Tribology Letters (2018) 66:128
https://doi.org/10.1007/s11249-018-1081-3

ORIGINAL PAPER

Acid Treatment of Diamond-Like Carbon Surfaces for Enhanced Adsorption of Friction Modifiers and Friction Performance

Arman Mohammad Khan[1] · **Xingliang He**[1] · **Hongxing Wu**[1,2] · **Michael Desanker**[3] · **Ali Erdemir**[4] · **Yip-Wah Chung**[1,5] · **Q. Jane Wang**[1]

Received: 10 June 2018 / Accepted: 4 September 2018

Abstract

Diamond-like carbon (DLC) is a class of amorphous carbon materials used as wear-resistant coatings in tribo-components. The chemical inertness of DLC surfaces, while important in many applications, makes them incompatible with additives in commercial lubricants. Specifically, DLC surfaces do not permit strong adsorption of friction modifier molecules. This study aims at improving the adsorption of these friction modifier molecules on DLC surfaces through an acid treatment. Water contact angle measurements show that such a treatment results in improved hydrophilicity of the DLC. XPS analysis demonstrates 50% increase in the uptake of ArmeenT, an organic friction modifier, on DLC after the acid treatment. This increased ArmeenT adsorption is accompanied by marked decrease in friction in micro-scale friction experiments.

Keywords DLC · Surface treatment · Surface adsorption · Friction modifiers

1 Introduction

DLC coatings find applications in many fields such as automotive components [1], biomedical implants [2], magnetic disk drives [3], and micro-electro-mechanical systems (MEMS) [4]. Structurally, DLC is a class of amorphous carbon materials composed of a network of sp^2- and sp^3-hybridized carbon atoms. The relative proportion of these two hybridized carbon types and DLC growth conditions influence chemical, mechanical, and physical properties. DLC coatings are broadly classified as hydrogenated amorphous carbon (*a*-C:H) having certain fractional content of hydrogen in them and tetrahedral amorphous carbon (*ta*-C) with no hydrogen content. The sp^3 fraction varies between 20 and 65% in *a*-C:H [5], while that in *ta*-C ranges from 5 to 90%. DLC coatings can be doped with other elements to modify their properties. Doping elements can either be metals such as tungsten [6], or non-metals such as nitrogen and sulfur [7, 8].

DLC coatings exhibit a wide range of tribological properties as a function of their chemical composition and hybridization state of carbon. For example, DLC coatings can achieve hardness ranging from 20 to 90 GPa and are used as wear-protective coatings [9–12]. Their friction behavior depends on internal and external factors [13]. Internal factors include the relative amounts of sp^2- and sp^3-hybridized carbon, the content of hydrogen, and other doping elements, whereas external factors include the relative humidity of the testing environment, sliding speed, and contact stress [14, 15]. As a result, the friction coefficient of DLC coatings under dry sliding conditions exhibits a wide range, from 0.001 to 0.7 [5]. For tribological components made of steels, one can achieve more predictable friction performance when lubricated with commercial lubricants. For the same tribological components coated with DLC, the situation becomes more complicated as lubricant additives

---

✉ Yip-Wah Chung
ywchung@northwestern.edu

✉ Q. Jane Wang
qwang@northwestern.edu

[1] Department of Mechanical Engineering, Northwestern University, Evanston, IL 60208, USA

[2] Key Laboratory of Education Ministry for Modern Design and Rotor Bearing Systems, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China

[3] Department of Chemistry, Northwestern University, Evanston, IL 60208, USA

[4] Energy Systems Division, Argonne National Laboratory, Lemont, IL 60439, USA

[5] Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA

such as friction modifiers in these lubricants were originally designed for iron-based surfaces.

