

PTFE 복합재료의 기계적, 마찰 특성에 대한 강화재료의 역할

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Role of Reinforcement Materials on Mechanical and Tribological Properties of PTFE Composites

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Abstract: The use of polytetrafluoroethylene (PTFE) in various industrial applications under extreme operating conditions makes it very important to determine the behavior of this material. The mechanical and wear properties of PTFE can be enhanced by adding filler materials. This study focused on both the mechanical and tribological properties of PTFE and its composites with a 25 wt% addition of carbon and glass fiber (GF). Glass transition temperature (T_g), hardness, tensile, and impact tests were carried out to determine the mechanical and physical properties of PTFE. In addition, abrasive wear tests were applied to obtain wear behavior. The tensile strength values of the pure and C/GF-filled PTFE were found as 28, 16.7, and 18.6 MPa, respectively. Tensile tests clearly showed that the filler materials led to a reduction of the tensile strength and elongation at break of the PTFE. Impact energy values were similarly decreased by the addition of filler materials. However, the carbon and GF additions significantly increased the abrasive wear resistance and T_g of the PTFE. Consequently, carbon and GF-filled PTFE would be a suitable candidate for use in tribological applications.

Keywords: polytetrafluoroethylene, carbon, glass fiber, wear behavior, mechanical properties.

Introduction

Polytetrafluoroethylene (PTFE) is an outstanding thermo-plastic with excellent mechanical properties e.g., good chemical resistance and self-lubricating, low coefficient of friction and surface energy, high thermal stability.¹⁻³ Because of its outstanding mechanical properties, PTFE is widely used as engineering plastic for many lubrication, anti-corrosion, anti-stick, sealing, electrical, and medical applications⁴⁻⁶ and has a significant effect in the development of manufacturing industry and in the transportation, aerospace, and other industries.⁷⁻¹²

However, PTFE exhibits poor wear resistance, which leads to early failure and leakage problems in sealing components. The mechanical and tribological properties of PTFE can be significantly enhanced by the addition of suitable filler materials.¹³⁻¹⁶ The most widely preferred fillers are carbon, glass

fibers, graphite, bronze and molybdenum disulfide (MoS_2) in different percentages to improve mechanical and tribological properties. Fillers can be combined to achieve high wear resistance and mechanical properties.¹⁷⁻²¹ Glass fiber (GF) is one of the most common fillers for PTFE and it presents good wear resistance, low creep, good compressive strength and excellent chemical compatibility.^{22,23} Carbon filler leads to low deformation under load, good tribological properties and thermal conductivity and low permeability.^{24,25} Graphite is a crystal modification of high purity carbon. Its flaky structure imparts excellent lubricity and increased wear resistance. Graphite can also be used with fillers such as carbon and GF.²⁶⁻²⁸ Bronze provides excellent wear resistance and thermal conductivity to PTFE. In addition, it can be combined with MoS_2 or graphite. Bronze-filled PTFE has poorer chemical resistance than other filled PTFEs.²⁶⁻²⁹ MoS_2 improves wear resistance and further lowers the coefficient of friction and is typically combined with other fillers such as glass and bronze.^{30,31} Generally, fillers can improve wear resistance by 10 to 500 times and increase the thermal conductivity by 2 to 3 times.³²⁻³⁴

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Teng *et al.* carried out tribological tests using stainless steel plate as the counter body. They reported that the tribological and mechanical properties of PTFE were improved dramatically by adding potassium titanate whiskers and GF fillers.³⁵ Zhang *et al.* analyzed the influences of several tensile rates on the thermal and mechanical properties and microstructure of GF-filled PTFE composites. The results showed that the thermal stability of the composites would be slightly enhanced and the tensile rate leads to improve the thermal expansion coefficient.³⁶ Song *et al.* researched the tribological behavior and PV limit of PTFE composites reinforced with chopped carbon fiber, MoS₂, and GF. They selected the ASTM 1045 standard ring steel as the counterpart in the wear experiments. The authors stated that the synergistic effect of MoS₂ and GF led to a great improvement in the tribological behavior and PV limit of the PTFE composites.³⁷ Huang *et al.* investigated GF-reinforced PTFE sliding against duplex steel at an elevated temperature. They found that a high wear rate was obtained during the direct contact of the PTFE and steel in the run-in stage. After removal of the upper PTFE layer, the embedded glass fibers became exposed and gradually came to move the main load. As a result, the wear rate was significantly reduced.³⁸ Bi *et al.* studied the friction behavior of PTFE at a pin-to-plate interface. In the wear experiments, PTFE was selected as the pin material and steel as the plate material. They found that the pressure affected the coefficient of friction and changed the deformed areas in the contact zone, and that the percentage of deformed zone characters could be estimated based on equivalent strain energy.³⁹

Previous studies have generally focused on either the mechanical properties or the tribological properties of PTFE composites. There are few studies in which both research fields are examined together. However, tribology studies have been focused on improving the adhesive wear resistance of PTFE. Researchers have carried out wear experiments using a metal disc as the counterpart. This study compensates for the lack of studies in the literature on GF- and carbon-reinforced PTFE. The aim was to determine the mechanical properties and abrasive wear behavior of carbon-filled and GF-filled PTFE composites.

Experimental

Production of Filled PTFE Composites. Carbon and GF were purchased from local suppliers. The carbon, in the form of carbon black, spherical-shaped particles (average 20 μm) was purchased from the Polyplast Company. The glass fiber, in the form of chopped, (average diameter of 15 μm and length of 500 μm) was supplied by Dost Chemistry Company. The SEM images of filler materials were given in Figure 1. In addition, physical properties of PTFE are given in Table 1.

