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"Ultralow" Sliding Wear PTFE Nanocomposites with Functionalized Graphene

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Abstract:

The dry friction and sliding wear behavior of sintered PTFE containing various amounts of functionalized graphene (GR) were studied in this work. GR was incorporated in 0, 0.25, 0.75, 1, 2 and 4 vol%, respectively. Sliding wear tests were performed in ring(metal)-on-plate(PTFE) (ROP) test rig under ambient temperature setting 1 m/s sliding speed and 1 MPa contact pressure. The dynamic coefficient of friction (COF) and specific wear rate (w_s) data were determined. Very low COFs (0.12-0.14) were measured for PTFE containing 2 or 4 vol% GR which was attributed to the formation of a tribofilm on the countersurface. w_s went through a maximum (peaked at doubling that of the unmodified PTFE at about 0.75 vol% GR) as a function of GR content. Ultralow w_s data in the range of 10^{-6} $mm^3/(N.m)$ were measured for the PTFE nanocomposites with 2 and 4 vol% GR. This was reasoned by the formation of a robust tribofilm, the development of which was followed by scanning electron microscopy (SEM) by inspecting the worn surface of PTFE nanocomposites and that of the steel ring of the ROP test rig. Fourier transform infrared spectroscopic results confirmed the formation of carboxyl groups in the tribofilm. They were supposed to react with the functional groups of GR and to create complexes with the metal countersurface ensuring the tribofilm with high adhesion and cohesion strengths.

Key words: Polytetrafluoro ethylene (PTFE); graphene; sliding friction and wear; tribofilm; wear mechanisms; tribochemistry; ring-on-plate testing (ROP)

1. INTRODUCTION

Polytetrafluoro ethylene (PTFE) and its composites are widely used in different applications where very low friction coefficient, excellent resistance to chemicals, and good thermal stability are required. Moreover, PTFE-based systems exhibit self-lubrication which is beneficial for maintenance-free sliding parts. Self-lubrication often manifests also in the formation of a so called transfer or tribofilm on the counterpart´ surface. As a consequence PTFE rubs, slides against PTFE and no more against the metal surface. However, PTFE, being a viscoelastic polymer, is prone for creep. Its resistance to sliding wear is moderate to low (specific wear rates in the range of 10^{-5}… 10^{-3} $mm^3/(N.m)$) [1 and references therein]. Owing to the aforementioned viscoelastic feature both the coefficient of friction (COF) and wear rate strongly depend on the sliding conditions (speed, pressure) and temperature. To overcome these disadvantages many micronscale fillers of various aspect ratios have been incorporated in PTFE and their effects on the friction and wear behavior tested [2 and references therein]. This strategy resulted in marked improvement in the resistance to sliding wear [2,3,4]. Initially, researchers were reserved to use nanofillers because their effect was thought too low to suppress wear and support the formation of the tribofilm [1,2]. Ultralow wear is usually quantified at a specific wear rate less than 10^{-5} $mm^3/(N.m)$, at least for PTFE. Note that this threshold is at about two orders of magnitude lower than that of plain PTFE measured at sliding speeds higher than 50 mm/s [1]. Onset of ultralow wear is associated with the development of a durable, thin tribofilm on both sliding surfaces. It is intuitive that a robust tribofilm should have very good adhesion to the counterpart (usually metal surface) and at the same time high resistance to shear (being the prevailing mechanical loading). Nanoparticles proved to be promising additives to enhance the strength [5], also in shear deformation, in various polymers. Therefore, they may be promising additives to improve the cohesive strength of the tribofilm. In fact, incorporation of alumina [6], serpentine [7] nanoparticles enhanced the wear resistance and even ensured ultralow wear performance of PTFE. Trials were made also to improve the wear performance of PTFE by using carbonaceous nanofillers such as carbon nanotube (CNT) [8] and graphene [9-10]. Graphene and its derivatives proved to be very attractive self-lubricating materials themselves to achieve low friction and low wear rates [11].

By contrast to former explanations, some present theories [12-15], emphasize the influence of tribochemistry on the formation of the tribofilm, more exactly on its “anchorage” to the metal countersurface. According to one of the tribochemical pathways proposed, PTFE macromolecules first undergo chain scissions and then the related macroradicals become “functionalized” by reacting with oxygen and subsequently with water from the surrounding atmosphere [13]. Another tribochemical scheme involves the formation of terminal unsaturations (double bonds) in the broken PTFE molecules which are transformed to carboxylic groups through reaction with water [14]. Irrespective of differences in the above reaction pathways, the final functional groups are carboxylic ones. They may participate in chelate complex formation with the ions of the metal surface whereby anchoring the wear debris to the surface [13]. The open question is now: how to improve further the cohesive strength of the tribofilm? Obviously such additives should be selected which bear the same functional groups evolved according to above schemes, which may enter in reaction with them, or which have possible ligands for the supposed complex formation. The latter aspect seems to be confirmed by the ultralow wear results measured for PTFE with alumina and silicate type nanofillers [6-7,12-15]. Suitable functional groups for complexing can be produced, however, also on carbonaceous nanofillers, such as CNT and graphene derivatives. For the functionalization researchers generally adapt modifications of the Hummers-Offeman method [16 and references therein]. After the acidic treatment the related nanofillers bear carboxyl, hydroxyl and epoxy groups, which all are promising for metal complexation. Moreover, hydroxyl and epoxy groups can react with the carboxyl groups formed in PTFE according to the above mentioned tribochemical pathways. Nowadays, functionalized CNT and graphene grades are available commercially. Further potential benefit of carbonaceous nanofillers is that they suppress creep [17] and may work as solid lubricants which are of great relevance in wear tests. Considering the fact that the tribofilm is generated by shear deformation, platy, disc-shaped nanofillers may possibly be more suited than any others in this respect. Accordingly, the research strategy of this work was to incorporate functionalized graphene (GR) in PTFE that should yield ultralow sliding wear at least beyond a given GR concentration. This strategy is reasoned by surmising multiple roles of functional GR:

i) support of the chemical anchorage of the tribofilm to the metal surface via its functional groups (enhancing the adhesive strength),
ii) reinforce the PTFE tribofilm via “grafting” of PTFE macroradicals onto its surface and trigger the reaction between carboxyl groups formed in PTFE and epoxy/hydroxyl groups of functionalized GR (enhancing the cohesive strength), and
iii) act as solid lubricant in form of exfoliated GR sheets (after peeled off during tribofilm formation).

It is intuitive that this combined effect depends on the amount of the available functional groups (functionalization) and the dispersion state of the GR, and thus in case of a given functionalization of GR also on its concentration in the PTFE matrix. To check this idea tests were run on the plain PTFE and PTFE/GR nanocomposites, respectively, in a ring(metal)-on-plate(PTFE) test rig. The GR content in the PTFE was varied between 0 and 4 vol.%.

