Adsorption of alcohols and fatty acids onto hydrogenated (a-C:H) DLC coatings

*R. Simič [1], M. Kalin [1] *, J. Kovač [2], G. Jakša [2]*

[1] University of Ljubljana, Faculty of Mechanical Engineering, Laboratory for Tribology and Interface Nanotechnology, Bogišićeva 8, 1000 Ljubljana, Slovenia

[2] Jožef Stefan Institute, Jamova 19, 1000 Ljubljana, Slovenia

* Corresponding author. Tel.: +386 1 4771 462. E-mail address:

mitjan.kalin@tint.fs.uni-lj.si

Abstract

Information about the interactions between lubricants and DLC coatings is scarce, despite there having been many studies over the years. In this investigation we used ToF-SIMS, XPS and contact-angle analyses to examine the adsorption ability and mechanisms with respect to two oiliness additives, i.e., hexadecanol and hexadecanoic acid, on an a-C:H coating. In addition, we analyzed the resistance of the adsorbed films to external influences like solvent cleaning. The results show that both molecules adsorb onto surface oxides and hydroxides present on the initial DLC surface and shield these structures with their hydrocarbon tails. This makes the surfaces less polar, which is manifested in a smaller polar component of the surface energy. We also showed that ultrasonic cleaning in heptane has no significant effect on the quantity of adsorbed molecules or on their chemical state. This not only shows the relatively strong adsorption of these molecules, but provides useful information for future experimental work. Of the two examined molecules, the acid showed a greater adsorption ability than the alcohol, which explains some of the previously reported better tribological properties in the case of the acid with respect to the alcohol.

1 Introduction

Diamond-like carbon (DLC) coatings are undoubtedly one of the fastest developing coatings for ensuring low friction and protecting the sliding surfaces of various mechanical components [1,2]. Because of their superior sliding properties, DLC coatings are now being widely used in many applications (e.g., IC engines, slider bearings, hard discs, etc.), most of which are lubricated in one way or another. Despite the good sliding properties of certain DLC coatings, even in the absence of any lubricant [3,4], the use of a lubricant seems inevitable, due to the better heat dissipation, extended service life and also due to the protection of parts that are not, or cannot be, coated.

In spite of more than 10 years of studies, information about the interactions between lubricants and DLC coatings is still very scarce; this of course hinders the effective implementation of such coatings. For DLC coatings, it is believed that the major problem related to lubrication is their high inertness, which limits the adsorption of the lubricants onto the surface [5]. This adsorption is one of the fundamental and well-understood mechanisms that affect the sliding characteristics of conventional steel and other metal surfaces.

Despite the believed non-reactivity of DLC, several studies have confirmed the existence of interactions between the lubricants and/or additives and the DLC. For example, there is empirical evidence of an improvement in the wear performance as the amount of unsaturation and the polarity of the base oil increases [6]. This was attributed to the polar-based adsorption onto the DLC, but the details for these interactions remain to be better understood. There have also been numerous studies of the tribolayer formation on DLC coatings from current

commercial additives like ZDDP and MoDTC, which were developed to work with metal systems. However, the results on their effectiveness in DLC contacts seem to exhibit significant scatter [7-10]. Therefore, it seems that commercial lubricants that are optimized to work best with metal contacts cannot always provide the optimum lubrication for DLC as well. Besides, to satisfy the ever more strict environmental standards, some of the compounds that are currently in use will have to be replaced with more environmentally friendly, organic compounds.

There are several studies confirming the beneficial effects of purely organic glycerol or glycerol-monooleate (GMO) in ta-C contacts [11,12]. In these studies the authors suggested tribo-induced surface hydroxylation, which helps with the intercalation of other alcohol molecules in the contact region and leads to a lowering of the friction. However, after exposing the surfaces to glycerol the increase of surface C-O bonds on DLC surface was detected even in the absence of a tribocontact [13]. To our best knowledge, however, in the available literature there are no results of DLC coatings being studied in combination with fatty acids, apart from our previous studies, where we used alcohols and fatty acids to prove and explain their beneficial effects in sliding contacts [14, 15]. We showed in these works, for example, that fatty acids better adsorb onto a-C:H than alcohols, so leading to a larger surface coverage, which is most probably the main cause for the lower wear of the coatings when the fatty acids are used as additives instead of the alcohols. The better adsorption properties of the acid compared to the alcohol were also confirmed using neutron reflectometry, where the thickness and the density of the adsorbed layers were determined [16,17]. Furthermore, the binding of the carboxylic acids to DLC was found to be more stable

than the binding of the alcohols to DLC surface as showed by *ab-initio* calculations using DFT [18].