The carbon and GF additives were added to the matrix at 25 wt% and pre-mixed for 10 min at 180 rpm using a mechanical stirrer. The mixtures were then dried at 100 °C for 2 h to remove moisture and other volatiles. The pre-mixed products were transferred to the extruder. The carbon- and GF-filled PTFE composites were fabricated by melt-blending with the

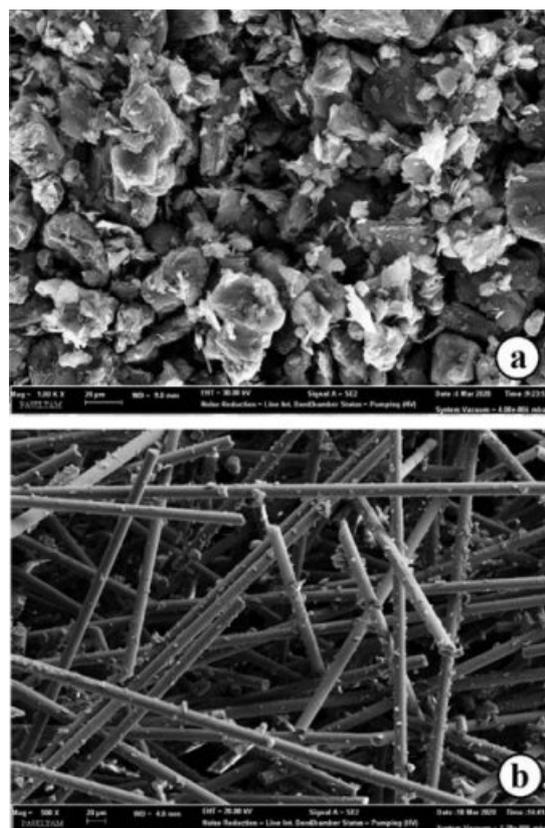


Figure 1. SEM images of filler materials: (a) carbon; (b) glass fiber.

Table 1. Physical Properties of PTFE

Chemical formula	Density	T_g	Melting point	Thermal conductivity	Molecular weight
(C ₂ F ₄) _n	2.15 g/cm ³	129.4 °C	335 °C	0.25 W/mK	100.01 g/mol

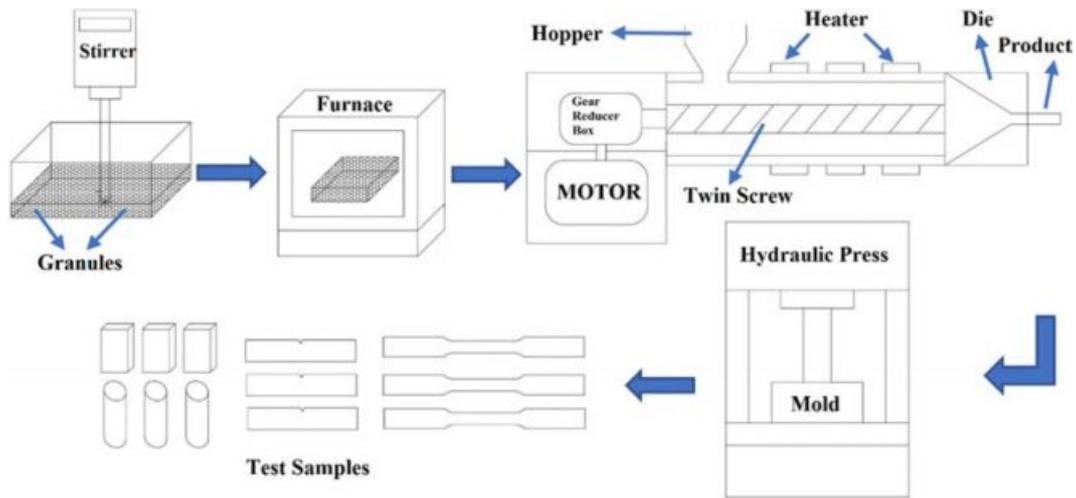


Figure 2. Schematic illustration of PTFE sample production.

twin screw extruder at 30 rpm screw speed. The temperature from the feed zone to the nozzle zone was 234-306-365-310 °C. The exit temperature was set at 40 °C. The extruded fibers were pelletized and press molding was used to produce the test samples. A schematic illustration of the sample preparation is given in Figure 2.

Determination of Glass Transition Temperature. Glass transition temperatures (T_g) of PTFE composites were measured on dynamic mechanical analyzer in single cantilever bending mode. Samples were cubic with a diameter of 16×10×4 mm. The temperature range, heating rate, and frequency were 50 to 180 °C, 3 °C/min, and 1 Hz, respectively.

Hardness Measurement and Wear Experiments of PTFE Composites. Shore D hardness measurements were carried out at three different points for each sample in accordance with ASTM standard D2240. The applied load was 50 N

and the hold time was 15 s.

The wear tests were performed in accordance with ASTM standard G99 using a pin-on-disk apparatus under dry test conditions. PTFE sample in Ø10×25 mm diameter was used as pin and a 200-grit abrasive paper with an abrasive disc was used as counter-face during the wear test. The wear test was carried out at 3 different distances of 120, 240, and 360 m under 3 different loads of 5, 10, and 15 N at a speed of 2 m/s. The pin-on-disk test apparatus is shown in Figure 3. The ultrasonic cleaner was used to clean contaminants on surface of samples before measuring.

