The present work attempted to understand the modification of wear resistance and coefficient of friction by incorporating nano-sized CNT and micro-sized silica particles in polyester composites. Wear mechanisms under the specific tribological condition were studied by scanning electron microscope observations.

MATERIALS AND METHODS

MATERIALS

The matrix material used in the present work was unsaturated polyester resin (UPR) with methyl ethyl ketone peroxide (MEKP) as the catalyst. Micro-sized silica (SiO_2) particles and carboxylic functionalized multi-walled carbon nanotubes (CNT) were the reinforcing agents employed in the hybrid polyester composites. The silica particles acquired from Sibelco Malaysia Sdn. Bhd. have an outer diameter in the range of 15-25 µm. The CNT were purchased from Nanostructured & Amorphous Materials Inc., the outer diameter is in the range of 10-30 nm and purity of 88%.

FABRICATION OF HYBRID POLYESTER COMPOSITES

Initially, silica particles were dispersed in the polyester resin using an ultrasonicator (UP100H, Hielscher) at 90% amplitude for 10 min. Then, the step was repeated by incorporating another reinforcing agent, CNT in the polyester resin. After dispersion, the mixture was put into the vacuum drying oven at 0.1 MPa for 30 min in order to evacuate most of the entrapped air. The same evacuation action was made for another 5 min after the catalyst was mixed into the mixture. Vacuum infusion method as in Figure 1 was used to produce cylindrical samples required for pin-on-disc tests in accordance with ASTM G99-05. Specimen pins were prepared from the fabricated cylindrical sample after post curing at room temperature for overnight and subsequently at 40ºC for 16 h. The compositions and nomenclature of the test samples are presented in Table 1.

DRY SLIDING WEAR TEST

Wear tests were carried out using pin-on-disc tester (TR-20LE, Ducom Instruments Pvt. Ltd.). The tests were carried out under dry conditions 20 N and 4 m/s at an interval of

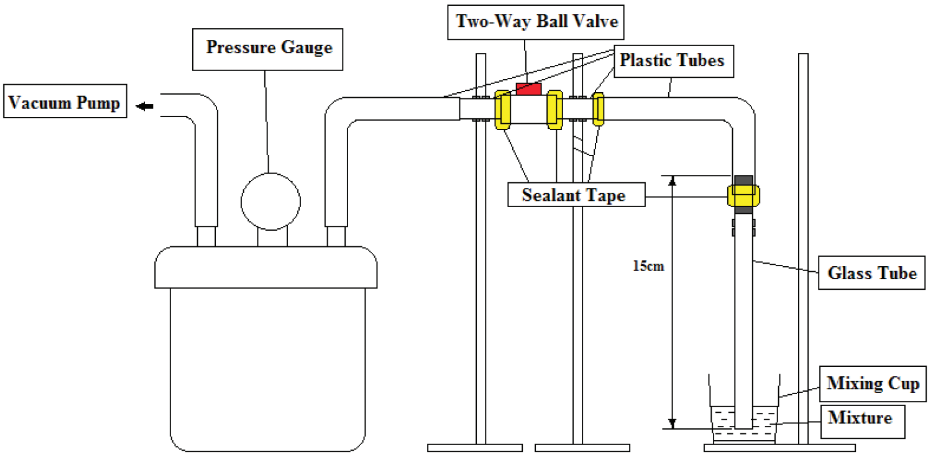

FIGURE 1. Vacuum infusion method

TABLE 1. Nomenclature of the test samples of different composition

Nomenclature	Composition (wt.%)		
	UPR	SiO_2	CNT
UPR/0.1	99.9	-	0.1
UPR/SiO_2	90	10	-
UPR/SiO_2/0.1	89.9	10	0.1

every sliding distance of 3600 m for total sliding distance of 28800 m. A grey cast iron (Grey Iron 4E) with 85.26 HRB (Flocast Australia Pty. Ltd.) was selected as countersurface material. The countersurface was polished to achieve a surface roughness of R_a 0.8, as recommended in ASTM G99-05. Intimate touch of pin on countersurface was ensured before the test began in order to avoid long break-in period. The coefficient of friction was directly obtained from the wear tester and the weight loss of samples due to wear was measured using digital balance.

