Friction Properties of Sisal Fiber/Nano-Silica Reinforced Phenol Formaldehyde Composites

Chun Wei,[1,2] Ming Zeng,[2,3] Xuemei Xiong,[2,3] Hongxia Liu,[1,2] Kun Luo,[1,2] Tianxi Liu[1]
[1]*Key Laboratory of New Processing Technology for Nonferrous Metals and Materials, Ministry of Education, Guilin University of Technology, Guilin 541004, China*

[2]*College of Materials Science and Engineering, Guilin University of Technology, Guilin 541004, China*

[3]*Guilin Electrical Equipment Scientific Research Institute Co. Ltd., Guilin 541004, China*

The friction-resistant sisal fiber/nano-silica phenol formaldehyde resin composites were prepared through compression molding. To enhance the bonding between the sisal fiber (SF) and polymer matrix, SF were treated with different surface modifiers. The worn surfaces of composites were observed by scanning electron microscope (SEM). The result shows that the matrix of nano-silica phenol formaldehyde resin can relieve the heat fade of the friction materials. Meanwhile sisal fibers treated with borax have effectively improved the friction and wear properties of the composites when the fiber content was 15%. POLYM. COMPOS., 36:433–438, 2015. © 2014 Society of Plastics Engineers

INTRODUCTION

Asbestos fibers are conventionally used in friction-resistant materials, for their excellent heat resistance and mechanical strength. However, it is known that asbestos is proved to be toxic in recent medical evidences, which indicates that asbestos fibers used in the manufacture of clutch and brake lining may cause lung diseases for those exposed to them. Therefore, the development of asbestos-free friction-resistant materials such as metal fibers and aramid pulp is in demand in many countries [1, 2]. Natural fibers have also become the alternative for the advantages of low cost, little process injury and low density, as well as being environmental friendly and biodegradable [3–5]. Recently natural fiber reinforced polymer composites have been commercially applied in automobile interior decoration and brake pads [6, 7].

Among various kinds of natural fibers, sisal fiber is one of the most widely used. It is obtained from the leaves of the Agave sisalana plants, which are readily available in tropical countries. During the past decade, sisal fiber has been increasingly used as an economical and environmentally friendly reinforcement material for polymer composites. However, the high moisture absorption, poor wettability and adhesion to the matrix as well as the low thermal stability during processing, limit the practical utility of sisal fiber reinforced composites. Many techniques have been employed to modify the surface of sisal fibers. For example, Yang et al. reported that the cohesiveness between sisal fibers and phenol formaldehyde could be improved when sisal fibers were treated with 3-aminopropyltriethoxy silane [8]. As a result, the mechanical properties of the composites were improved, and water-resistance of the composites can be simultaneously improved by the treatment of silane. Megiatto et al. modified the sisal fiber surface with chlorine dioxide and followed with furfuryl alcohol and poly (furfuryl alcohol), which were used to prepare composites with phenolic thermoset matrix. Scanning electron microscopy (SEM) images revealed that the treated fibers exhibited fiber/matrix bonding at the interface [9]. Sangthong and Pongprayoon studied the mechanical properties of unsaturated polyester resin reinforced by admicelle-treated sisal fibers, where the tensile and flexural properties, impact strength and hardness of the composite were improved [10]. Gilberto et al. modified cellulose nanocrystals (or whiskers) and microfibrillated obtained from sisal fibers with *n*-octadecyl isocyanate ($C_{18}H_{37}NCO$), where the surface chemical modification with *n*-octadecyl isocyanate allows dispersion of the nanoparticles in organic solvents and may allow processing of nanocomposite films from a

Correspondence to: Chun Wei; e-mail: 1005668130@qq.com or Tianxi Liu; e-mail: txliu@fudan.edu.cn
Contract grant sponsor: National Natural Science Foundation of China; contract grant numbers: 51163003, 21264005, 51263005; contract grant sponsor: Guangxi Universities' Talent Highland; contract grant sponsor: Guangxi Funds for Specially-appointed Expert; contract grant sponsor: Guangxi National Natural Science Foundation; contract grant number: 2013DXNSFDA019008.
DOI 10.1002/pc.22957
Published online in Wiley Online Library (wileyonlinelibrary.com).

casting/evaporation technique for a broad range of polymeric matrices [11].