The applied load on the specimen was recorded during the wear test for the calculation of the friction coefficient. The friction coefficient was calculated using eq. (1).

$$\text{The coefficient of friction is } \mu = \frac{F}{P} \quad (1)$$

The frictional force and the normal load on the specimen are symbolized by F and P , respectively. eq. (2) explains how to calculate volume loss from the weight loss.

$$\text{Volume loss (mm}^3\text{)} = \frac{\text{Weight loss(g)}}{\text{Density(g/mm}^3\text{)}} \quad (2)$$

Eq. (3) was used to define the specific wear rate.

$$\text{Specific wear rate (mm}^3\text{/Nm)} = \frac{\text{Volume loss(mm}^3\text{)}}{\text{Sliding distance(m)} \times \text{Load(N)}} \quad (3)$$

Tensile and Izod Pendulum Impact Tests of PTFE Composites. Mechanical tests have a vital role in the evaluation of the basic properties of materials, in the development

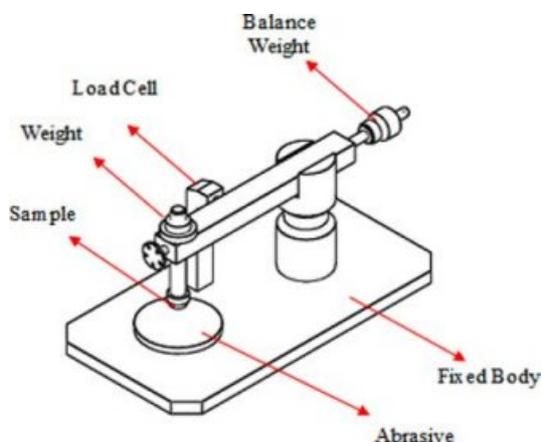


Figure 3. Schematic view of wear test machine.

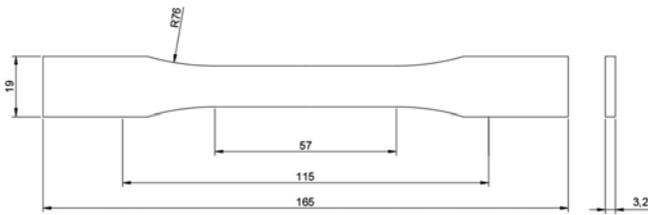


Figure 4. Dimensions of tensile test specimen.

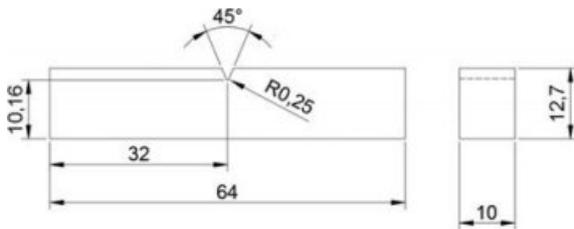


Figure 5. Dimensions of impact test specimen.

of new materials, and in quality and control of the products to be used in industry. Tensile testing is the fundamental test for obtaining the mechanical characteristic of a material and is widely preferred to acquire basic design knowledge about the

strength of materials. Moreover, it is an acceptance test for the specification of materials.

An effective method to investigate the effect of filler materials on the fracture behavior of PTFE is to subject this material to impact testing. The Izod test is the one of the most common standards for impact testing. It is very useful to deduce from fundamentals for fracture mechanics of a material.

Tensile and impact tests of the filled PTFE composites were carried out in accordance with ASTM D638 and ASTM D256, respectively. Tensile and Izod impact test specimens are given in Figure 4 and Figure 5, respectively.

Results and Discussion

Microstructure of Filled PTFE Composites. Figure 6 shows the scanning electron microscopy (SEM) micrograph of the PTFE-based composites. Surface images show the carbon (C) and GF used as reinforcing material. Upon examining Figure 6(a), it can be seen that the energy dispersive X-ray spectroscopy (EDS) analysis taken over the entire surface shows only C and fluorine (F). In Figure 6(b), only F and silicon (Si)