Finally, the specific wear rate, W was calculated according to the following equation.

$$W = \frac{\Delta m}{\rho \times F \times 1}, \tag{1}$$

where Δm is the mass loss (g), ρ is the density (g/cm^3), F is the sliding load (N) and L is the sliding distance (m).

SURFACE EXAMINATION

In order to understand the possible mechanism under the specific sliding condition, worn surfaces of specimen pins were investigated using Carl Zeiss (Evo® 60) scanning electron microscope (SEM). The wear tracks on the cast iron counter surfaces were also observed using Meiji Techno Co., Ltd. (EMZ-8TR) zoom stereo microscope.

EXPERIMENTAL DETAILS

The experimental design of the dry sliding tests was conducted as per the historical data design. There were three parameters taken in consideration, reinforced agents, CNT (A), SiO_2 (B) and sliding distance (C). These parameters were at different levels, CNT (A) and SiO_2 (B) were at three levels while sliding distances (B) were at eight levels. All control parameters and their levels are tabulated in Table 2. Statistical analysis of variance (ANOVA) was applied for the purpose of determining the percentage contribution of each control parameter and their interactions in the experimental results. The statistical analysis was performed using Design-Expert statistical software (Statistics Made Easy, version 7.0.0, Stat-Ease, Inc., Minneapolis, MN).

RESULTS AND DISCUSSION

WEAR BEHAVIOR

Variation of specific wear rates of polyester composites is presented in Figure 2. A running- in wear was observed at the beginning of sliding test on all samples as it is obvious for polyester composites (Zhang et al. 2007) and it is presumed that after the run-in stage, all composite samples test system was stable. The sample containing only CNT (UPR/0.1) has the shortest run-in period where the specific wear rate tends to stable after sliding distance of 7200 m. Meanwhile, specific wear rates of all polyester composites were decreasing as the sliding distance increased. Furthermore, the samples with only CNT (UPR/0.1) exhibit the lowest specific wear rate as the sliding distance increased and a continuous transfer film of composite material is found to adhere to the countersurface (Figure 3(a)). The continuous transfer film may retard further removal of materials from test sample. Tranfer films were also observed on the countersurface when tested with UPR/SiO_2 and UPR/SiO_2/0.1 samples but the appearances of transfer films were discontinuous

TABLE 2. Control factors and levels used in the experiment

Levels	Control factor		
	A: CNT (wt. %)	B: SiO_2 (wt. %)	B: Sliding distances (×100 m)
I	0.1	0	36
II	0	10	72
III	0.1	10	108
IV	-		144
V	-		180
VI	-		216
VII	-		252
VIII	-		288

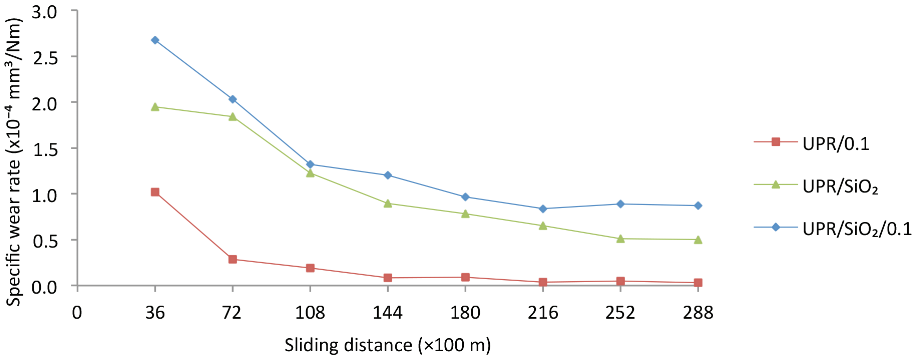

FIGURE 2. Comparison of wear rates of various polyester composites at different sliding distances under dry sliding at 4 m/s, 20N

(Figure 3(b) and 3(c)). The presence of silica particles may scale off transfer films during wear process (Song & Zhang 2006). Hence, wear protection was reduced due to discontinuous transfer film.