In recent years, oil palm, coir, kenaf, jute, bamboo, hemp, betel palm, and pineapple leaf fibers have been used as reinforcement materials for improving the wear resistance of the natural fiber/polymer composites [12–19]. However, to our knowledge, only few recent studies have been paid on the wear resistance of sisal fiber composites [7, 20, 21].

Herein, we present an asbestos-free friction-resistant materials, a composite of sisal fibers and nano-silica phenol formaldehyde resin. Meanwhile, different surface modifiers were used to enhance the bonding between the sisal fiber (SF) and polymer matrix. We focused on the effect of sisal fiber treatment and contents on the friction and wear properties of sisal fibers/nano-silica phenol formaldehyde composites, where the experimental results indicate that sisal fibers are qualified to replace asbestos fibers.s

EXPERIMENTAL

Materials

Sisal fibers were kindly provided by Guangxi Sisal Company. The nano-silica modified phenolic resin was purchased from Wuhan Haibaolong Composite Material (the content of nano-silica was 15%). Pure phenolic resin was supplied by Guilin Electrical Equipment Scientific Research Institute, and KH550 (g-amine propyl triethoxysilane) and borax were purchased from Wuhan Huachang Application Technology Institute.

Sisal Fiber Pretreatment

Alkali Treated Sisal Fiber (ATSF). Sisal fibers were immersed in a solution of 2% NaOH for 6 h, washed thoroughly with water to remove the excess of NaOH, and dried at 80°C.

Organosilane Treated Sisal Fiber (SCSF). Sisal fibers were soaked in a solution of 2% aminosilane (KH550, g-amine propyl triethoxysilane) in 95% alcohol for 5 min at a pH value of 4.5–5.5, and kept in air for 30 min. Then, allowed the hydroxyl groups of sisal fiber to react with the silanols of KH550 in an oven at 100°C for 2 h.

Flame Retardant Treated Sisal Fiber. Here, the method described by Xu et al. [7] was used. The alkali treated sisal fiber was immersed in $Na_2B_4O_7$-HCHO-$NaHSiO_3$ solution (10 wt%) for 4 h, dried in the air, and annealed at 150°C for 1 h.

Preparation of Composites

The sisal fibers (SF), phenol formaldehyde resin (PF) and fillers were blended on a roll machine, then the

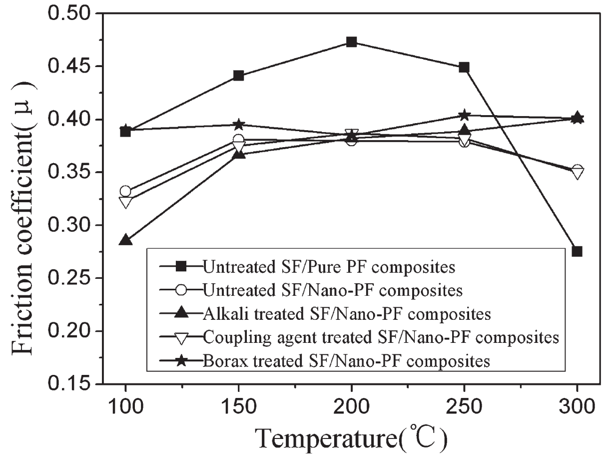

FIG. 1. The effect of the fiber treatment on the wear riction coefficient of the fiber composites.

mixture was smashed and SF/PF composites were fabricated by compression molding under 160–170°C and 15MPa for 5 min. Afterward, the composites were post-cured at 140, 160, and 180°C for 3 h, respectively.