2. EXPERIMENTAL

2.1. Materials

Exfoliated graphene nanoplatelets (GR, Grade M-25) were obtained from XG Sciences (East Lansing, MI, USA) which exhibited an average particle size of 25 µm, specific surface area in the range of 120-150 m^2/g, and a thickness of 6-8 nm. The atomic oxygen and its residual acid contents of this GR was at about 1% and 0.5 wt.%, respectively. It is noteworthy that GR grades with higher oxygen contents, linked with the presence of carboxyl, hydroxyl and epoxy groups, are also available. According to our abovementioned research strategy they might be more suited as additives. Our intention was, however, to use a less functionalized graphene which allows the evaluation of the GR concentration on the sliding wear properties and tribofilm formation in a larger concentration range. A modified PTFE powder (TFM 1700) which was obtained from 3M/Dyneon (Neuss, Germany) was used as the base polymer to be blended with the GR. Solvent blending was utilized with a perfluorinated solvent (perfluoroheptane (PFH)) which was supplied by Pelchem SOC Ltd (Pelindaba, South Africa) to disperse the graphene nanoplatelets with the unprocessed PTFE powder. GR was incorporated to the PTFE up to 4 vol.%, more exactly nanocomposites with 0, 0.25, 0.75, 1, 2 and 4 vol.% GR were prepared.

2.2. Specimen preparation

The required amount of GR nanoplatelets was dispersed in 250 ml PFH for 2 hours (h) in an ultrasonic bath (power: 100 W) at 30 °C. After sonication the GR/PFH dispersion was blended with 50 g of the PTFE powder. The related dispersion was stirred for 1 h at 20 °C. After stirring, the PFH was filtered off, to be recycled, and the PTFE/GR blended powder was collected. The composite powder was further baked at 70 °C for 24 h to remove any residual solvent. This procedure was followed for each volume fraction loading of GR per batch.

Disc samples with a 55 mm diameter and an approximate 3 mm thickness were cold pressed (13 MPa, 23 °C) in a stainless steel mold. The required pre-form pressure (13 MPa), maintained for 3 min, was exerted using a 20 ton hydraulic press (Hytec, Kempton Park, South Africa). Sintering of the discs was performed in a sintering oven (Carbolite HRF-L; Hope Valley, United Kingdom) fitted with a Shinko (JCS, Osaka, Japan) temperature controller. The sintering occurred at 380 °C for 240 min (Figure 1) to allow for coalescence of the compacted composite powder. The temperature cycle of the sintering oven is given in Figure 1.

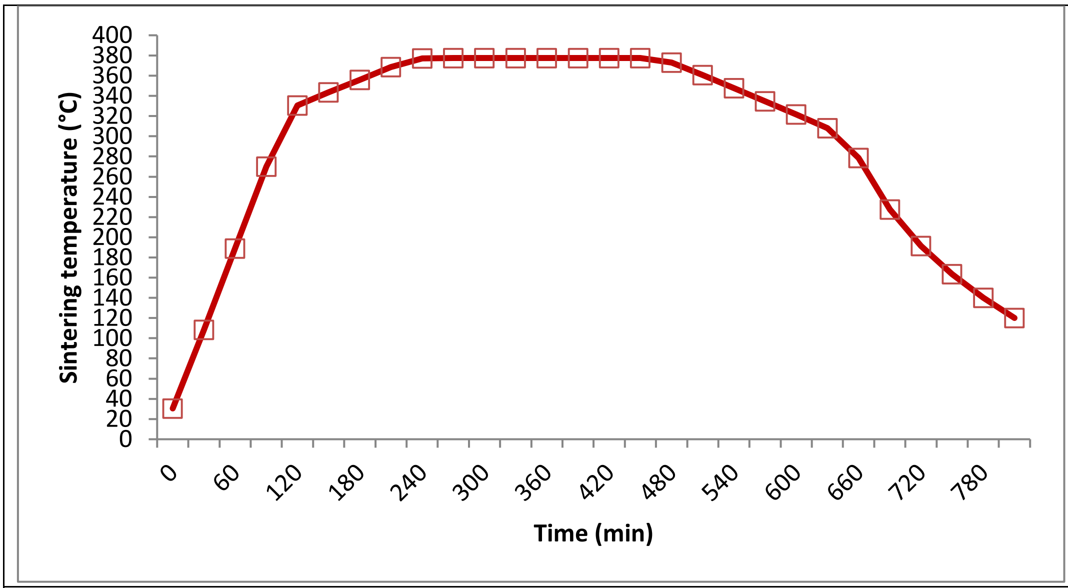


Figure 1 : Heating profile for sintering program

2.3. Tribological testing

Dry sliding friction and wear tests were performed on a ring-on-plate (ROP; SOP 3000, Werner Stehr Tribologie, Horb am Neckar, Germany) test rig. In ROP testing a fixed PTFE plate was pressed against a rotating metal ring. The PTFE plate samples were cut to the dimensions of 20 x 9 x 3 mm^3 (length x width x thickness). In the tests 100 Cr6 rings with an average surface roughness of Ra ≈ 0.2 µm were used as counterparts. The tribological tests were carried out under dry sliding conditions at room temperature using following parameters: pressure p = 1 MPa, sliding speed v = 1 m/s and testing time t = 4 hours. At least three specimens were tested on each test rig. As results the averaged coefficient of friction (COF) and specific wear rate (w_s) were determined for each PTFE/GR system. Equation (1) was used for the calculation of w_s:

$$w_s = \frac{\Delta m}{L \cdot \rho \cdot F_N} \left[\frac{mm^3}{N \cdot m} \right] \qquad (1)$$

where Δm is the gravimetrically measured weight loss, L is the overall sliding distance, ρ is the density determined by the buoyancy technique in water, and F_N is the normal load applied. F_N was computed by considering the specimens´ dimension to reach 1MPa pressure. For ROP configuration a line contact with 1 mm width was accepted to set the above nominal contact pressure.

2.4. Morphology, tribofilm formation and characteristics

Dispersion of GR platelets in PTFE was studied on cryofactured surfaces of the corresponding nanocomposites. Specimens were fractured across their thickness in different planes in order to get information on eventual enrichment or depletion of the GR locally.

Morphology of the worn PTFE surfaces and film formation on the counterparts were inspected using ultra-high resolution field emission scanning electron microscope (SEM) SUPRATM 40VP (Carl Zeiss SMT AG, Jena, Germany) operating with 10 kV acceleration voltage, a working distance of less than 10 mm, and a secondary electron detector. The respective surfaces were sputter-coated for 80 s with gold prior to SEM analysis.