During lubrication with a formulated lubricant, friction modifier molecules are expected to adsorb onto the surface and form a low-shear-strength layer, resulting in friction reduction in the boundary and mixed lubrication regimes. The adsorption is facilitated by dipole interactions between the polar end of these friction modifier molecules and oxide/surface hydroxyl groups covering a typical metal surface such as steel. Because of the chemical inertness and non-polar nature of DLC coatings, these friction modifier molecules show poor adsorption on DLC surfaces [16]. Kano et al. [17] observed that no tribochemical film was formed on a DLC surface when tested in a fully formulated SAE 5W-30 lubricant containing an organic friction modifier. They attributed this observation to the inactive chemical nature of DLC coatings. De Barros Bouchet et al. [18] found that hydrogenated DLC coatings showed better friction performance in the presence of lubricant additives as compared to non-hydrogenated ones. Kano et al. [19] examined the friction performance of various DLC/DLC and DLC/steel contact pairs in the presence of glycerol mono-oleate, an organic friction modifier. They found that the *ta*-C/*ta*-C pair gave substantially lower friction coefficient than those of *a*-C:H/*a*-C:H and *ta*-C/steel. The reason was ascribed to the formation of a tribofilm consisting of OH-terminated species resulting from the thermal degradation of the glycerol mono-oleate followed by reaction with carbon dangling bonds of the *ta*-C surface. In that study, tribofilm formation occurred after a short run-in phase, which was hypothesized to expose the carbon dangling bonds of a *ta*-C surface. These studies demonstrate that the adsorption of friction modifier molecules on DLC is highly variable.

The study presented in this paper is motivated by the need to generate DLC surfaces with enhanced adsorption of friction modifiers to achieve improved boundary friction performance. Our approach was inspired by the early work on the synthesis of graphite oxide. Graphite has been traditionally oxidized by an acid treatment using the Hummers method [20], while other oxidizing agents were used to oxidize carbon nanotubes and carbon nanofibers [21]. In our work, we explore how the acid treatment affects the polar nature and surface roughness of these DLC surfaces. These results will then be compared with the adsorption uptake of a typical friction modifier and friction performance before and after the treatment.

2 Materials and Methods

DLC coatings (*a*-C:H) were deposited on silicon substrates using plasma-enhanced chemical vapor deposition with methane as the precursor. Deposition details can be found in [22]. The thickness of the DLC coating was about one µm.

We used the “improved method” as presented in [23] to perform acid treatment of DLC surfaces. First, a 9:1 (162:18 mL) mixture of concentrated sulfuric acid (H_2SO_4) and concentrated phosphoric acid (H_3PO_4) was added to 8.1 g of potassium permanganate ($KMnO_4$). DLC samples measuring about 5×5 mm^2 were then immersed into this solution. This treatment was carried out as a function of temperature (25 °C, 50 °C, 70 °C, and 90 °C) and time (5 min, 15 min, 60 min, and 240 min) with continuous stirring. After removal from the solution, each sample was rinsed thoroughly with deionized water.

Water contact angles of DLC surfaces were measured immediately after the treatment on an ORBIT DSA25 Contact Angle Meter using 1 µL deionized water drops. A white light interferometer (ZYGO NewView™ 7300) was used to collect quantitative surface topography information of the DLC surfaces. Chemical states of DLC surfaces as well as the quantification of friction modifier adsorption were obtained with a Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectrometer, using the Al Kα line at 1486.6 eV, with photoelectrons being collected at an emission angle normal to the sample surface.

We used a commercially available alkyl-amine-based friction modifier, ArmeenT (from AkzoNobel), to evaluate the effectiveness of surface acid treatment by micro-scale friction tests. ArmeenT was dip-coated onto the DLC surface by immersing DLC-coated substrates in ArmeenT (liquid) at 120 °C for 5–60 min. Kimberly-Clark Kimtech delicate-task wipers were used to remove excess liquid from the surface right after the dip-coating process. Subsequent micro-scale friction tests were performed at room temperature using a Micro Materials NanoTest system under different loads (10 mN, 20 mN, 40 mN, and 60 mN). Friction tests were conducted with a spherical steel tip (2 mm diameter) sliding on the DLC surface at 1 µm/s for 300 µm, with simultaneous recording of the normal and lateral forces. The averaged friction coefficients were extracted from the friction-time curves.