Figures 4, 5 and 6 show the wear surface SEM micrographs of UPR/0.1, UPR/SiO_2 and UPR/SiO_2/0.1 samples, respectively. In wear surface of UPR/0.1 sample, material waves (Figure 4(a)) were developed from cracks originating from wear track and appeared perpendicular to the sliding direction. The introduction of CNT obstructs the propagation of cracks into the polyester matrix to some extent by consecutive development of smooth facet and wave front. The generation of small wave fronts slow down the material removal via microcracks and fragmentation of materials (Figure 4(b)), as evidenced by other researchers (Zhang et al. 2007).

The sample containing only silica (UPR/SiO_2) showed the absence of wave front on wear surface, as shown in Figure 5. In terms of wear damage, material removal occurred through cracking at filler/matrix interface followed by dislodging of silica particles which abrades the polyester matrix and causes further material removal.

Figure 6 shows the SEM wear surface on UPR/SiO_2/0.1 sample where the mix mode of material wave phenomena

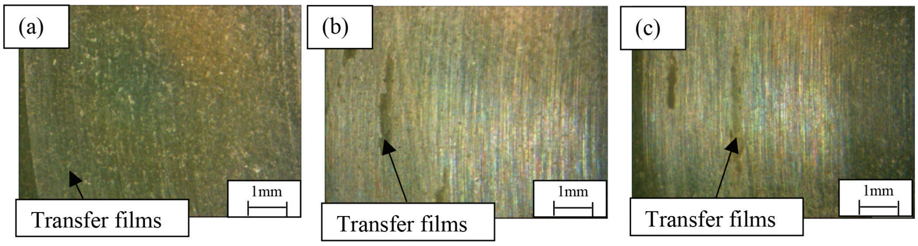

FIGURE 3. Countersurfaces after dry sliding test (a) UPR/0.1, (b) UPR/SiO_2 and (c) UPR/SiO_2/0.1 (4 m/s, 20N)

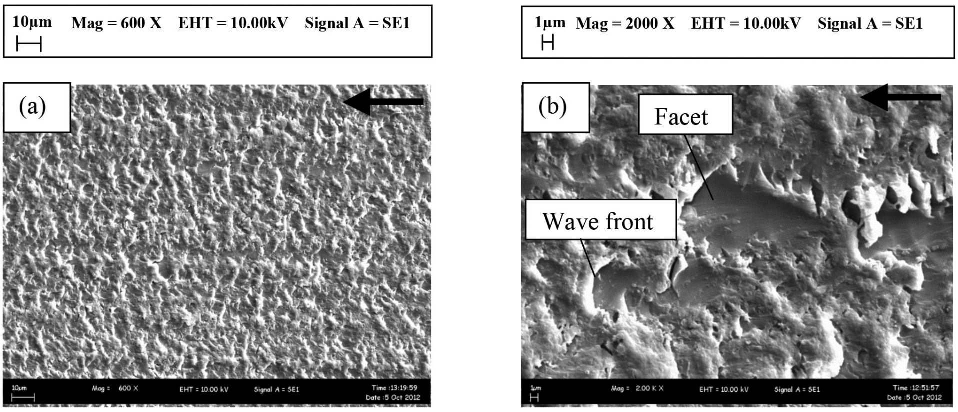

FIGURE 4. SEM of wear surfaces on sample UPR/0.1 (4 m/s, 20N). Arrows in micrographs indicate the sliding direction during wear test