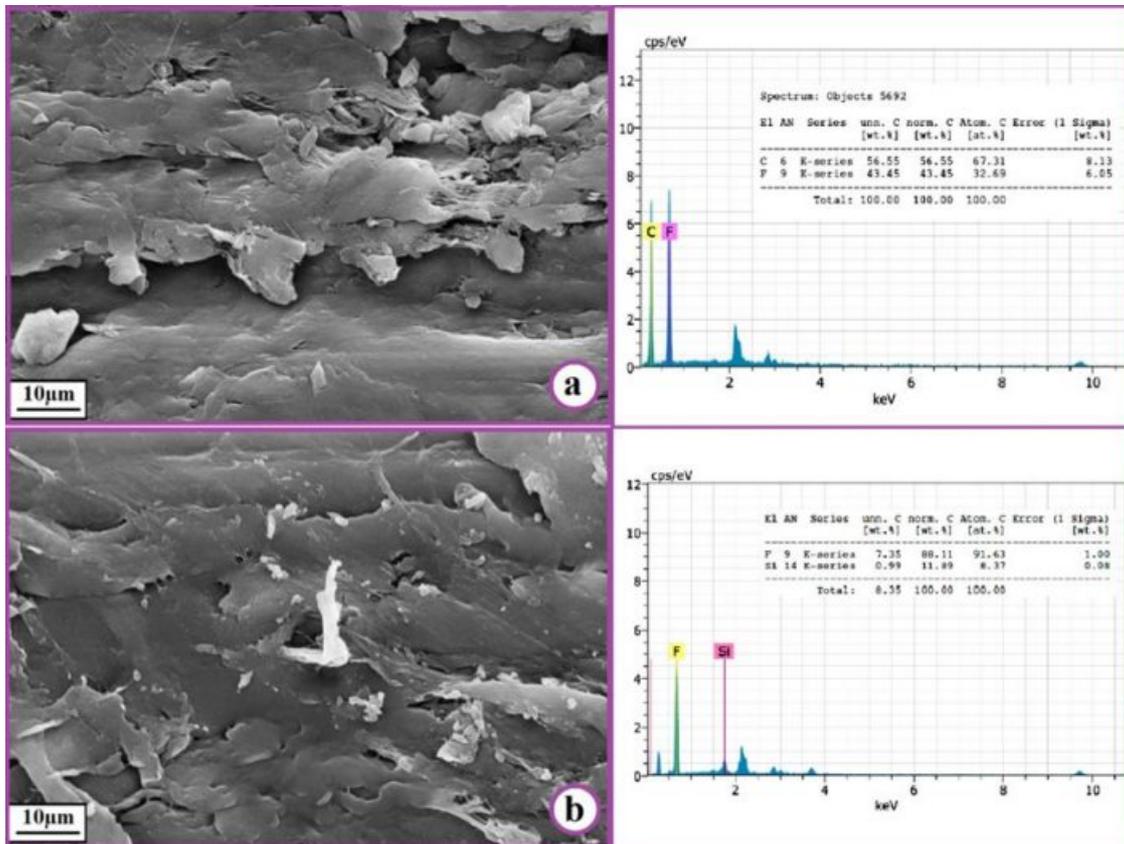


Figure 6. Microstructure and EDS analysis of filled PTFE: (a) C-filled; (b) GF-filled.

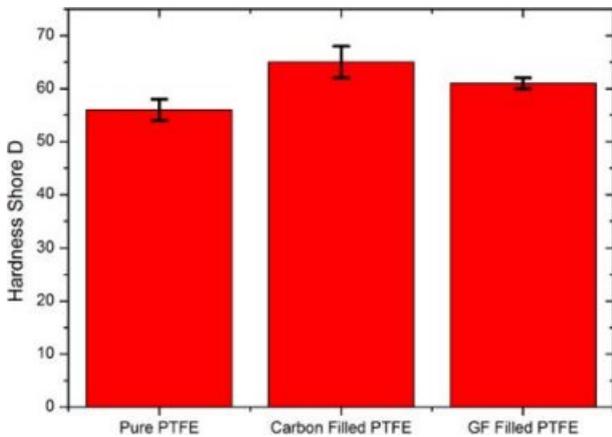


Figure 7. Hardness values of filled PTFE composites.

were determined. The other peaks are the gold (Au) and palladium (Pd) from the coating applied for SEM image acquisition. Thus, the EDS analysis and SEM images confirmed the desired reinforcement of PTFE.

Hardness Measurement. Hardness is one of the key parameters used for evaluation of wear behavior.³⁸ The effect of reinforcement materials on hardness is given in Figure 7, which reveals that the GF and C filler materials led to increased hardness of the PTFE. Pure PTFE had a Shore D hardness of 56, whereas the GF reinforcement increased the hardness to 61 Shore D and the C reinforcement increased the hardness to 65 Shore D.

Glass Transition Temperature Properties of PTFE Composites. Figure 8 presents $\tan \delta$ - temperature curves for the pure PTFE and PTFE composites. Glass transition tem-

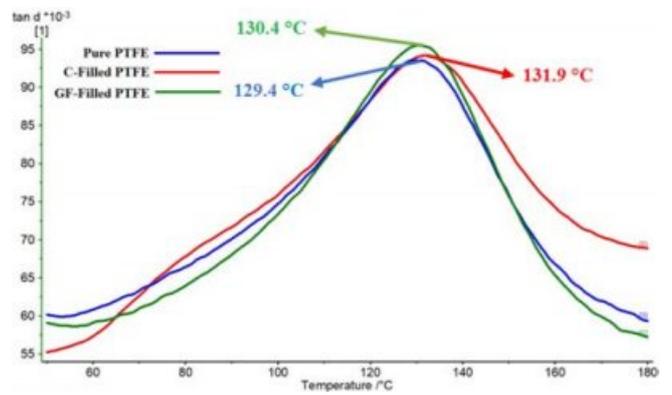


Figure 8. Glass transition temperature curves of PTFE composites.

perature of pure PTFE was obtained as 129.4 °C. However, the addition of filler materials on PTFE didn't influence significantly on the T_g . GF and C fillers lead to increase T_g only 1 °C and 2.5 °C, respectively. All samples displayed fairly sharp and well-defined glass transition temperature relaxation. Moreover, Figure 8 compares the values of $\tan \delta$ of the pure PTFE and PTFE composites. The results show that the PTFE composites possessed higher $\tan \delta$ values compared to pure PTFE. The higher value of $\tan \delta$ means higher energy damping behavior or lower elasticity. This reduction in carbon and GF filled PTFE' elasticity (increase in $\tan \delta$) can be ascribed to the role of filler materials. Carbon and GF lead to restrict the energy storage ability of PTFE.

Tribological Properties of PTFE Composites. Figures 9 and 10 show the results of the wear tests for the pure PTFE and PTFE composites with 25 wt% added contents of C and GF