3 Results and Discussion

3.1 Water Contact Angles and Surface Topography

Figure 1a, b shows how the water contact angle of DLC surface is affected by the acid treatment as a function of temperature and time, respectively. Figure 1c provides visual evidence for the marked increase in hydrophilicity due to the treatment at 90 °C for 240 min. These results indicate that treatment at modest temperatures (50–90 °C) for short times (5–15 min) are sufficient to produce strongly hydrophilic DLC surfaces.

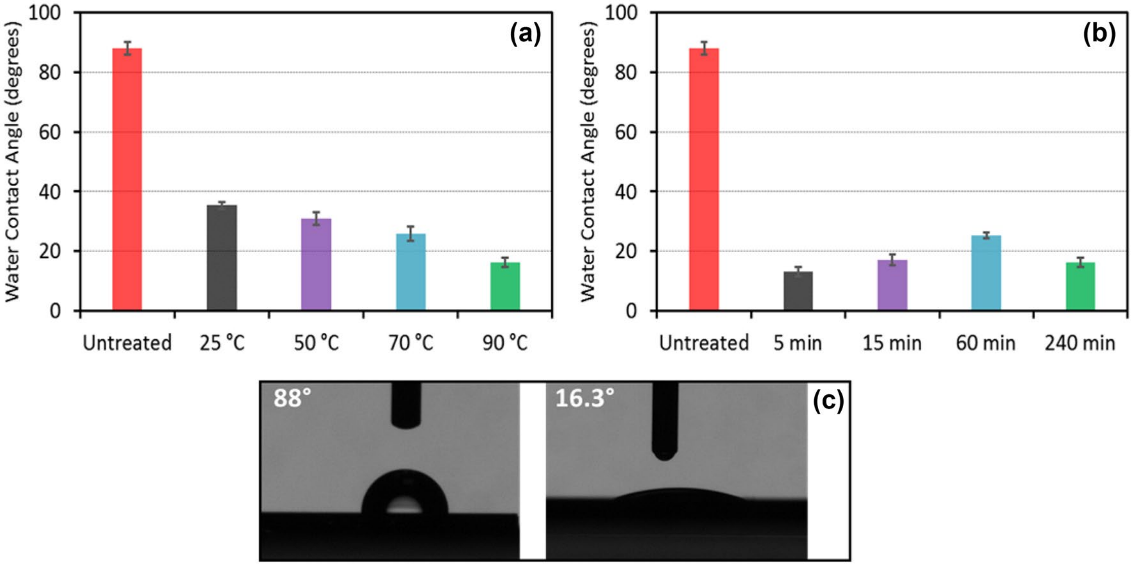

Fig. 1 **a** Water contact angles of DLC surfaces treated for 240 min at different temperatures; **b** water contact angles of DLC surfaces treated at 90 °C for different durations; **c** comparison of the water contact angle before (left) and after (right) the acid treatment performed at 90 °C for 240 min

Figure 2 shows results of surface roughness measurements before and after the treatment. The measurements were conducted on four samples for all the cases shown, with sampling area of 702 µm × 520 µm. The surface roughness is statistically the same before and after the acid treatment, confirming that the marked change in hydrophilicity is due to surface chemical rather than topographical changes.

3.2 XPS Analysis of Treated and Untreated DLC Surfaces

Figure 3a shows the C 1s XPS spectra obtained from the DLC surface before and after the acid treatment (90 °C for 15 min). There is a small peak shift to larger binding energy of 0.5 ± 0.1 eV after the acid treatment. The C 1s peak asymmetry suggests the existence of multiple binding states. Deconvolution of the C 1s peak into three components around 284 eV (due to C–C and C=C), 286 eV (due to C–O), and 288 eV (due to C=O) gives excellent