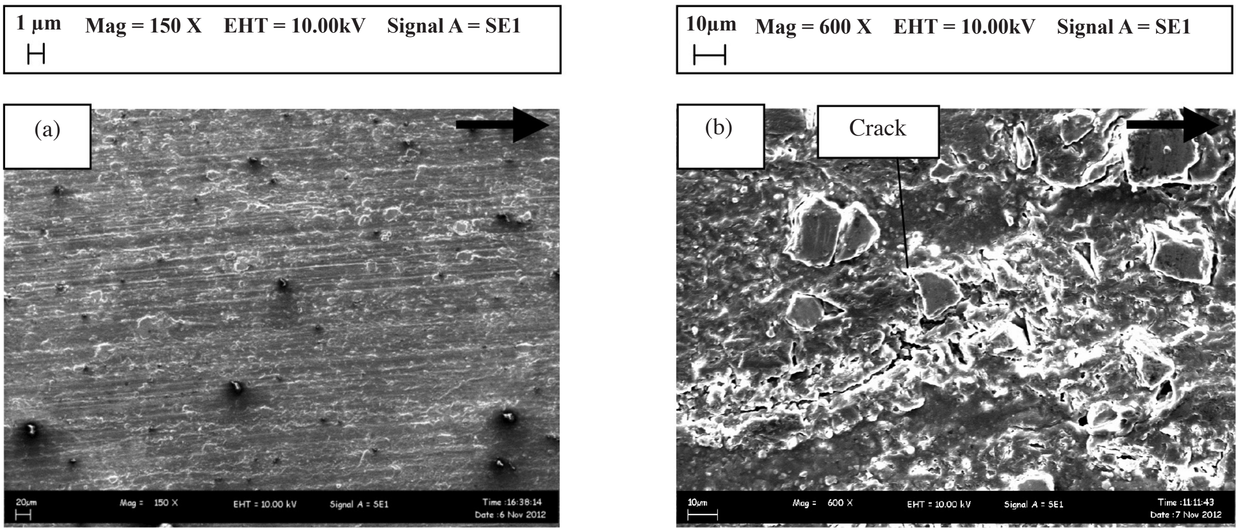

FIGURE 5. SEM of wear surfaces of sample UPR/SiO$_2$ (4 m/s, 20N). Arrows in micrographs indicate the sliding direction during wear test