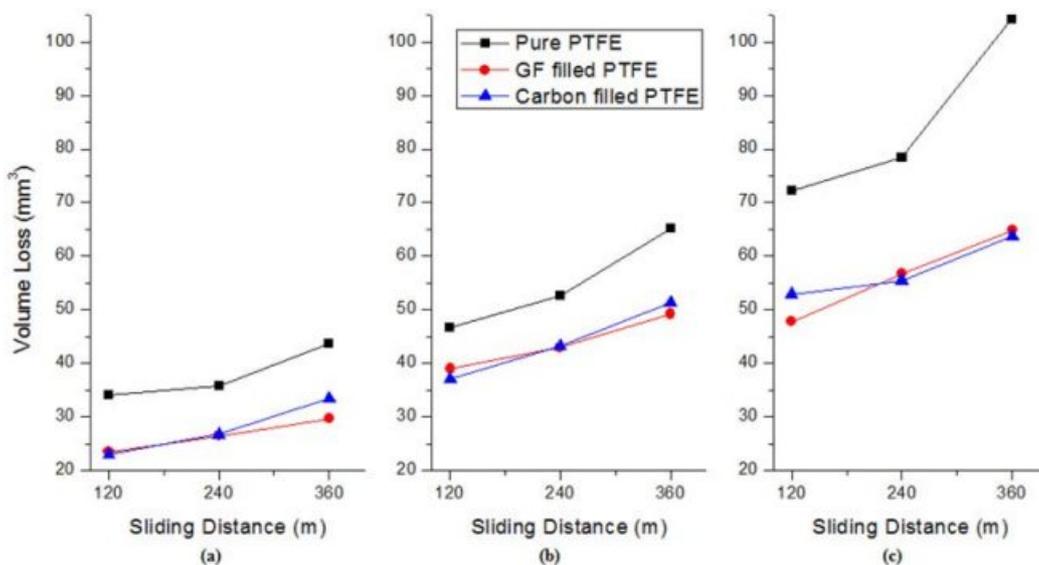


Figure 9. Volume loss as function of sliding distance and applied load: (a) 5 N; (b) 10 N; (c) 15 N.

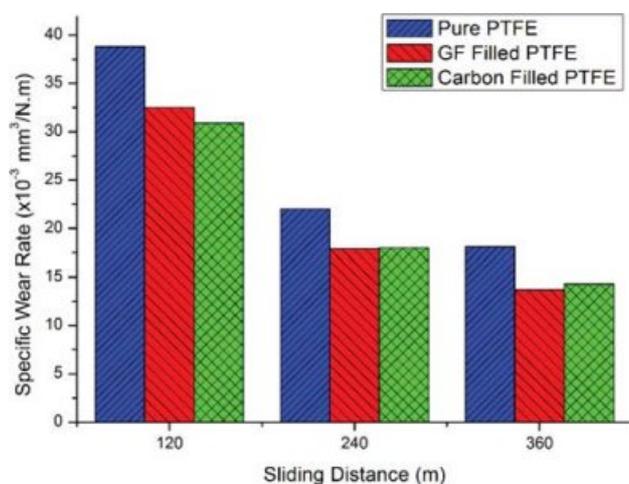


Figure 10. Specific wear rate of PTFE composites as function of sliding distance (load 10 N).

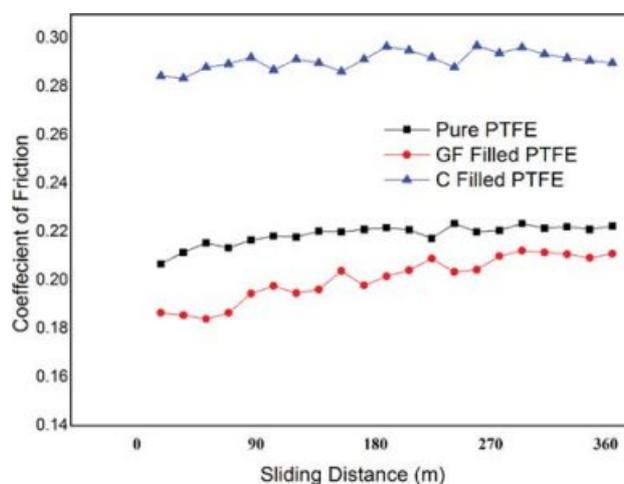


Figure 11. Variation in the friction coefficient according to sliding distance.

tested against the abrasive paper. There is a clear reduction in wear volume for the PTFE composites compared to the pure PTFE, although it appears only slightly dependent on the reinforcement materials that were used in the experiments. However, it is clearly seen in Figures 9 and 10 that the reinforcement materials improved the abrasion resistance of the PTFE. In the case of the composites, for a given 25 wt% C and GF, the specific wear rate decreased sharply with increasing sliding distance. Furthermore, the sliding distance and applied load significantly influenced the volume loss. The volume loss increased with increasing sliding distance and applied load. Applied load and sliding distance define wear mechanisms.⁴⁰⁻⁴⁴ Contact time between the wear surfaces was increased with increasing sliding distance. Therefore, higher volume loss was obtained with higher sliding distance. In the adhesive wear tests that were carried out with a metal disc as the counterpart, the C reinforcement improved the wear resistance of PTFE more than the GF reinforcement.^{14,24,25} However, when tests were carried out with abrasive paper, no significant difference in effect was found between the C and GF reinforcements.

The variation in the CoF according to the sliding distance under a constant load for pure PTFE and GF- and C-filled PTFE is described in Figure 11. The average friction coefficient of pure PTFE was about 0.22, which is obviously less than that of the C-filled PTFE, and was very close to that of the GF-filled PTFE. Nevertheless, the friction coefficient of the G-filled PTFE increased slightly during the friction process, which had obvious fluctuations, with an average value of about 0.2, whereas, for the pure and C-filled PTFE, the friction coefficient curve was typically flat and smooth. Consequently, C

reinforcement increased the friction coefficient of PTFE, while GF reinforcement decreased it.