Testing

Charpy impact testing of the composites specimens (10 mm × 4 mm × 120 mm) was carried out by using an impact tester (Chengde tester company, China, Model XJJ-5) according to the National standard GB1043-93. Three-point bending tests were performed in a computer controlled electronic universal testing machine (Jinan tester company, China) at a pressing speed of 2 mm min^{-1} and a gauge length of 64 mm following the national standard GB9341-2000. The sample size was also 10 mm × 4 mm × 120 mm.

The friction test was commenced on a constant speed (D-SM) tester. The friction disk is made of cast iron (HT250) with a hardness of 210 HB. The tester offers a friction temperature range of 100–300°C, which is automatically adjusted. The load was 0.98 MPa on each slider and the speeds were in the interval of 480 r min^{-1}. The friction tests were carried out at 100, 150, 200, 250, 300°C and each test lasted for 10 min. Thermogravimetric analysis was carried out on a NETZSCH STA 449C thermal analysis instrument. Samples were analyzed in range of 50–700°C at a rate of 10°C min^{-1}.

The Vickers hardness test was conducted on the MH-6 microhardness tester. A JSM-5600 LV scanning electron microscope (SEM) was used to observe the morphology of worn surfaces which were sputtered with a thin layer of gold.

RESULT AND DISCUSSION

Effect of Sisal Fiber Treatment on the Friction and Wear Properties

To show the excellent performance of the nano-silica modified phenolic resin, we also used the pure phenolic

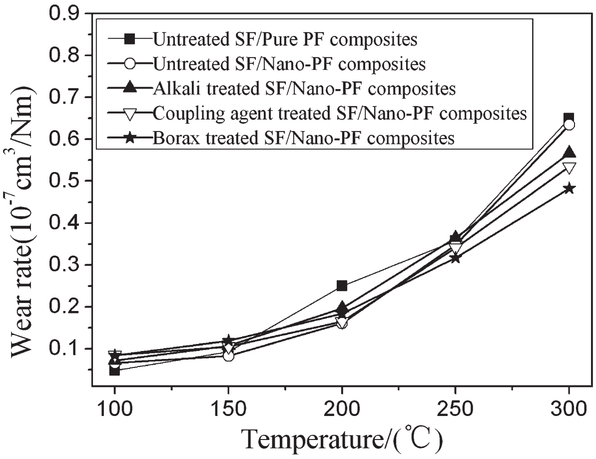

FIG. 2. The effect of the fiber treatment on the rate of the fiber composites.

resin to prepare SF/pure PF composites, the comparative result are shown in Figs. 1 and 2. From the figures, the friction coefficient of SF/pure-PF and nano-silica filled SF/PF composites decreases with temperature, while the wear rate of them appeared to increase. When the temperature of the friction disk came to 300°C, the friction coefficient of the SF/pure PF composites decreased sharply, and heat fade appeared. In contrast, the friction coefficient of the nano-silica filled composite was stable which show that nano-silica can improve the thermal stability of the SF/PF composites, and presents better wear resistance at different temperatures, indicative of the improvement on thermal stability.

Figures 1 and 2 showed the effect of sisal fiber treatment on the friction and wear properties of the SF/nano-PF composites under different temperatures (the sisal fiber content is 15 wt%), where the friction coefficient of untreated fiber composites decreased obviously at high temperature, in contrast to the treated fiber composites. This was due to the improvement of interfacial adhesion by surface treatment, where the borax treated fiber showed stable friction coefficient at variant temperatures,