Fourier transform infrared (FTIR) spectroscopic measurements were performed on a Nicolet 510 spectrometer (Madison, Wisconsin, USA). The tribofilm was scratched from the ring surface and mixed with KBr and pressed into disks. PTFE/GR sheet samples were tested in attenuated total reflection (ATR) mode using ZnSe crystal. FTIR spectra were recorded at 4 cm^{-1} spectral resolution in the wavelength range of 4000-600 cm^{-1}.

3. RESULTS AND DISCUSSION

3.1. GR dispersion

Figure 2 shows SEM pictures taken from the top, middle and bottom sections of the PTFE nanocomposite disc containing 2 vol.% GR (designated as PTFE/GR-2). One can recognizes that the GR platelet stacks are rather homogenously distributed across the thickness. Accordingly, no segregation phenomenon occurred during preparation of the samples. Similar results were obtained for all PTFE/GR nanocomposites. This finding is very important with respect to the interpretation of the sliding wear tests.

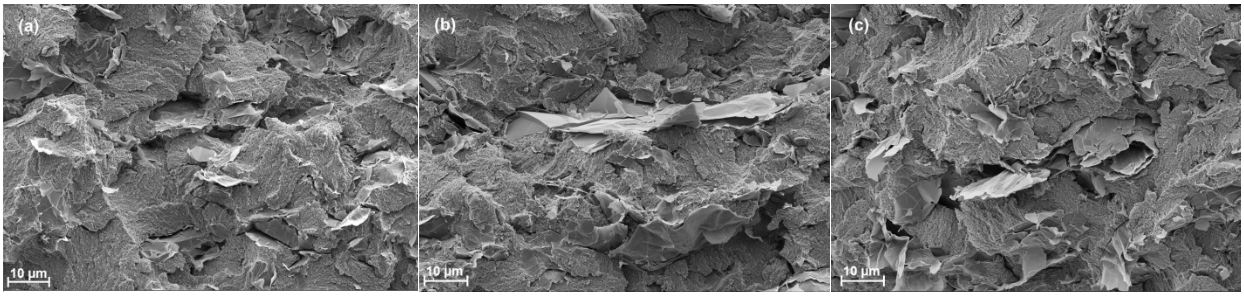


Figure 2. SEM pictures taken from the top (a), middle (b), and bottom section (c) of PTFE/GR-2. Note: fracture surfaces were produced by cutting of the disc specimens cooled by liquid nitrogen

3.2. Sliding friction and wear

Mean values of the dynamic coefficient of friction (COF) are given in Figure 3. One can observe that the value of COF is monotonically decreasing with increasing GR content before leveling off at 2vol% GR and above. In this GR range the related COF is very low (0.12-0.14) suggesting the development of a tribofilm on the countersurface. The tribofilm formation will be confirmed later.

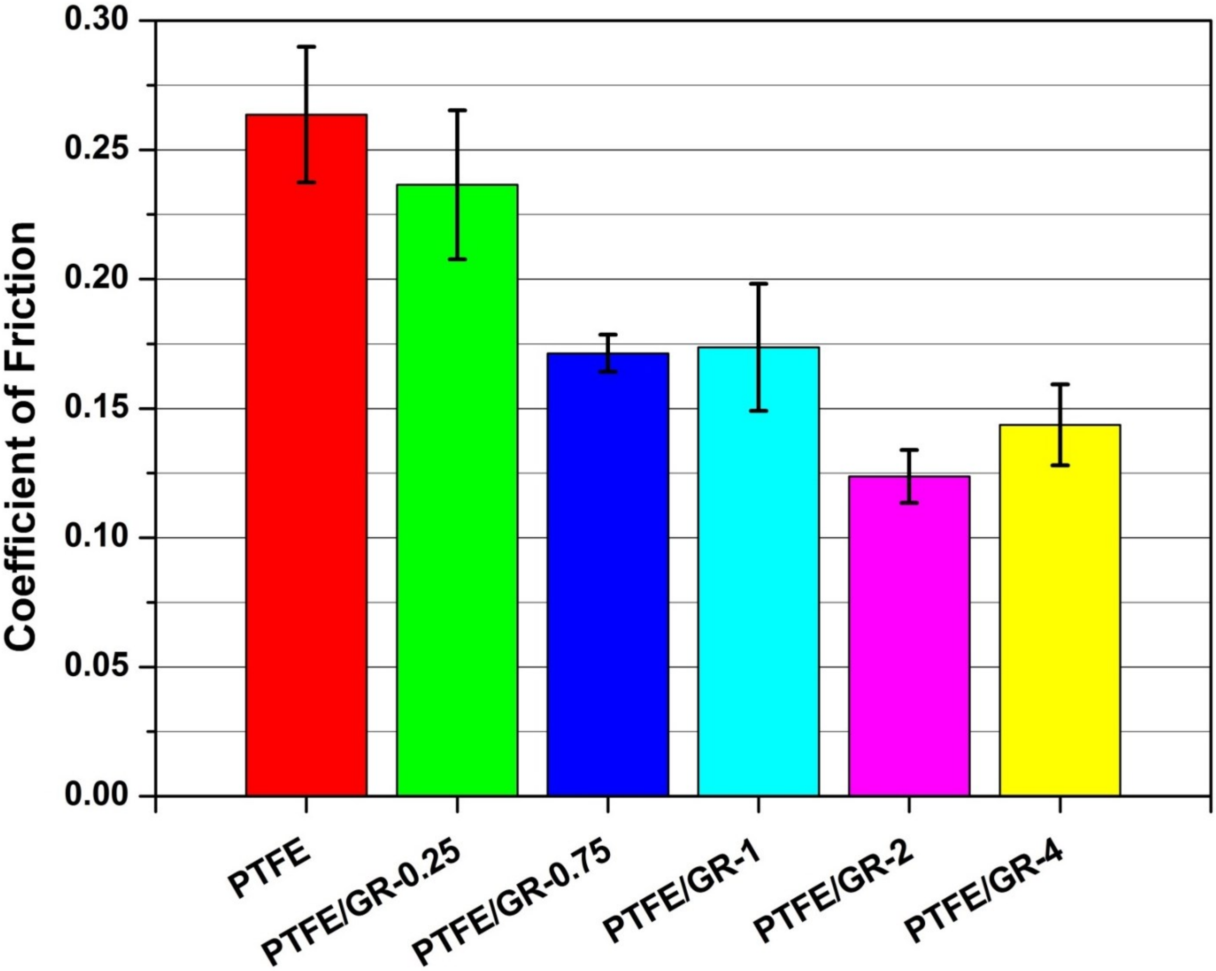


Figure 3. Steady state dynamic COFs measured in ROP testing conditions for the PTFE/GR nanocomposites

An interesting feature in the course of the COF as a function of elapsed time was observed in ROP testing. The scatter in the measured COFs was markedly reduced, i.e. the related traces smoothed, with increasing GR content – cf. Figure 4. The possible reason of this may be linked with the self-lubrication behavior of GR.