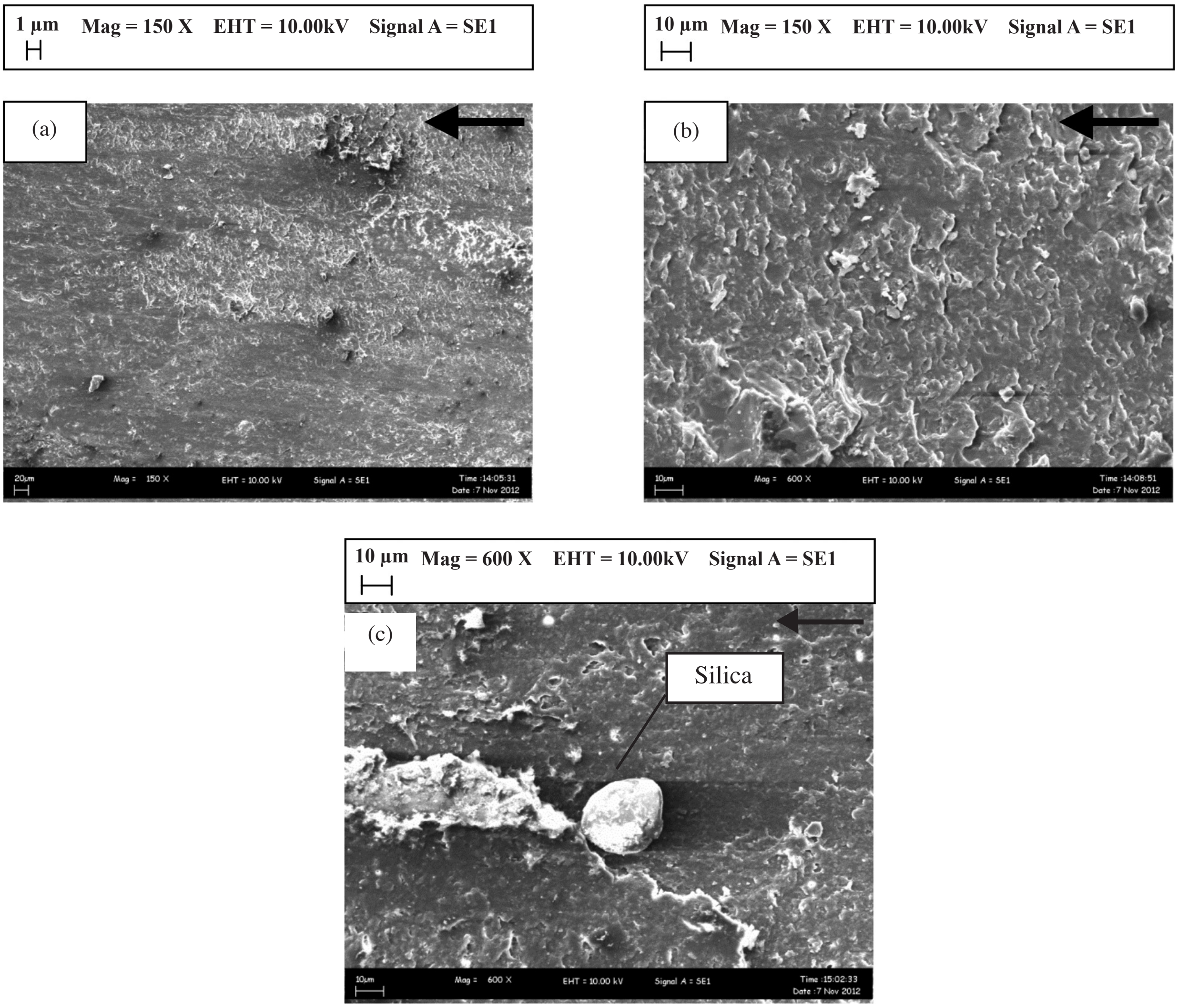

FIGURE 6. SEM of wear surfaces of sample UPR/SiO$_2$/0.1 (4 m/s, 20N). Arrows in micrographs indicate the sliding direction during wear test

and nominal wear phenomena was observed. The presence of large and edged silica particles (Figure 6(c)) causes worn out of matrix resulting in starvation of material waves in some regions of the wear surface. In addition, agglomeration of CNT and silica particles caused by poor particulate dispersion has weakened the interfacial bonding between fillers and matrix (Men et al. 2008). Among the tested samples, material removal through a combination of abrasion from silica and fracture from CNT generated the highest wear rate in the CNT/silica hybrid composite (UPR/SiO_2/0.1). Adherence of a discontinuous yet discrete transfer film on the countersurface also supports the fact of a low wear resistance (Figure 3(c)).

Figure 7 shows the coefficient of friction (COF) of the composite samples obtained from the wear tests. The sample incorporated with only CNT (UPR/0.1) exhibits the highest values of COF as compared with other composites throughout the wear test. Meanwhile, composites containing SiO_2, with and without CNT, show an approximately 50% reduction in COF as compared with UPR/0.1. Although a smooth transfer film was formed on countersurface during the wear test of UPR/0.1, the material waves generated rough ridges and valleys on wear surface at microscopic level (Figure 4(a) and 4(b)) resulted in a high value of COF. Silica particulate reinforced composites, with and without CNT, did not form a continuous transfer film due to tearing of films by silica particles; however, the microscopic wear surfaces of both samples showed least rough surfaces where friction force was minimized (Stachowiak 2005).

ANALYSIS OF EXPERIMENTAL RESULTS

In order to find out the characteristics of variables reinforced agents and sliding distance, statistical analysis of variance (ANOVA) was applied. Tables 3 and 4 are the results of ANOVA for specific wear rate and COF. This analysis provides at least 95% confidence for all results in responses, specific wear rate and coefficient of friction. The P value in Tables 3 and 4, the reinforced agents, SiO_2 and sliding distance are the controlling factors on the specific wear rate and COF. In addition, it is evident that reinforced agent, SiO_2 and sliding distance are controlling the responses predominantly.