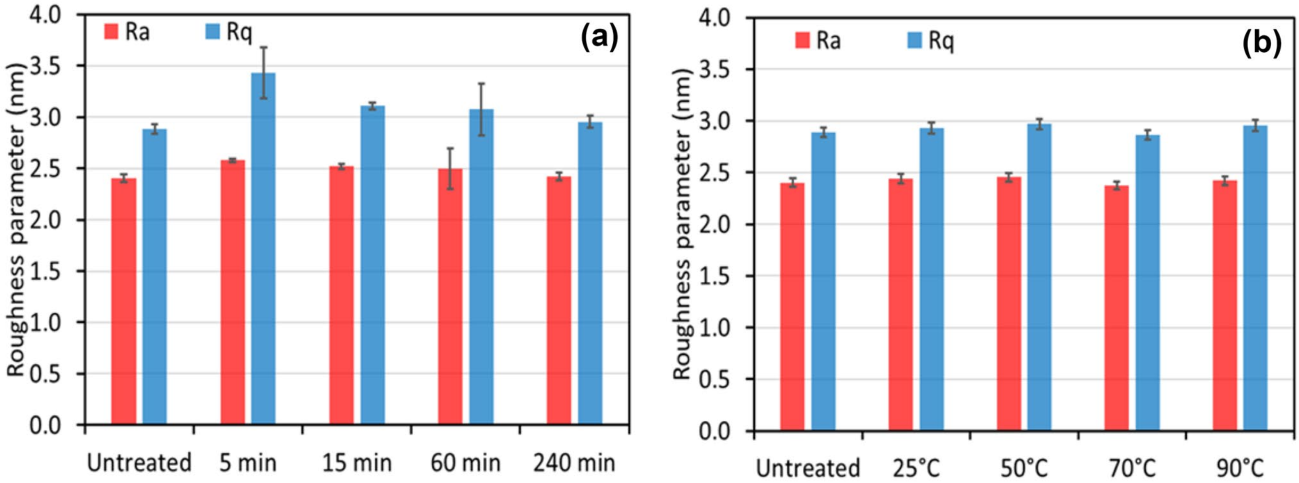

Fig. 2 Roughness of DLC surfaces treated **a** for 240 min at different temperatures, **b** at 90 °C for different durations

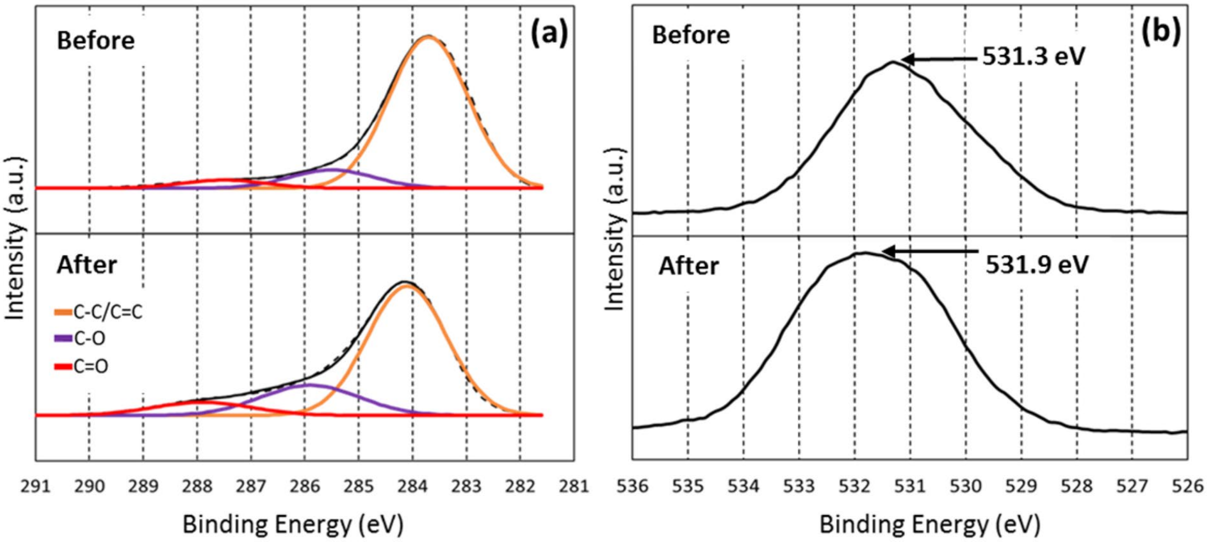

Fig. 3 XPS **a** C 1s and **b** O 1s core level spectra obtained from the DLC surface before and after acid treatment (90 °C for 15 min)

fit to the data. Results of the deconvolution show that the fraction of oxidized carbon (C–O and C=O) signal increases from about 15% for the untreated surface to 29% for the treated surface.