Figure 12 shows SEM images of the worn surfaces of pure PTFE and PTFE composites with C and GF contents of 25 wt%. As seen in Figure 12(a), the worn surface of the pure PTFE shows a pattern of scratched and flaked-off matrix material. Moreover, wear debris appears on the worn surface of the PTFE. Figure 12(b) shows the worn surface of the 25 wt% C-filled PTFE, which exhibits exposed carbon fillers and short, criss-crossed cracks caused by the peeling of the PTFE matrix. Where the cracks are expanded, the fillers exposed to the counterface were finally removed, as shown in Figure 10(b). The exposed carbon fillers acted as hard particles and reduced the counterface contact area; thus, the volume loss of the C-filled PTFE decreased significantly. As shown in Figure 12(c), the worn surface of the 25 wt% GF-filled PTFE was smoother than that of the C-filled PTFE. The SEM image shows exposed GF on the worn surface. The exposed GF led to the reduction of the contact area and friction coefficient. The resistance of the composite to plowing was improved, as the composite hardness increased with the GF reinforcement, which also contributed to the decrease in the friction coefficient and wear rate of the GF-filled PTFE. Similarly, the sloughed GFs also acted as needle roller bearings to further reduce the volume loss. The wear experiment results showed that the usage of reinforcement materials enable to use polymers in tribological applications.⁴⁵⁻⁴⁷

Tensile and Impact Properties of PTFE Composites. Figure 13 presents the results of the tensile tests for the pure PTFE and PTFE composites with C and GF contents of

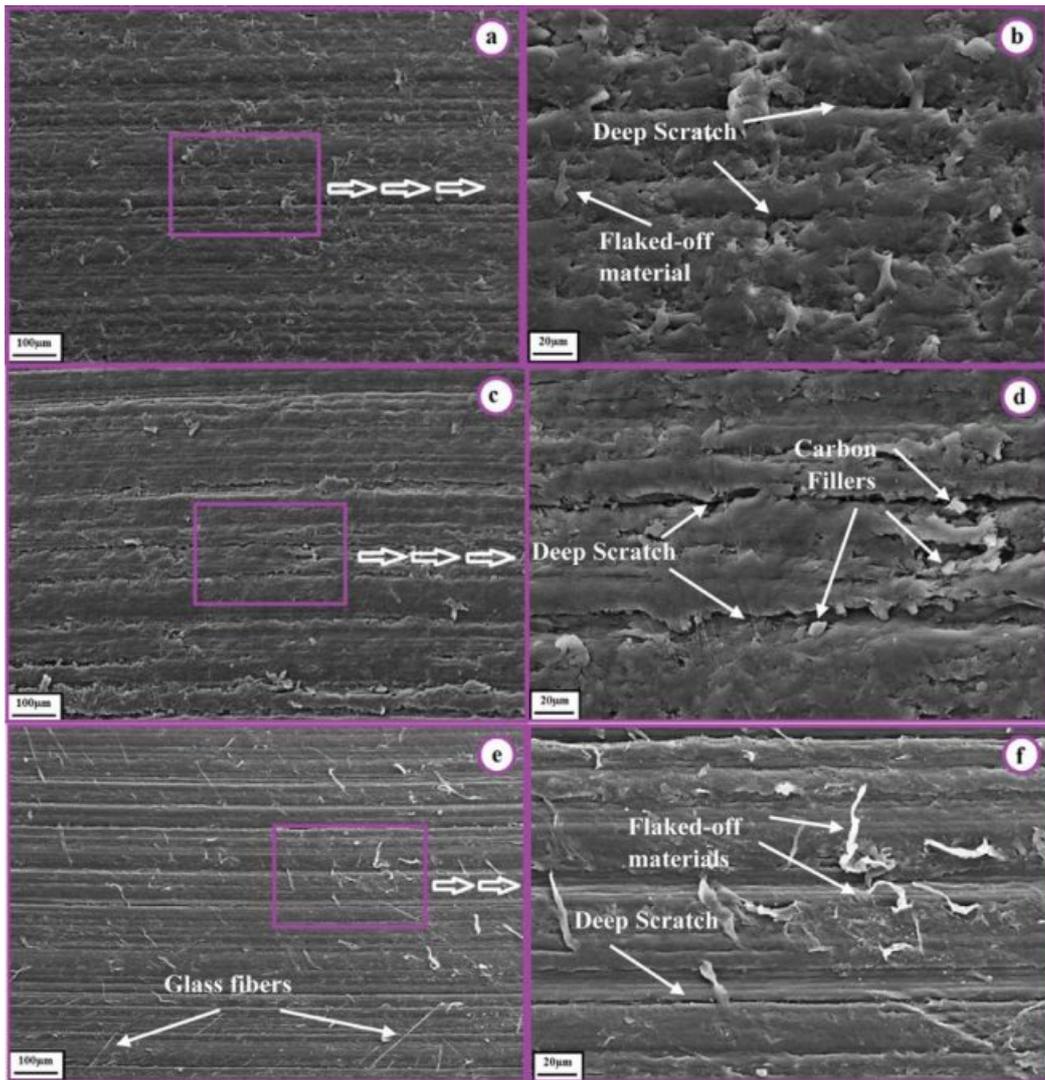


Figure 12. SEM images of worn surfaces: (a) pure PTFE 250x; (b) pure PTFE 1000x; (c) carbon-filled PTFE 250x; (d) carbon-filled PTFE 1000x; (e) GF-filled PTFE 250x; (f) GF-filled PTFE 1000x.