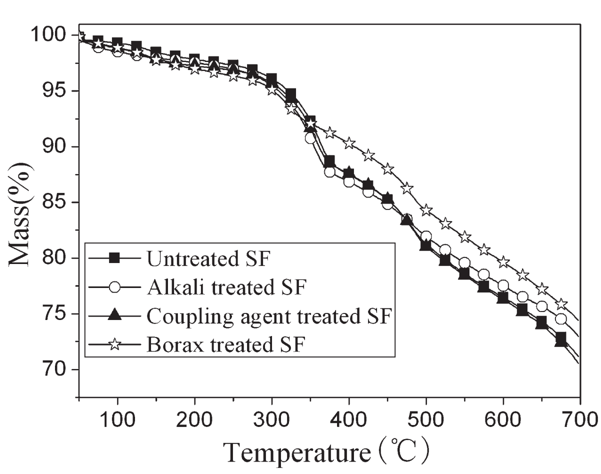

FIG. 3. The thermo-gravimetric curves of treated fiber composites.

TABLE 1. Effects of SF treatments on mechanical properties of composite friction materials.

Treatment method	Impact strength (kJ m^{-2})	Flexural strength (MPa)	Flexural modulus (GPa)	Vickers hardness (kgf mm^{-2})
Untreated SF	4.29	64.90	10.05	31.78
Alkali treated SF	5.03	68.77	12.69	32.41
Coupling agent treated SF	5.04	71.26	11.32	38.47
Borax treated SF	4.98	69.20	11.25	37.08

especially at 250–300°C. The reaction of fibers with formaldehyde and borax possibly formed a network structure that anchors the boron atoms onto the surface of fibers, leading to an enhanced resistance to thermal decomposition. The presence of borax can absorb the frictional heat and thus prevent the sisal fiber from decomposing. The friction stability also was significantly correlated with the thermal stability of the composites; Fig. 3 showed the TG curves of the SF/PF composite, where two decomposition platforms were presented. The first at 350°C corresponded to degradation of sisal fiber, and the second platform at 480°C was attributed to the degradation of composites. Apparently, the initial decomposition temperature for the composite with treated fibers shifted to higher temperature compared to untreated fiber composites, and the carbon residual rate of the borax treated fiber composite (74.25%) was also higher than the one with untreated fibers (70.97%). The improved thermal stability was associated with the superior thermal stability of treated fiber.

Table 1 showed the effect of various surface treatment of SF on the mechanical properties of the friction composites.

The enhancement of the mechanical properties was likely owing to the reduced hydrophilicity of the cellulosic SF, which improved the wetting and interfacial bonding between the fibers and matrix. Among different treatments, coupling agent treated SF/nano-PF composites present the highest impact strength (5.04 kJ m^{-2}) and bending strength (71.26 MPa), with the increments of 17.48 and 9.79% to the untreated SF/nano-PF samples, due to additional sites of mechanical interlocking generated by the resin–fiber interface interactions.

Effect of Sisal Fiber Contents on the Friction and Wear Properties

Figures 4 and 5 showed the friction and wear behavior of SF/nano-PF composites with different fiber contents, where the friction coefficient increased with fiber content at 150°C. At 300°C, the friction coefficient reached a maximum point when the content of sisal fiber was at 15 wt%, and then began to decease. The wear rate increased significantly with the increase of surface temperature of

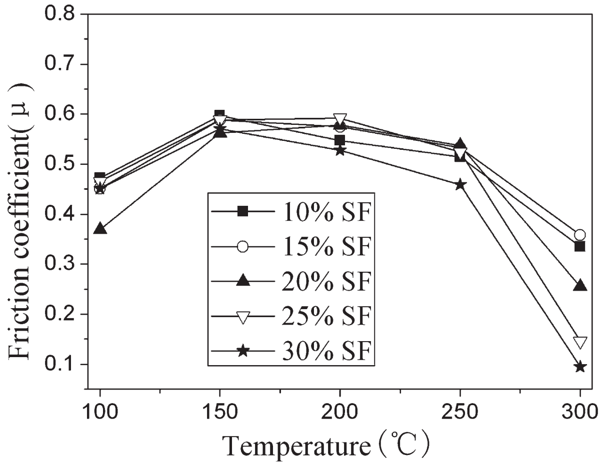

FIG. 4. The influence of sisal fiber content on the friction coefficient of the fiber composites.