Figure 3b shows the O 1s XPS spectra obtained from the DLC surface before and after the acid treatment. Oxygen adsorption on a typical DLC surface is common [23]. There are three notable O 1s features. First, the peak is unusually broad, with full-width at half-maximum of 3.2–3.4 eV. This shows that there are multiple oxygen bonding states, most likely due to a mixture of O–H and C–O bonding. Second, the O 1s peak shifts to larger binding energy by 0.5 ± 0.1 eV due to acid treatment, same as the C 1s peak shift. This rigid peak shift suggests a decrease in work function induced by the formation of surface dipoles. Third, the integrated intensity of the O 1s peak after the acid treatment is greater than that before the treatment. Given that the XPS sampling depth is much less than the DLC film thickness and that the acid treatment is not expected to vastly disrupt the carbon film, we assume the carbon signal intensity to be constant. By scaling the O 1s signal to a constant C 1s integrated intensity, we calculate that the oxygen content increases by about 50% due to the acid treatment.

XPS does not provide definitive chemical state information about oxygen incorporated onto the DLC surface. Regardless, the observed work function decrease suggests that surface dipoles have been formed by oxygen incorporation. The increased polar nature of the DLC surface is consistent with the marked decrease of water contact angle after the acid treatment, as shown in Fig. 1c.

3.3 XPS Analysis of ArmeenT Adsorption

To compare the amount of ArmeenT adsorbed on the DLC coating surface before and after acid treatment using the same dip-coating procedure, we performed XPS measurements of the N 1s and C 1s core levels from these surfaces immediately after the procedure. The acid treatment was conducted at 90 °C for 15 min, and the dip-coating time was set at 15 min for all samples. Each N 1s spectrum has been normalized by the C 1s integrated intensity from the corresponding sample to eliminate run-to-run variation in XPS intensities. Due to atmospheric adsorption, nitrogen was present on the DLC surface even before ArmeenT dip-coating. This background nitrogen signal was subtracted from each N 1s spectrum to facilitate comparison. Based on the relative sensitivity factors, one can convert these integrated signal counts into atomic percentages within the XPS probing depth. Figure 4a compares the N atomic percentages obtained ArmeenT adsorbed on untreated DLC sample (2.7%) and three independently treated DLC samples (average = 3.9%). The electron kinetic energy corresponding to the N 1s peak is about 1100 eV, and the sampling depth at this energy is about 2 nm, or 10 atomic layers. Assuming that ArmeenT molecules are present on the surface only, this means that the surface coverage of ArmeenT after acid treatment of DLC is about 39%, compared with 27% before acid treatment. Therefore, the ArmeenT uptake by DLC increases by almost 50% due to the acid treatment. Note the decrease of the N atomic percentage after rinsing with toluene, by 20–25% for the three surfaces for which we have data, likely due to wash-off of multilayers. The