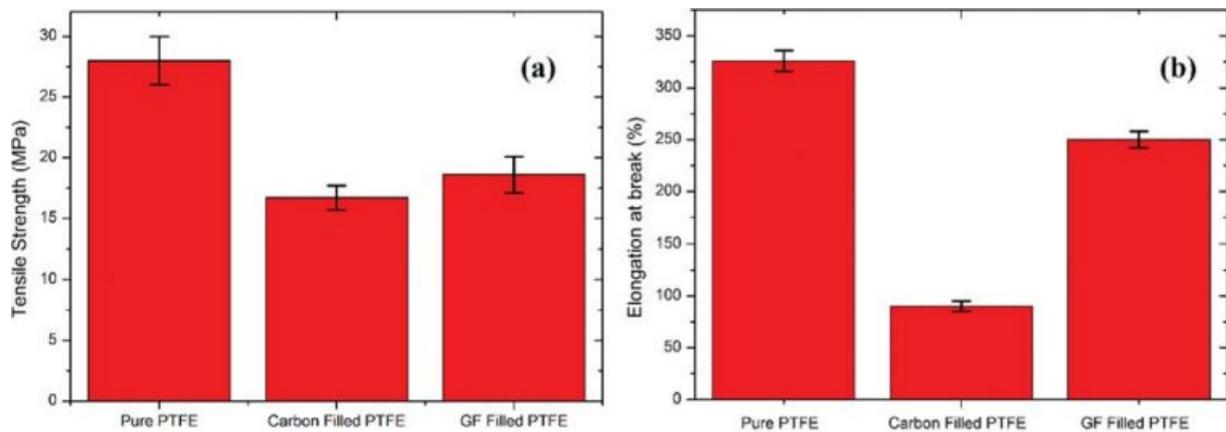


Figure 13. Tensile strength and elongation at break of pure PTFE and PTFE composites.

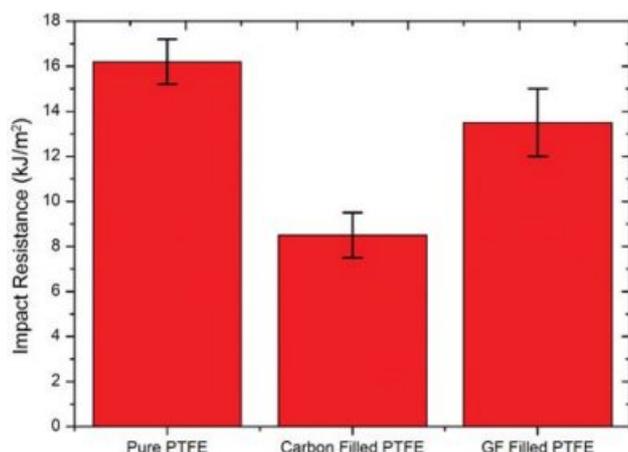


Figure 14. Impact test results of pure PTFE and PTFE composites.

25 wt%. The tensile strength values of the pure and C-/GF-filled PTFE were obtained as 28, 16.7 and 18.6 MPa, respectively. Tensile tests clearly showed that the filled materials led to reduction of the tensile strength of the PTFE. Likewise, the filler materials also caused a reduction in the elongation of the pure PTFE. It was noted that pure PTFE showed the highest tensile strength and the highest elongation values.

The Izod impact test results of the PTFE and PTFE composites are given in Figure 14. Impact energy values of the pure and the C-/GF-filled PTFE were obtained as 16.5, 8.5 and 13.5 kJ/m², respectively. The use of filler materials within the PTFE served to reduce the impact energy. In particular, the carbon filler reduced impact energy significantly. Consequently, Filler materials led to reduction of mechanical properties of PTFE unlike other polymers.⁴⁸⁻⁵⁰

Conclusions

In this paper, PTFE composites reinforced with carbon and GF were fabricated and the effects of the filler materials on the mechanical and tribological properties were investigated.

Tensile tests clearly demonstrated that the filler materials led to a reduction of the PTFE tensile strength and elongation. The tensile strength values of the pure and C-/GF-filled PTFE were found as 28, 16.7 and 18.6 MPa, and values of elongation were obtained as 325, 80 and 250%, respectively. Tensile tests clearly showed that the filler materials led to reduction of the tensile strength of the PTFE. The T_g of pure PTFE was 129.4 °C. The additives did not significantly affect the T_g , which was found as 130.4 and 131.9 °C for GF- and C-filled PTFE, respectively. The Izod impact test results showed that

the filler materials within the PTFE served to reduce the impact energy. Impact energy values of the pure and the C-/GF-filled PTFE were obtained as 16.5, 8.5 and 13.5 kJ/m², respectively. In particular, the carbon filler reduced impact energy significantly. The reinforcement materials also reduced the volume loss and wear rate significantly. Therefore, C and GF fillers improved the wear resistance of PTFE. However, no significant difference in effect was found between the C and GF reinforcements, although the GF-filled PTFE provided a lower friction coefficient.