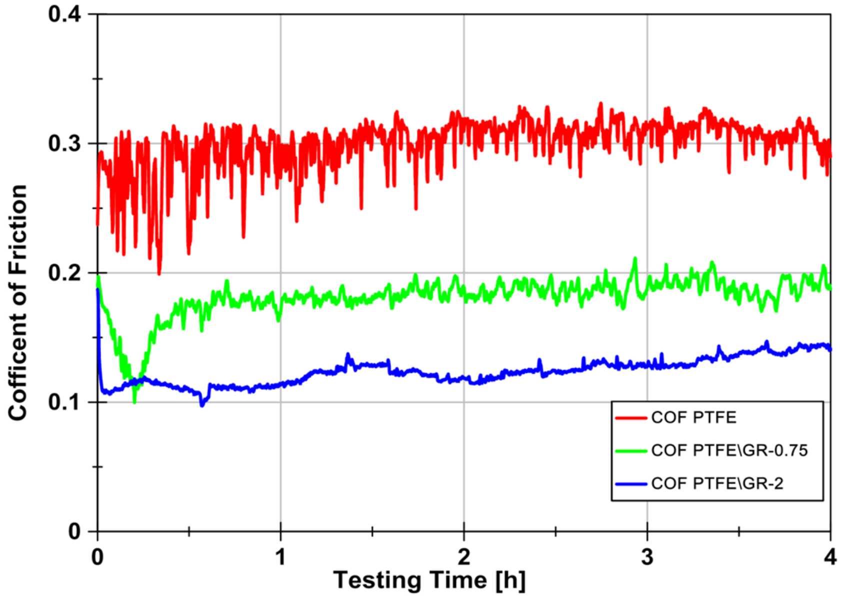


Figure 4. COF vs. time in ROP test monitored for PTFE and its GR nanocomposites with 0.75 and 2 vol% GR, respectively

The specific wear rate (w_s) data, received from ROP tests are displayed in Figure 5.