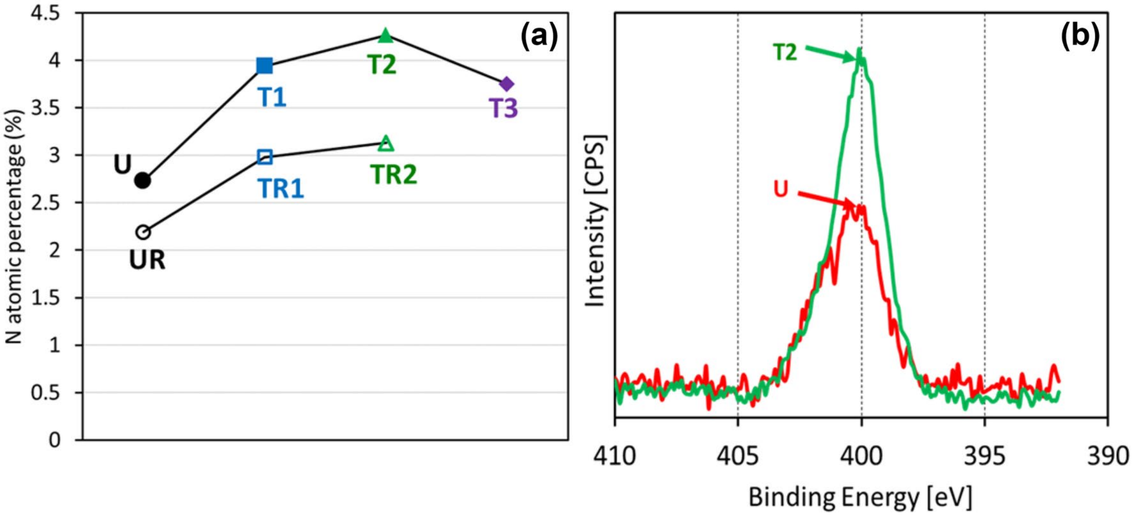

Fig. 4 **a** Comparison of nitrogen atomic percentage due to ArmeenT dip-coating on DLC coatings with and without acid treatment, before and after rinsing with toluene. U = DLC sample without acid treatment; T1, T2, T3 = DLC samples with acid treatment (90 °C for 15 min); UR, TR1, TR2 = corresponding DLC samples after rinsing with toluene; **b** N 1s spectrum after ArmeenT dip-coating on U and T2

enhanced amine adsorption on DLC after acid treatment by almost 50% remains valid. Figure 4b shows that the N 1s peak occurs at ~400 eV for ArmeenT dip-coating on the untreated and treated DLC surfaces, the major difference between the two being the enhanced intensity for the treated case. The N 1s peak position also signifies that the N atom of the adsorbed friction modifier molecule is close to neutral on the untreated and treated DLC surfaces.

3.4 Micro-scale Friction Measurements

To explore how increased ArmeenT adsorption may affect friction, we performed micro-scale friction experiments on these DLC samples under varying normal loads. Figure 5a compares the micro-scale coefficient of friction of a spherical steel tip sliding on untreated DLC with that on DLC after acid treatment (90 °C for 15 min) as a function of dip-coating time in ArmeenT at different loads. The friction results from untreated DLC without ArmeenT dip-coating are included as a reference. Results presented in Fig. 5a were averaged from the friction-time curves over five repeating tests, with values reproducible within ± 5%. Figure 5b shows friction-sliding distance curves at 60 mN load for untreated and treated DLC after dip-coating in ArmeenT for 60 min, along with data for untreated DLC for comparison. These results show that treated DLC