References

1. Z. Wang, S. Wu, and J. Ni, *Proc. Inst. Mech. Eng. Part J.-J. Eng.*, **232**, 607 (2018).
2. Q. Zhao, Y. Liu, and C. Wang, *Appl. Surf. Sci.*, **252**, 1620 (2005).
3. R. Zhou, P. Yuan, Y. Wang, J. G. Hunsberger, A. Elkahoun, Y. Wei, P. D.-Williams, J. Du, G. Chen, and H. K. Manji, *Neuropsychopharmacol.*, **34**, 1395 (2009).
4. T. Hubáček, O. Lyutakov, V. Rybka, and V. Švorčík, *J. Mater. Sci.*, **45**, 279 (2010).
5. M. Fineschi, T. Gori, G. Sinicropi, and A. Bravi, *Heart*, **90**, 490 (2004).
6. J. S. Choi, J. Y. Sohn, and J. Shin, *Polym. Korea*, **38**, 457 (2014).
7. J. Y. Sohn, B. H. Park, J. M. Song, Y. M. Lee, and J. Shin, *Polym. Korea*, **37**, 649 (2013).
8. N. Wang, H. Wang, J. Ren, G. Gao, S. Chen, and Y. Yang, *J. Appl. Polym. Sci.*, **136**, 47774 (2019).
9. L. J. van Rooyen, H. Bissett, M. C. Khoathane, and J. K. Kocsis, *J. Appl. Polym. Sci.*, **133**, 43369 (2016).
10. F. Li, K. A. Hu, J. L. Li, and B. Y. Zhao, *Wear*, **249**, 877 (2001).
11. DuPont, *Teflon® PFA Fluoropolymer Resin Properties Handbook*, DuPont Fluoroproducts, Wilmington, 1998.
12. S. Kaner and T. Sekercioglu, *Polym. Korea*, **41**, 827 (2017).
13. L. H. Lee, "Polymer Wear and Its Control", in *American Chemical Society*, M. J. Comstock, Editor, Washington, Vol **287**, p 27 (1985).
14. J. Khedkar, I. Negulescu, and E. I. Meletis, *Wear*, **252**, 361 (2002).
15. K. Jotaki, M. Miyatake, T. Stolarski, S. Sasaki, and S. Yoshimoto, *Tribol. Int.*, **113**, 291 (2017).
16. F. Song, Q. Wang, and T. Wang, *Tribol. Int.*, **104**, 392 (2016).
17. W. G. Sawyer, K. D. Freudenberg, P. Bhimaraj, and L. S. Schadler, *Wear*, **254**, 573 (2003).
18. M. Conte and A. Igartua, *Wear*, **296**, 568 (2012).
19. J. Girard, N. Joset, A. Crochet, M. Tan, A. Holzheu, P. Brunetto, and K. Fromm, *Polymer*, **8**, 208 (2016).
20. J. C. Seferis, *Polym. Compos.*, **7**, 158 (1986).
21. C. Liu, K. Chan, J. Shen, C. Liao, K. Yeung, and S. Tjong, *Polymer*, **8**, 425 (2016).
22. F. Luo, B. Tang, Y. Yuan, Z. Fang, and S. Zhang, *J. Alloy Compd.*, **769**, 1034 (2018).

23. Y. Zhang, K. Kou, S. Zhang, and T. Ji, *J. Polym. Res.*, **26**, 214 (2019).
24. Y. Wang and Z. Yin, *Ind. Lubr. Tribol.*, **71**, 22 (2019).
25. S. Bhargava, M. E. Makowiec, and T. A. Blanchet, *Wear*, **444**, 203163 (2020).
26. C. A. G. S. Valente, F. F. Boutin, L. P. C. Rocha, J. L. Vale, and C. H. Silva, *Tribol. Trans.*, **63**, 356 (2020).
27. F. L. Yin, H. Ji, and S. L. Nie, *Proc. Inst. Mech. Eng. Part J-J. Eng.*, **233**, 1729 (2019).
28. R. Gheisari and A. A. Polycarpou, *Wear*, **436**, 203044 (2019).
29. A. Charfi, S. Neili, M. Kharrat, and M. Dammak, *J. Thermoplast. Compos. Mater.*, <http://doi.org/10.1177/0892705719875203> (2019).
30. A. H. Wang, J. Xia, Z. X. Yang, and D. H. Xiong, *Opt. Laser Technol.*, **116**, 171 (2019).
31. M. Trabelsi, M. Kharrat, and M. Dammak, *T. Indian I. Metals*, **69**, 1205 (2016).
32. E. Dhanumalayan and G. M. Joshi, *Adv. Compos. Hybrid Mater.*, **1**, 247 (2018).
33. D. M. Price and M. Jarratt, *Thermochim. Acta*, **392**, 231 (2002).
34. D. Gong, Q. Xue, and H. Wang, *Wear*, **148**, 161 (1991).
35. X. Teng, L. L. Wen, W. Tang, X. Zhao, and C. Chen, *High Perform. Polym.*, **30**, 752 (2018).
36. Y. Zhang, K. Kou, C. Pan, Z. Li, and T. Ji, *J. Appl. Polym. Sci.*, **136**, 48175 (2019).
37. F. Song, Q. Wang, and T. Wang, *Tribol. Int.*, **104**, 392 (2016).
38. R. Huang, S. Ma, M. Zhang, J. Yang, D. Wang, L. Zhang, and J. Xu, *Materials*, **12**, 1082 (2019).
39. Z. Bi and D. W. Mueller, *Friction*, **7**, 268 (2019).
40. I. Ovali, H. Karakoc, and H. Cinici, *Manuf. Eng.*, **79**, 19 (2016).
41. A. E. P. A. Baradeswaran and A. E. Perumal, *Compos. Part B-Eng.*, **54**, 146 (2013).
42. A. Abdollahi, A. Alizadeh, and H. R. Baharvandi, *Mater. Design*, **55**, 471 (2014).
43. A. Yazdani and E. Salahinejad, *Mater. Design*, **32**, 3137 (2011).
44. R. K. Goyal and M. Yadav, *J. Appl. Polym. Sci.*, **127**, 3186 (2013).
45. X. Hu, X. Yan, Y. Ma, and Y. Bai, *Polym. Korea*, **41**, 68 (2017).
46. M. V. Chernets, S. V. Shilko, M. I. Pashechko, and M. Barshch, *J. Frict. Wear*, **39**, 361 (2018).
47. R. Kaundal, A. Patnaik, and A. Satapathy, *Proc. Inst. Mech. Eng. Part L-J. Mat.*, **232**, 893 (2018).
48. C. Liu, C. Long, L. Chen, J. Liu, T. Cao, and J. Zhang, *Polym. Korea*, **40**, 836 (2016).
49. U. R. Hashim and A. Jumahat, *Mater. Res. Express*, **6**, 025303 (2018).
50. R. A. Mohammed, *Mater. Res. Express*, **6**, 125314 (2019).