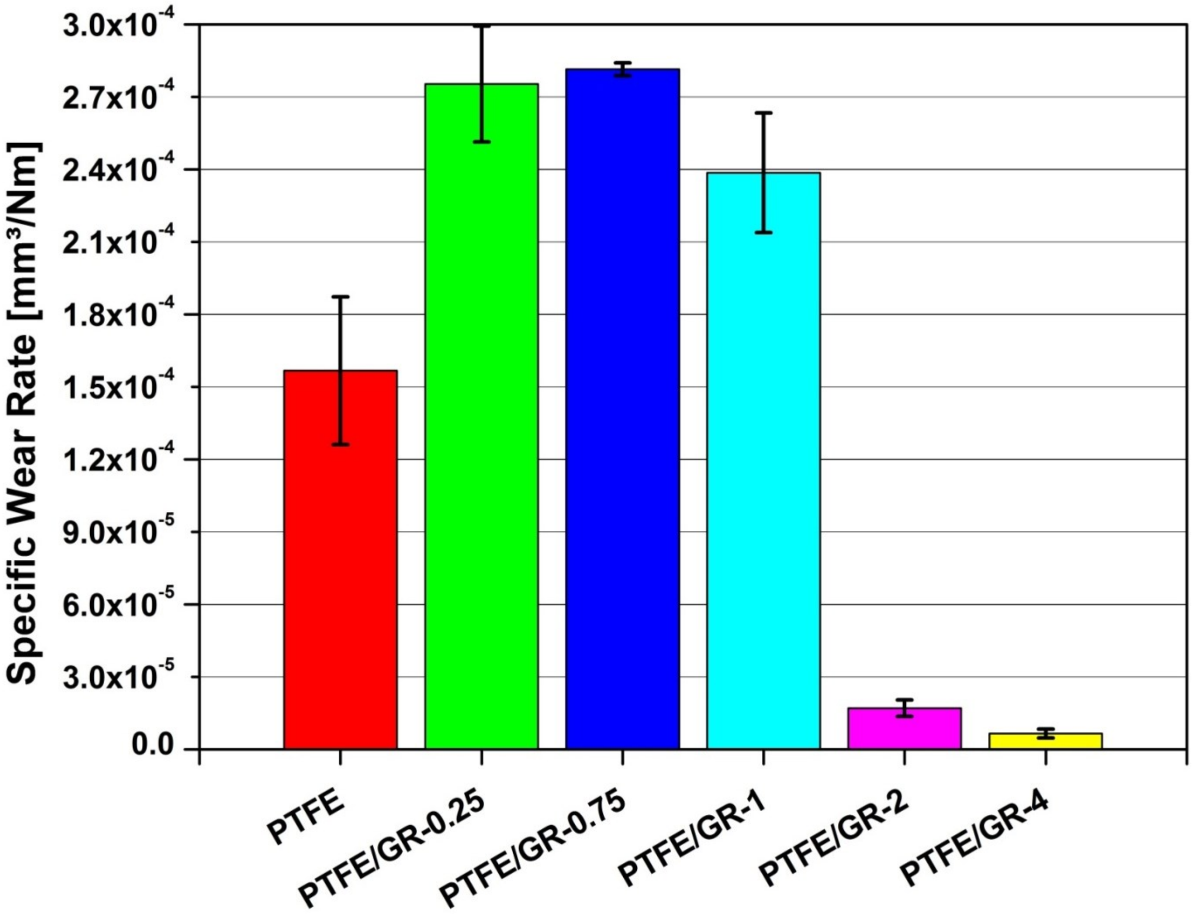


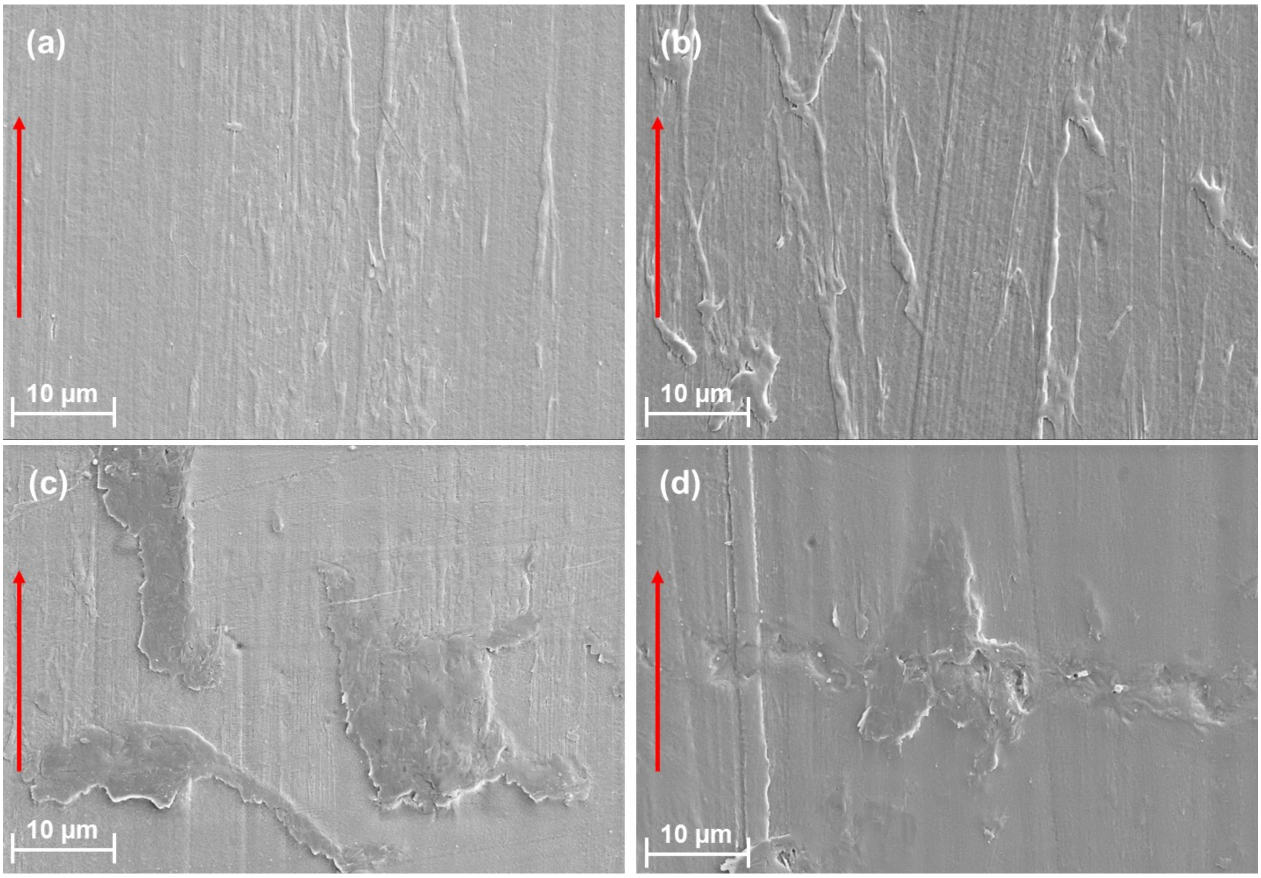
Figure 5. Specific wear rate measured in ROP testing conditions for the PTFE/GR nanocomposites

Note that the w_s values are going through a maximum as a function of the GR content for the PTFE/GR nanocomposites. The most striking finding is that PTFE/GR-2 and -4 show ultralow w_s values. These w_s data lay at 1.70×10^{-5} and 6.61×10^{-6} $mm^3/(N.m)$ for the PTFE/GR-2 and PTFE/GR-4, respectively. These data confirm that the criterion of "ultralow wear" is met and thus the attribute "ultralow" adequately used in the title of this paper. Attention should be paid to the fact that many polymers, even without any additives, exhibit similar low wear rates (e.g. [18]) and not referred to as "ultralow wear" systems. This is due to the fact that the considered threshold, i.e 1×10^{-5} $mm^3/(N.m)$, is strictly related to PTFE. Recall that PTFE has low resistance to sliding wear as emphasized in the introduction section.

The observed ultralow wear should be linked with the formation of a transfer or tribofilm on the metal countersurface. In order to clarify this aspect and to reason the appearance of the maximum in w_s as a function of GR loading the worn surfaces of the PTFE nanocomposites and that of the counterparts (i.e. steel rings) were subjected to SEM inspection.

3.3. Wear mechanisms

Figure 6 displays characteristic SEM pictures taken from the worn surface of PTFE and its GR-filled nanocomposites.



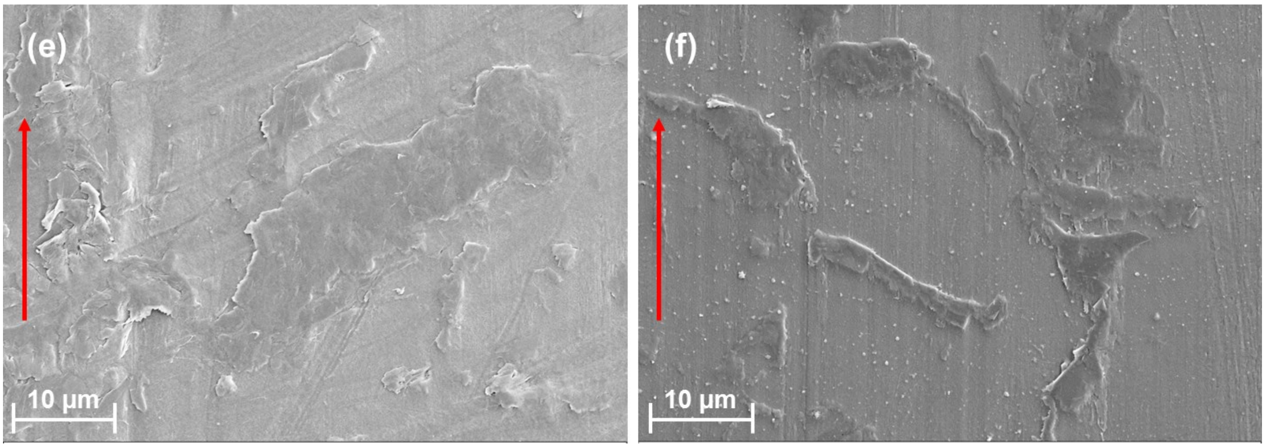


Figure 6. SEM pictures taken from the worn surfaces of PTFE and PTFE/GR nanocomposites. Designations: a) PTFE, b) PTFE/GR-0.25, c) PTFE/GR-0.75, d) PTFE/GR-1, e) PTFE/GR-2 and f) PTFE/GR-4. Note: sliding direction is indicated by arrow.