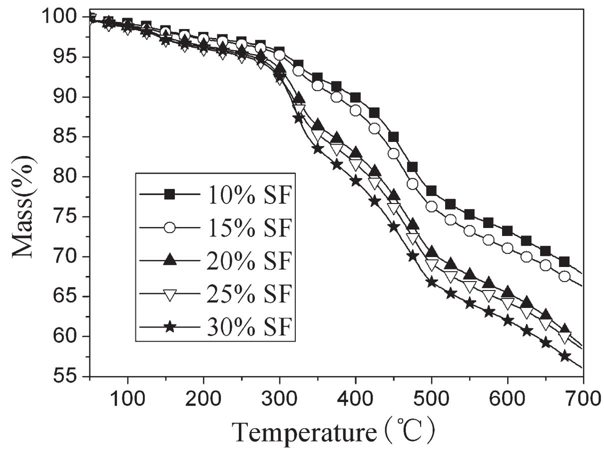

FIG. 6. The influence of sisal content on the thermal property of the fiber composites.

friction disk at all the tested contents of sisal fiber. The exposed fibers on the wear surface bare the majority of the friction loads, but when the fiber content was too high, defects probably occurred in the composites for the worse dispersion of fibers in matrix, which bring with the decrease of interfacial bonding force. In this case, the transfer film formed on the surface of composites could be destroyed, and the tribology properties of the material could be affected. The TG curves of the composites with different fiber contents shown in Fig. 6 reveal that the thermal stability of the SF/nano-PF composites decreased significantly, when the fiber content exceeded 15%, indicating that heat fade obviously occurred under high temperature.

As shown in Table 2, the impact strength of SF/nano-PF composites increased from 3.52 to 4.21 kJ m^{-2} when the content of SF increased from 10 to 20 wt%. However, further addition of SF would result in a decrease of impact strength, where the same trend was present for the flexural strength. At low fiber content, the fibers were not likely to be evenly distributed in the matrix so that the load transfer may not work properly; but too high fiber content possibly leaded to poor wetting of fibers, where the initiation and propagation of cracks will occur.

With the addition of sisal fiber, the Vickers hardness of the fiber composites was found to decrease slightly, due to the softness of sisal fiber itself. However, it is beneficial to the reducing of the noise when braking.

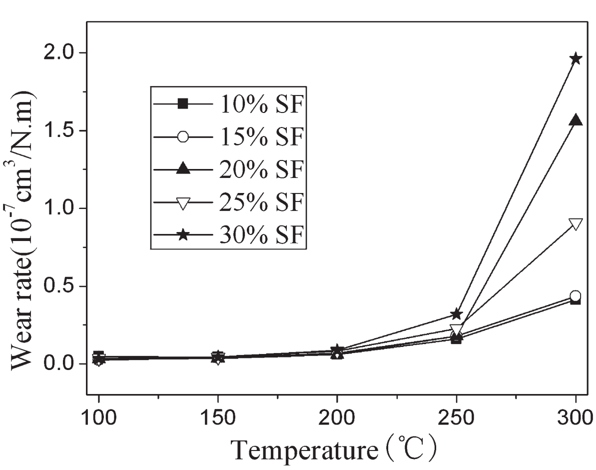

FIG. 5. The influence of sisal fiber content on the wear rate of the fiber composites.

SEM of the Worn Surface of the Fiber Composite Materials

Eriksson and Jacobson argued that the even distribution of the actual contacting area was critical for the transfer of the friction force [22]. Contact plateaus consist of two parts, primary plateaus and secondary plateaus. The primary plateaus were first formed due to the slower removal of the mechanically stable and wear resistant ingredients of the specimen. The uniform distribution and favorable primary plateaus were the necessary condition of an excellent brake pad. The observation in Fig. 7a illustrated that untreated fibers were pulled out from the matrix when the worn surface was exfoliated severely, with tiny abrasive dusts on the worn surface, as the arrow signified in Fig. 7a In addition, the fiber was not completely covered with phenol formaldehyde resin and there existed voids between SF and resin matrix (Fig. 7a) indicative of poor interface adhesion. In contrast, the worn surface of treated fiber composites was smoother, and only some slight scratches were observed on the worn surface

TABLE 2. Effects of SF content on mechanical properties of composite friction materials.