The design expert software had generated a regression models in order to understand the relationship between the control parameters (CNT, SiO_2 and sliding distance) and responses (specific wear rate and COF). The following are the regression models fitted to specific wear rate and COF.

Specific wear rate (mm^3/Nm),

$$W = +0.63 + 0.15 \times A + 0.56 \times B - 0.66 \times C. \qquad (2)$$

Coefficient of friction,

$$COF = +0.48 - 9.438E\text{-}03 \times A - 0.12 \times B + 0.016 \times C. \qquad (3)$$

A R^2 value of 0.8487 shows the specific wear rate whereby it indicates that 84.87% of the variability in the response can be explained. As for coefficient of

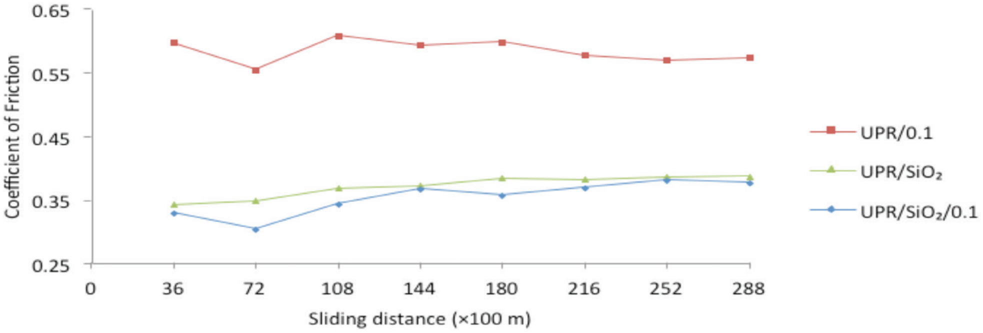

FIGURE 7. Comparison of coefficient of friction of various polyester composites under dry sliding at 4 m/s, 20N

TABLE 3. ANOVA table for specific wear rate

Source	SS	df	MS	F Value	P value	
Model	9.87	3	3.29	37.40	< 0.0001	Significant
A	0.37	1	0.37	4.24	0.0528	
B	5.08	1	5.08	57.73	< 0.0001	
C	4.44	1	4.44	50.44	< 0.0001	
Residual	1.76	20	0.088			
Cor Total	11.63	23				

TABLE 4. ANOVA table for coefficient of friciton

Source	SS	df	MS	F Value	P value	
Model	0.27	3	0.088	267.46	< 0.0001	Significant
A	0.001425	1	0.001425	4.31	0.0509	
B	0.21	1	0.21	644.07	< 0.0001	
C	0.03	1	0.002693	8.15	0.0098	
Residual	0.006606	20	0.003303			
Cor Total	0.27	23				

friction, the R^2 value is 0.9757. In other words, 97.57% of coefficient of friction variation can be explained for this model. From the regression models (2), it shows that reinforced agent, SiO_2 has the highest effect, leading the other control parameters, reinforced agent, CNT and sliding distance. However, the sliding distance has the most significant influence on COF and it was followed by reinforced agents, CNT and SiO_2.