Comparing the SEM pictures in Figure 6 one can observe the appearance of rugged and patchy pattern with increasing GR content up to 0.75 vol% GR. At higher GR loadings some patchy appearance still can be resolved but the corresponding fragments are well "ironed" into the worn surface. Accordingly, the overall surface roughness goes through a maximum which suggests a similar trend as found for w_s. A further noteworthy aspect is that above 1 vol% GR the GR particles, clearly visible as white spots already at this magnification, appear finely and homogeneously dispersed in the worn surfaces (cf. Figure 6e and 6f). This suggest that 2 or more vol.% reinforcing GR, when well distributed and likely aligned, can efficiently enhance the shear strength of the PTFE. Until this threshold GR particles (platelet agglomerates), though well dispersed in the PTFE matrix, have not the necessary reinforcing effect. On the contrary, the related agglomerates may trigger debonding of the matrix, along with some fibrillation, which all contribute to wear. The onset of patches hints for the development of worn sections which are likely held together by the reinforcing action of GR platelets. The formation and break away of these patches from the worn surface (cf. Figure 6c and 6d) are in the framework of a dynamic process during sliding wear. Its manifestation may be the reduced scatter of the dynamic COF when monitored as a function of time (cf. Figure 4). The peel off, break away of the patches are hampered when the homogenously dispersed GR with smaller interparticle distance and better adhesion to the PTFE matrix (via the supposed chemistry) can overtake the role of an efficient nanoscale reinforcement.

3.4. Tribofilm formation

During ROP testing only small deposited PTFE debris could be observed on the countersurface (Figure 7). These debris, fragments are agglomerated from rolls. Accordingly, roll formation is the first wear mechanism. This is in concert with the appearance of the worn surfaces in the previous section (cf. Figure 6a and 6b). A closer look on the patchy debris reveals that the GR particles are causing cavitation (debonding) in the PTFE, as already suggested when reasoning the wear increment below 0.75 vol% GR content.

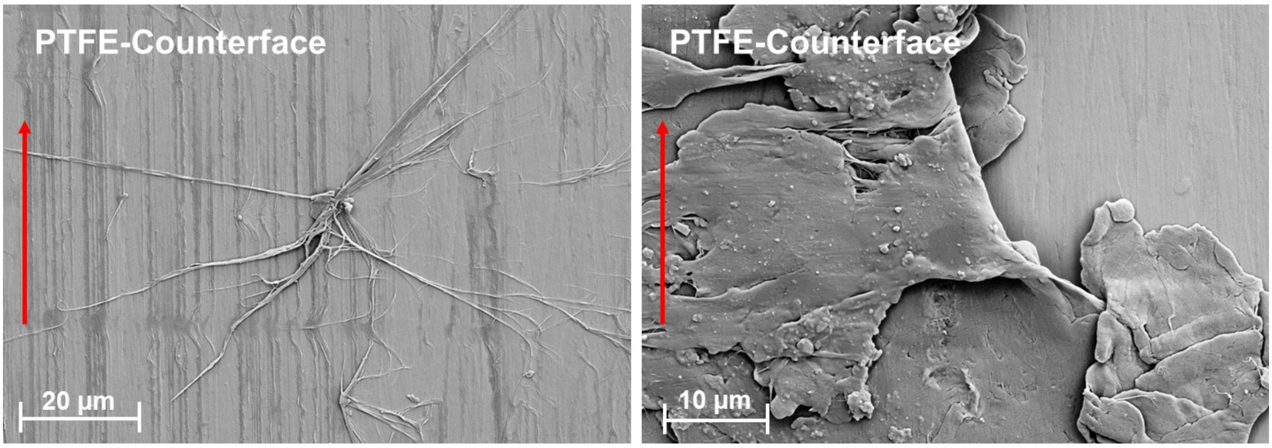


Figure 7. SEM pictures from the roll countersurface used in ROP to wear against PTFE. Note: sliding direction is indicated by arrow.

The countersurface is becoming more and more covered with PTFE with increasing amount of GR content in the nanocomposite. This can be seen already in case of PTFE/GR-0.25 (Figure 8a). In the patch adhering to the metal surface massive fibrillation can be observed (Figure 8b) which follows the debonding, and it is associated with enhanced wear. Recall that dynamic patch formation with debonding and fibrillation were made responsible for the initial increment in w_s with increasing GR content up to 0.75 vol% GR.

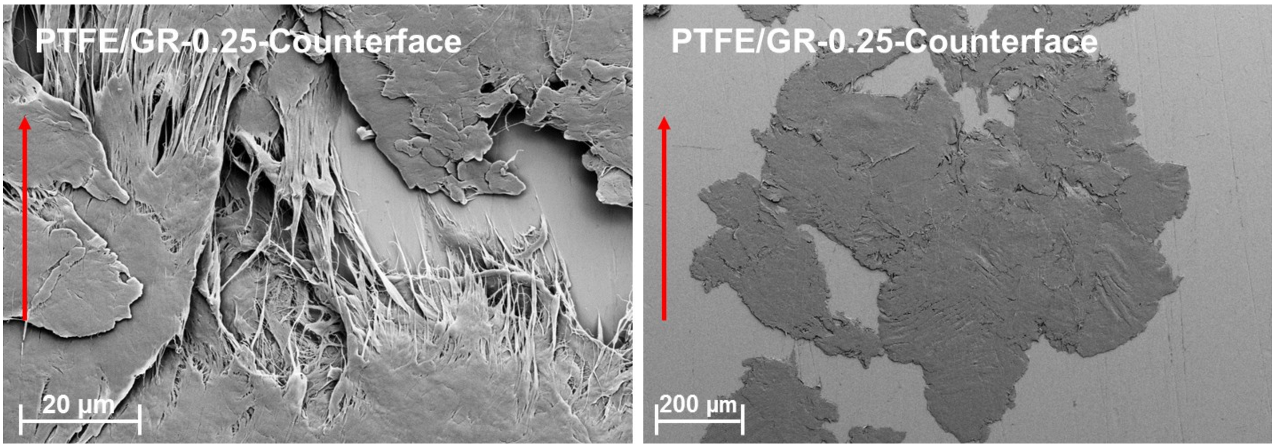


Figure 8. SEM pictures from the roll counterface used in ROP to wear against PTFE/GR-02.5. Note: sliding direction is indicated by arrow.

Unlike in case of PTFE/GR-1 (cf. Figure 9a), the surface of the metallic ring is practically fully covered by the tribofilm after testing of PTFE/GR-4 (cf. Figure 9b). The fine structure of the continuous tribofilm is well resolved in Figure 9c at high magnification. Though in the tribofilm some debonding-induced hole formation can still be resolved, the cohesive strength of the PTFE owing to reinforcing effect of GR is high enough to avoid massive breakage and peel off.