Sisal fiber content (%)	10	15	20	25	30
Impact strength (kJ m^{-2})	3.52	4.02	4.21	4.17	4.20
Flexural strength (MPa)	54.48	59.24	65.98	61.81	62.27
Flexural modulus (GPa)	12.01	11.71	10.92	9.59	9.29
Density (g cm^{-3})	1.87	1.86	1.83	1.81	1.73
Vickers hardness (kgf mm^{-2})	33.88	32.61	31.97	30.58	29.70

 DOI 10.1002/pc

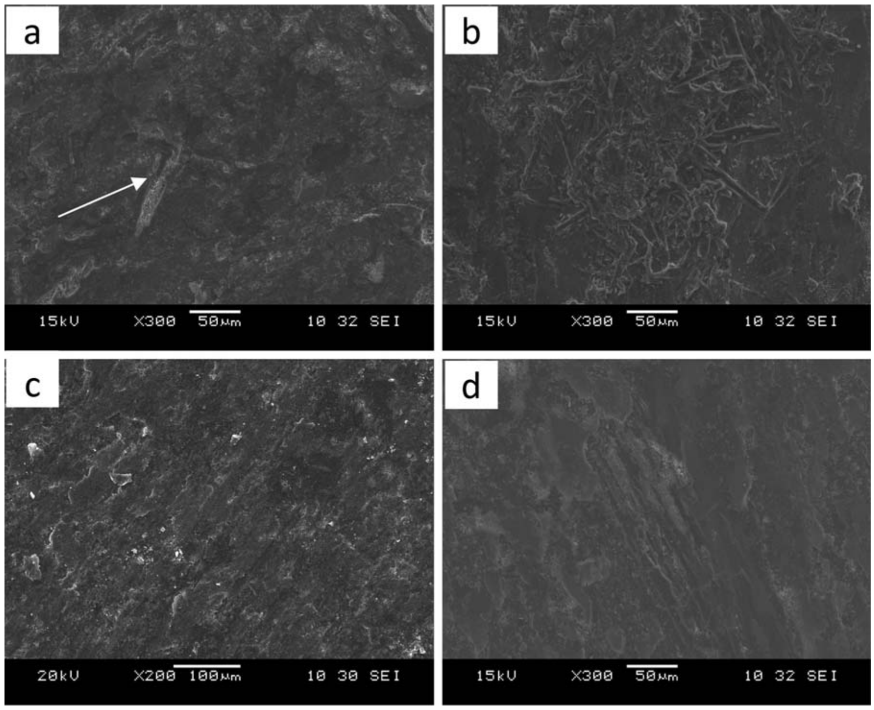

FIG. 7. SEM photographs of the worn surface of SF/Nano-PF composites: (a) Untreated SF/Nano-PF composites, (b) Borax treated SF/Nano-PF composites, (c) 10%SF composites, (d) 30%SF composites.

(Fig. 7b). This is because the treated SF had no pectin on the surface. The surface of treated SF favored the incorporation with other component, increasing the adhesion area and interface interaction strength between resin and fiber. As a result, high abrasion resistance of the composites was observed. The secondary plateau was composed of molten abrasive dust, where the friction coefficient was stable. As a kind of plant fiber, the sisal fiber was carbonized immediately at above 200°C, playing the similar role of carbon fibers on improving the fade resistance and braking stability of the composites.