CONCLUSION

In conclusion, specific wear rate of polyester nanocomposite (UPR/0.1) decreased while the microcomposite (UPR/SiO_2) and hybrid composite (UPR/SiO_2/0.1) increased with the increasing sliding distance. This was attributed to the different wear phenomena of the composites which were showed through the distinctive features observed on the wear surface in SEM micrographs. For the nanocomposite, the formation of continuous transfer film on countersurface results in the enhancement of wear resistance of the composite. Unlike the nanocomposite, the presence of dislodged silica on wear surface was responsible for abrasion and increases the wear rate of the microcomposite; whilst the wearing of the hybrid composite was the concomitant of the wear phenomena of both nano- and micro- composites. In terms of COF, UPR/0.1 has the highest COF owing to the rough ridge and valley configurations on the wear surface whereas the relatively smooth surfaces and absence of material waves in some regions of wear surfaces of UPR/SiO_2 and UPR/SiO_2/0.1 reduced the COF values. According to the ANOVA, the reinforced agent, SiO_2 has the highest contributing effect compare with sliding distance and reinforced agent on specific wear rate and COF. Further research is required on different sliding conditions for tribological applications of hybrid polyester composites.

ACKNOWLEDGEMENTS

The authors are highly grateful for the financial support provided by Universiti Teknikal Malaysia Melaka (UTeM) under grant No. (PJP/2011/FKP(4B)/S00871).

REFERENCES

Ahir, S.V. & Terentjev, E.M. 2007. Polymers containing carbon nanotubes: Active composite materials. In *Polymeric Nanostructures and Their Applications*, edited by Nalwa, H.S. USA: American Scientific Publishers.

Bayer, R.G. 2004. *Engineering Design for Wear*. New York: Marcel Dekker, Inc. pp. 1-2.

Bugnicourt, E., Galy, J., Gerard, J. & Barthel, H. 2007. Effect of sub-micron silica fillers on the mechanical performances of epoxy-based composites. *Polymer* 48: 1596-1605.

Chauhan, S.R., Kumar, A. & Singh, I. 2010. Sliding friction and wear behavior of vinylester and its composites under dry and water lubricated sliding conditions. *Materials and Design* 31: 2745-2751.

Chen, H., Jacobs, O., Wu, W., Rudiger, G. & Schadel, B. 2007. Effect of dispersion method on tribological properties of carbon nanotube reinforced epoxy resin composites. *Polymer Testing* 26: 351-360.

Feyzullahoglu, E. & Saffak, Z. 2008. The tribological behavior of different engineering plastics under dry frction conditions. *Materials and Design* 29: 205-211.

Kanchanomai, C., Noraphaiphipaksa, N. & Mutoh, Y. 2011. Wear characteristic of epoxy resin filled with crushed-silica particles. *Composites: Part B* 42: 1446-1452.

Laurent, C. & Peigney, A. 2004. Carbon nanotubes in composite materials. In *Encyclopedia of Nanoscience and Nanotechnology*, edited by Nalwa, H.S. USA: American Scientific Publishers.

Ma, P.C., Siddiqui, N.A., Mrom, G. & Kim, J.K. 2010. Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: A review. *Composites: Part A* 41: 1345-1367.

Men, X.H., Zhang, Z.Z., Song, H.J., Wang, K. & Jiang. W. 2008. Functionalization of carbon nanotubes to improve the tribological properties of poly(furfuryl alcohol) composite coatings. *Composites Science and Technology* 68: 1042-1049.

Song, H.J. & Zhang, Z.Z. 2006. Study on the tribological and hydrophobic behaviors of phenolic coatings reforced with PFW, PTFE and FEP. *Surface & Coatings Technology* 201: 1037-1044.

Stachowiak, G.W. 2005. *Wear: Materials, Mechanisms and Practice*. New York: Wiley. pp. 291-315.

Xing, X.S. & Li, R.K.Y. 2004. Wear behavior of epoxy matrix composites filled with uniform sized sub-micron spherical silica particles. *Wear* 256: 21-26.

Zhang, L.C., Zarudi, I. & Xiao, K.Q. 2007. Novel behavior of friction and wear of epoxy composites reinforced by carbon nanotubes. *Wear* 261: 806-811.

Department of Engineering Material
Faculty of Manufacturing Engineering
Universiti Teknikal Malaysia Melaka
Hang Tuah Jaya

76100 Durian Tunggal, Melaka
Malaysia

Received: 4 April 2013
Accepted: 10 January 2014

*Corresponding author; email: cmm@student.utem.edu.my