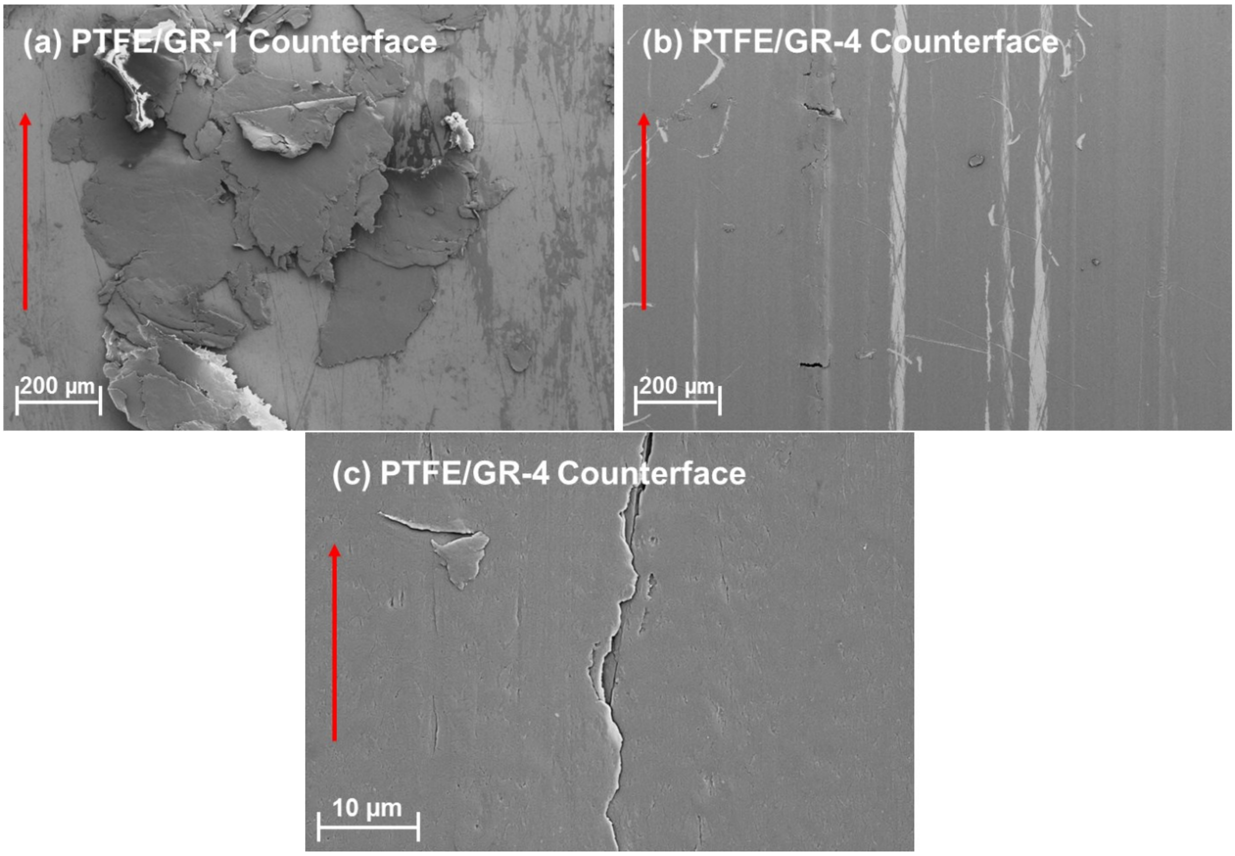


Figure 9. SEM pictures from the roll counterface used in ROP to wear against PTFE/GR-1 (a) and PTFE/GR-4 (b, c). Note: sliding direction is indicated by arrow.

The above scenario has confirmed that our research philosophy was correct. Functionalized graphene may support the formation of a tribofilm on the counterface and thus to yield ultralow sliding wear performance. Recall that it has been supposed that the functional groups of GR in interplay with the tribochemistry of PTFE should be strongly involved in this process. FTIR spectra taken from the unworn plate and tribofilm patches, peeled off the steel ring after testing of PTFE/GR-1, seem to support this hypothesis (cf. Figure 10).

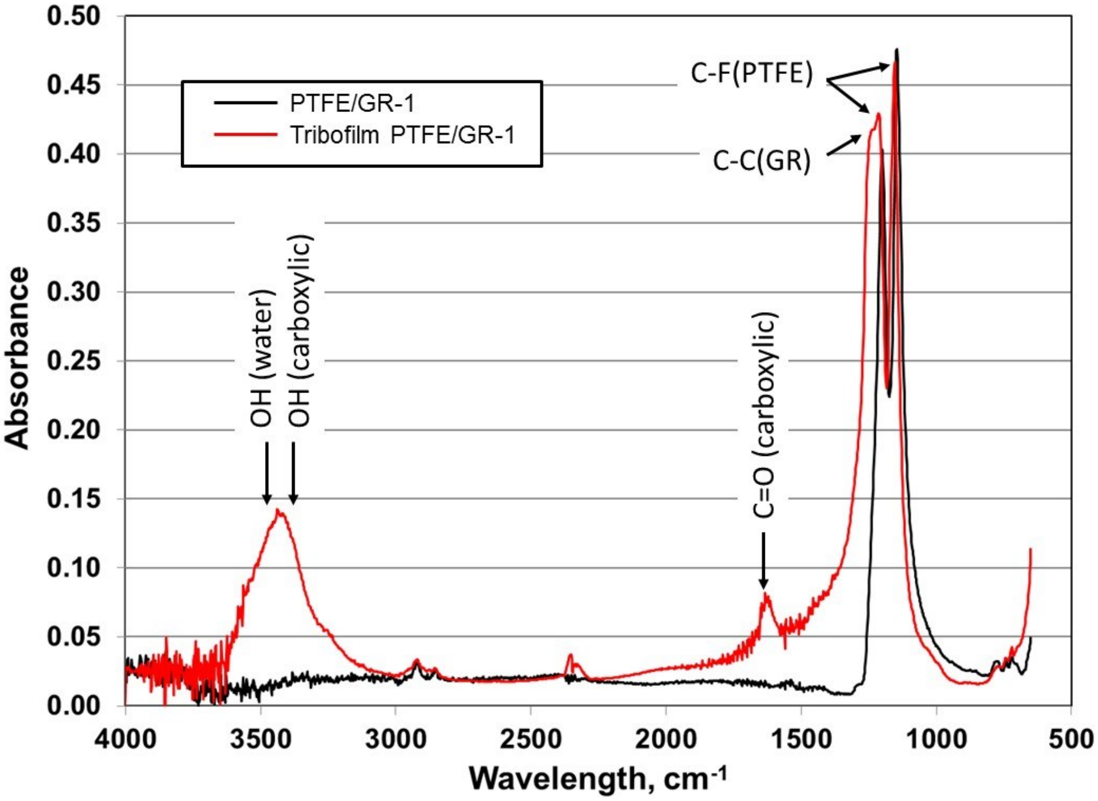


Figure 10. FTIR spectra taken from “fresh” PTFE/GR-1 (in ATR mode (black)) and from the related tribofilm developed on the surface of the steel ring during ROP (KBr technique, transmission mode (red))