When the fiber content was 10 wt%, the worn surface of the fiber composites was even (Fig. 7c), indicating that the reinforcing effect was obvious at this content. The cohesiveness among the resin, fiber and filler is good too. When the sisal fiber content was increased to 30 wt%, there were some microcracks and pits, which were caused by the exfoliation of the fiber and filler. The wear mechanism was consisted of fatigue wear and adhesive wear. As the fiber content increases, more defects appeared in the interior of the composite, making the composites appear stressed when working under the loads. Under such a situation, fatigue cracks were produced, the large fatigue cracks exfoliate from the surface, and holes at the worn surface appear.

CONCLUSIONS

The addition of nanosilica in the phenol formaldehyde resin can relieved the heat fade occurred in the friction process, the surface treatment of sisal fibers was able to improve the interface adhesion between fibers and resin. Among the treatments, the borax treated fibers showed the best heat resistance, consistent friction coefficient and low wear rate under different temperatures. The influence of the fiber content on the friction and wear properties of the composites was also investigated. Under the experimental conditions, the optimal fiber content was 15 wt%. Our results also suggest that the sisal fiber is promised to replace the asbestos on the fabrication of brake composites.

REFERENCES

1. H. Jang, K. Ko, S.J. Kima, R.H. Baschb, and J.W. Fash, *Wear*, **256**, 406 (2004).
2. S.J. Kim and H. Jang, *Tribol. Int.*, **33**, 477 (2000).
3. A.K. Bledzki and J. Gassan, *Prog. Polym. Sci.*, **24**, 221 (1999).
4. J.C.M. de Bruijn, *Appl. Compos. Mater.*, **7**, 415 (2000).
5. D.N. Saheb and J.P. Jog, *Adv. Polym. Tech.*, **18**, 351 (1999).
6. P. Wambua, J. Ivens, and I. Verpoest, *Compos. Sci. Technol.*, **63**, 1259 (2003).
7. X. Xu, G.X. Cheng, and F.Q. Liu, *Wear*, **262**, 736 (2007).
8. G.C. Yang, H.M. Zeng, and J.J. Li, *Fibre Reinf. Plast. Compos.*, **3**, 12 (1997).
9. J.D.J. Megiatto, F.B. Oliveira, D.S. Rosa, C. Gardrat, A. Castellan, and E. Frollini, *Macromol. Biosci.*, **7**, 1121 (2007).

10. S. Sangthong and T. Pongprayoon, *Compos. A Appl. S.*, **40**, 687(2009).
11. S. Gilberto, B. Julien, and D. Alain, *Langmuir*, **26**, 402 (2010).
12. B.F. Yousif and N.S.M. El-Tayeb, *Surf. Rev. Lett.*, **6**, 1095 (2007).
13. B.F. Yousif, *P. I. Mech. Eng. J-J. Eng.*, **223**, 51 (2009).
14. C.W. Chin and B.F. Yousif, *Wear*, **267**, 1550 (2009).
15. N. Chand and U.K. Dwivedi, *Wear*, **261**, 1057 (2006).
16. N. Chand and U.K. Dwivedi, *J. Mater. Process. Tech.*, **183**, 155 (2007).
17. D. Rouison, M. Sain, and M. Couturier, *Compos. Sci. Technol.*, **66**, 895 (2006).
18. W.L. Lai and M. Mariatti, *J. Reinf. Plast. Comp.*, **27**, 925 (2008).
19. M. Maniruzzaman, M.A. Rahman, M.A. Gafur, and H. Fabritius, *J. Compos. Mater.*, **46**, 79 (2012).
20. Q.H. Mu, C. Wei, and S.Y. Feng, *Polym. Compos.*, **30**, 131 (2009).
21. C. Wei, M. Zeng, X.M. Xiong, and F.A. Zhang, *Plast. Rubber Compos.*, **29**, 61 (2010).
22. M. Eriksson and S. Jacobson, *Tribol. Int.*, **33**, 817 (2000).

 DOI 10.1002/pc