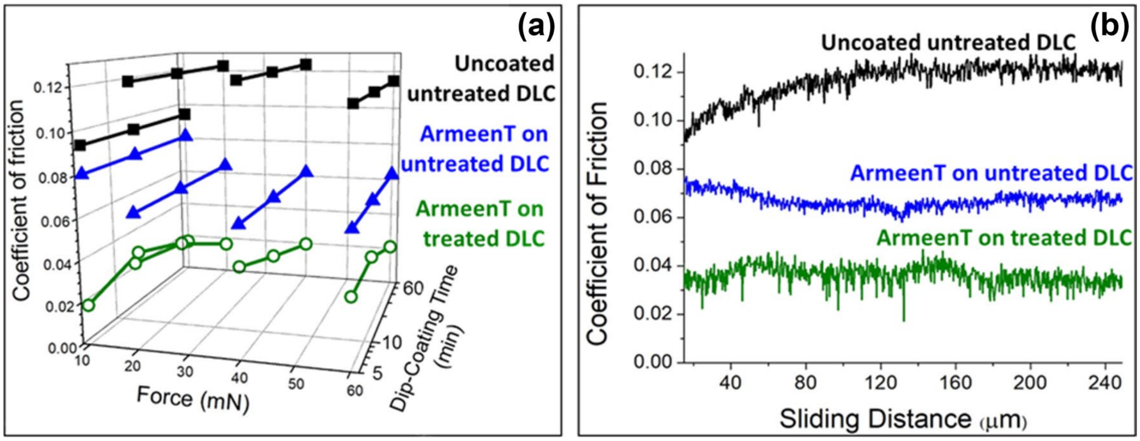

Fig. 5 Friction coefficient comparison for DLC surfaces **a** tested at normal loads of 10–60 mN and dip-coating duration of 5–60 min at 120 °C; **b** friction-distance plots at 60 mN normal load (DLC acid treatment at 90 °C for 15 min; ArmeenT dip-coating time = 60 min)

surface after ArmeenT dip-coating gives 50% lower coefficient of friction compared with the untreated DLC surface under the same dip-coating and micro-scale friction measurement conditions. Together with the XPS results, one may conclude that this is the result of increased ArmeenT adsorption on the treated DLC surface.

4 Conclusions

A modified acid treatment has been explored to make DLC surfaces more compatible with organic friction modifiers. The surface modification process was analyzed, and friction performance was evaluated. Following conclusions can be drawn:

1. The acid treatment makes the DLC surface more hydrophilic. Optical microscopy and surface roughness measurements demonstrate no significant changes in surface topography, thus confirming that the change in the hydrophilicity of DLC arises not from topographic changes, but from the modification of the chemical nature of the surface.
2. Comparison of XPS spectra of DLC taken before and after acid treatment shows a rigid shift of 0.6 eV for O 1s and C 1s core levels to larger binding energies due to the surface acid treatment of the DLC, suggesting work function decrease of the same magnitude. This signifies an increased concentration of surface dipoles, making the surface more polar, which is consistent with the observed improvement in hydrophilicity. Deconvolution of C 1s XPS reveals that the content of oxidized carbon (C–O and C=O) is nearly doubled because of the acid treatment.
3. XPS analysis shows that acid treatment of DLC improves its adsorption uptake of ArmeenT, an organic friction modifier, by about 50%. This improved uptake is also reflected in lower friction coefficient obtained from such treated DLC surfaces compared with untreated ones.

Acknowledgements The authors gratefully acknowledge US Department of Energy for the research support under Contract DE-EE0006449 and US National Science Foundation for research support under Grant CMMI-1662606. We sincerely thank AkzoNobel for the generous supply of friction modifier used in this research. This work also made use of the EPIC facility of Northwestern University's NUANCE Center, which has received support from the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF ECCS-1542205), the MRSEC program (NSF DMR-1720139) at the Materials Research Center, the International Institute for Nanotechnology (IIN), the Keck Foundation, and the State of Illinois (through the IIN).