In Figure 10 the PTFE backbone related peaks (C-F) are well resolved in the range of 1150-1200 cm^{-1} for both fresh and tribofilm PTFE/GR-1. The tribofilm, however, shows two additional well developed absorption bands, peaked at 1650 and 3380 cm^{-1}, respectively. The former one can be assigned to carbonyl/carboxylic groups which have an essential role in the supposed chelation/complexation process. The peak at 3380 cm^{-1} in linked to the presence of OH groups of carboxyl and/or water [13]. Recall that the latter had a prominent role in the tribochemical pathways proposed [13-14], as well. An additional shoulder at 1250 cm^{-1} can be attributed to the stretching vibration of C-C groups of GR, which confirms its presence in the analyzed tribofilm One can thus conclude that in the development of the tribofilm chemical reactions have been involved, in fact. Further studies are needed, however, to demonstrate the proposed coupling between the functional groups of the graphene and those generated in the PTFE during tribological testing. An indirect support for that would be if a higher functionalized GR than in the present case would yield the required tribofilm formation at lower concentration.

4. CONCLUSION

This work devoted to study the sliding wear performance of sintered PTFE containing various amounts of functionalized graphene (GR). GR was incorporated by a solvent-assisted technique up to 4 vol%. Sliding wear tests were run in ring-on-plate(PTFE) (ROP) test rigs.

Very low COFs values were found for PTFE/GR nanocomposites above 2 vol% GR content. This was attributed to tribofilm formation resulting in sliding of PTFE against PTFE and to the beneficial solid lubricant effect of “flattened” GR platelets.

The specific wear rate went through a maximum as a function of GR content. The initial increment was attributed to a dynamic wear process in which GR platelet agglomerates caused debonding with follow-up fibrillation thereby enhancing the wear. Reduction in the specific wear, reaching low values in 10^{-6} $mm^3/(N.m)$ range, was owing to the formation of a robust tribofilm on the steel counterface. For its high cohesive strength, reflected in high resistance to shear, the reinforcing action of closely spaced GR platelets, chemically bonded to the PTFE matrix, was made responsible. This information was deduced from extensive SEM work focused on both worn surface of the PTFE nanocomposites and steel counterface of the ROP test rig. For the adhesion of the tribofilm to the steel surface and cohesion strength of the tribofilm tribochemical reactions were suspected, in which the functional groups GR may play an important role. The fact that tribochemistry was at work was deduced from infrared spectra showing the formation of carbonyl/carboxylic groups.

Literature:

1 Ye J, Khare HS, Burris DL. Transfer film evolution and its role in promoting ultra-low wear of a PTFE nanocomposite. Wear 2013; 297: 1095-1102.

2 Burris DL, Santos K, Lewis SL, Liu X, Perry SS, Blanchet TA, Schadler LS, Sawyer WG. Polytetrafluoroethylene matrix nanocomposites for tribological application in “Tribology of Polymeric Nanocomposites” 2nd ed. (Eds.: Friedrich, K., Schlarb, A.K), Butterwort-Heinemann, Oxford, 2013, Ch. 17, pp. 571-617.

3 Chen B, Luan D, Huang J, Zhang J. Enhanced thermal conductivity and wear resistance of polytetrafluoroethylene composites through boron nitride and zinc oxide hybrid fillers. J. Appl Polym Sci 2015; 132:42302.

4 Unal H, Yetgin SH, Miramoglu A, Sumer M. The effect of test parameters on friction and wear performamnceof PTFE and PTFE composites. J Reinf Plast Compos 2010; 29:1978-1986.

5 Chow WS, Mohd Ishak ZA. Polyamide blend-based nanocomposites: A review. Express Polym Lett 2015; 9:211-232.

6 Burris DL, Zhao S, Duncan R, Lowitz J, Perry SS, Schadler LS, Sawyer WG. A route to wear resistant PTFE via trace loadings of functionalized nanofillers. Wear 2009; 267:653-660.

7 Jia Z, Yang Y. Self-lubricating properties of PTFE/serpentine nanocomposites against steel at different loads and sliding velocities. Composites B. 2012; 43:2072-2078.

8 Vail JR, Burris DL, Sawyer WG. Multifunctionality of single-walled carbon nanotube-polytetrafluoroethylene nanocomposites. Wear 2009; 267:619-624.

9 Kandanur SS, Rafiee MA, Yavari F, Schrameyer M, Yu Z-Z, Blanchet TA, Koratkar N. Suppression of wear in graphene polymer composites. Carbon 2012; 50:3178-3183.

10 Bhargava S, Koratkar N, Blanchet TA. Effect of platelet thickness on wear of graphene-polytetrafluoroethylene (PTFE) composites. Tribol Lett 2015; 59:17.

11 Berman D, Erdemir A, Sumant AV. Graphene: a new emerging lubricant. Mater Today 2014; 17(1): 31-42.

12 Krick BA, Ewin JJ, Blackman GS, Junk CP, Sawyer WG. Environmental dependence of ultra-low wear behavior of polytetrafluoroethylene (PTFE) and alumina composites suggests tribochemical mechanisms. Tribol Intern 2012; 51:42-46.

13 Harris KL, Pitenis AA, Sawyer WG, Krick BA, Blackman GS, Kasprzak DJ, Junk CP. PTFE tribology and the role of mechanochemistry in the development of protective surface films. Macromolecules 2015; 48:3739-3745.

14 Onodera T, Kawasaki K, Nakakawaji T, Higuchi Y, Ozawa N, Kurihara K, Kubo M. Effect of tribochemical reaction on transfer-film formation by poly(tetrafluoroethylene). J Phys Chem. C 2014; 118:11820-11826.

15 Khare HS, Moore AC, Haidar DR, Gong L, Ye J, Rabolt JF, Burris DL. Interrelated effects of temperature and environment on wear and tribochemistry of an ultralow wear PTFE composite. J Phys Chem C. 2015; 119:16518-16527.

16 Pedrazzoli D, Dorigato A, Conti T, Vanzetti L, Bersani M, Pegoretti A. Liquid crystalline polymer nanocomposites reinforced with in-situ produced graphene oxide. Express Polym Lett 2015; 9:709-720.

17 Bhattacharyya A, Chen S, Zhu M. Graphene reinforced ultra high molecular weight polyethylene with improved tensile strength and creep resistance. Express Polym Lett 2014; 8:74-84

18 Pei X, Friedrich K. Sliding wear properties of PEEK, PBI and PPP. Wear 2012; 274-275:452-455