References

1. Johnston, S.V., Hainsworth, S.V.: Effect of DLC coatings on wear in automotive applications. Surf. Eng. **21**(1), 67–71 (2013)
2. Dearnaley, G., Arps, J.H.: Biomedical applications of diamond-like carbon (DLC) coatings: a review. Surf. Coat. Technol. **200**(7), 2518–2524 (2005)
3. Casiraghi, C., Robertson, J., Ferrari, A.C.: Diamond-like carbon for data and beer storage. Mater. Today **10**(1–2), 44–53 (2007)
4. Luo, J.K., Fu, Y.Q., Le, H.R., Williams, J.A., Spearing, S.M., Milne, W.I.: Diamond and diamond-like carbon MEMS. J. Micromech. Microeng. **17**(7), S147–S163 (2007)
5. Erdemir, A., Donnet, C.: Tribology of diamond-like carbon films: recent progress and future prospects. J. Phys. D Appl. Phys. **39**(18), R311–R327 (2006)
6. Rincón, C., Zambrano, G., Carvajal, A., Prieto, P., Galindo, H., Martínez, E., Lousa, A., Esteve, J.: Tungsten carbide/diamond-like carbon multilayer coatings on steel for tribological applications. Surf. Coat. Technol. **148**(2), 277–283 (2001)
7. Freyman, C.A., Chen, Y., Chung, Y.-W.: Synthesis of carbon films with ultra-low friction in dry and humid air. Surf. Coat. Technol. **201**(1–2), 164–167 (2006)
8. Cutiongco, E.C., Li, D., Chung, Y.-W., Bhatia, C.S.: Tribological behavior of amorphous carbon nitride overcoats for magnetic thin-film rigid disks. J. Tribol. **118**(3), 543–548 (1996)
9. Heimberg, J.A., Wahl, K.J., Singer, I.L., Erdemir, A.: Superlow friction behavior of diamond-like carbon coatings: time and speed effects. Appl. Phys. Lett. **78**(17), 2449–2451 (2001)
10. Grill, A.: Review of tribology of diamond-like carbon. Wear **168**, 143–153 (1993)
11. Donnet, C., Grill, A.: Friction control of diamond-like carbon coatings. Surf. Coat. Technol. **94–95**, 456–462 (1997)
12. Donnet, C.: Recent progress on the tribology of doped diamond-like and carbon allow coatings: a review. Surf. Coat. Technol. **180–186**, 100–101 (1998)
13. Donnet, C., Erdemir, A.: Tribology of Diamond-Like Carbon Films: Fundamentals and Applications. Springer Science & Business Media, New York (2007)
14. Konicek, A.R., Grierson, D.S., Sumant, A.V., Friedmann, T.A., Sullivan, J.P., Gilbert, P.U.P.A., Sawyer, W.G., Carpick, R.W.: Influence of surface passivation on the friction and wear behavior of ultrananocrystalline diamond and tetrahedral amorphous carbon thin films. Phys. Rev. B **85**(15), 155448 (2012)
15. Enke, K., Dimigen, H., Hübsch, H.: Frictional properties of diamondlike carbon layers. Appl. Phys. Lett. **36**(4), 291–292 (1980)
16. Kalin, M., Velkavrh, I., Vižintin, J., Ožbolt, L.: Review of boundary lubrication mechanisms of DLC coatings used in mechanical applications. Meccanica **43**(6), 623–637 (2008)
17. Kano, M., Yasuda, Y., Ye, J.P.: The effect of ZDDP and MoDTC additives in engine oil on the friction properties of DLC-coated and steel cam followers. Lubr. Sci **17**, 95–103 (2004)
18. de Barros' Bouchet, M.I., Martin, J.M., Le-Mogne, T., Vacher, B.: Boundary lubrication mechanisms of carbon coatings by MoDTC and ZDDP additives. Tribol. Int. **38**(3), 257–264 (2005)
19. Kano, M., Yasuda, Y., Okamoto, Y., Mabuchi, Y., Hamada, T., Ueno, T., Ye, J., Konishi, S., Takeshima, S., Martin, J.M., De Barros Bouchet, M.I., Mognee, T.L.: Ultralow friction of DLC in presence of glycerol mono-oleate (GNO). Tribol. Lett. **18**(2), 245–251 (2005)
20. Hummers, W.S. Jr., Offeman, R.E.: Preparation of graphitic oxide. J. Am. Chem. Soc. **80**(6), 1339–1339 (1958)
21. Wepasnick, K.A., Smith, B.A., Schrote, K.E., Wilson, H.K., Diegelmann, S.R., Fairbrother, D.H.: Surface and structural

characterization of multi-walled carbon nanotubes following different oxidative treatments. Carbon **49**(1), 24–36 (2011)
22. Erdemir, A.: The role of hydrogen in tribological properties of diamond-like carbon films Surf. Coat. Technol. **146–147**, 292–297 (2001)
23. Marcano, D.C., Kosynkin, D.V., Berlin, J.M., Sinitskii, A., Sun, Z., Slesarev, A., Alemany, L.B., Lu, W., Tour, J.M.: Improved synthesis of graphene oxide. ACS Nano **4**(8), 4806–4814 (2010)