However, despite intense research on the lubrication of DLC, the general interaction mechanisms are still not defined. This means that the process of efficient implementation is being hindered. An understanding of these interactions is required to enable systematic improvements in DLC lubrication and the consequent effective introduction of DLC coatings into real systems.

The main aim of this work was to study the adsorption mechanisms of alcohols and fatty acids on a-C:H coatings. Since most of the ex-situ chemical characterization techniques, like SIMS, XPS, Raman etc., require removal of the excess lubricant, we also investigated how solvent cleaning (rinsing and sonication) might affect the quantity of adsorbed molecules, their chemical state and their surface properties. In order to achieve the objectives of this research, we used a variety of cleaning procedures for the samples. We performed a ToF-SIMS analyses to prove the existence of the adsorbed molecules and to examine the effect of the cleaning. The XPS analyses served for the chemical bonding characterization, while the contact-angle measurements enabled analyses of the wetting properties and their correlation with the presence of adsorption layers.

2 Experimental

2.1 Materials

The substrates for the coating deposition were ultra-flat silicon blocks, $50 \times 50 \times 10$ mm^3 in size, with one side polished to a surface roughness of $R_q = 0.3$ nm (Yamanaka Semiconductor

Co., Japan). A 53-nm-thick, non-doped, a-C:H coating (32 at.% H, 35–40 % sp^3 bonded C) was deposited onto the polished side of the silicon blocks using a 13.56-MHz radio-frequency plasma-assisted CVD (RF PACVD) process. Being a typical and widely used DLC coating with superior tribological properties over a broad range of conditions, this coating was selected in this study to enhance our knowledge about the lubrication mechanisms of this coating and to complement the results obtained in our previous studies.

High-purity, deuterated hexadecanol and deuterated hexadecanoic acid (98 atom % D, Sigma-Aldrich Co., LLC.) were used as the surface-active agents to study the reaction of the DLC coating with the hydroxyl and carboxyl end-groups that are commonly present in various oils and additives. Deuterium labeling enabled an additional confirmation of the adsorption during the ToF-SIMS analyses. Both types of molecules were dissolved into PAO6 oil (Neste Oil, Espoo, Finland) in a concentration of 20 mmol/l, which corresponds to mass concentrations of 0.66 wt.% and 0.69 wt. % for the hexadecanol and hexadecanoic acid, respectively. This particular concentration was selected to match the concentration that gave the best results when used in tribological systems in our previous studies [1,2].

The samples were not exposed to any solvent prior to the experiment so as to avoid any contamination and passivation of the surfaces with the cleaning solvents. Any dust particles that may have been present on the surface were removed by a stream of dry air. Test samples were exposed to the prepared solutions for one week. The samples were then rinsed with heptane to remove the base oil and the non-bonded polar molecules. To ensure that the majority of non-bonded molecules were removed, some of the samples were additionally sonicated in heptane. Since the effect of sonication in this case is not known, the duration of

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the ultrasonic cleaning was varied from 0 to 180 s in order to investigate how the sonication affects the amount of adsorbed molecules. The sample surfaces A, B and C were thus exposed to the polar molecule solutions, rinsed with heptane and then sonicated for 180 s, 60 s and 30 s, respectively (Fig. 1). Sample surface D was not sonicated and remained only rinsed. One additional sample, denoted by E, was not exposed to either the hexadecanol or the hexadecanoic acid, but to pure PAO oil only, and then rinsed with heptane. The sample surface denoted by F was not exposed to polar molecules or PAO oil and was only rinsed with heptane. Therefore, the samples E and F served as references. Table 1 contains a list of all the samples, their denotations and the applied cleaning procedures.

2.2 ToF-SIMS

The samples that were prepared and cleaned as described above were first analyzed using ToF-SIMS (TOF.SIMS 5, ION-TOF, Germany). The analyses were performed in an ultra-high vacuum of approximately 10^{-7} Pa. A liquid metal ion gun (LMIG) was used to create a beam of bismuth clusters Bi_3^+ (primary ions) with an energy of 30 keV, which was then used for surface sputtering over an area of 100×100 μm^2. The beam current was 0.6 pA and the total measuring time to acquire the SIMS spectra was 120 s. The dose of the primary ions during the measurements was 4×10^{12} ions/cm^2 (static regime). High-resolution mass spectra of the positive and negative secondary ions were recorded from two places on each of the sample surfaces (A-F). The SIMS spectra were processed with the software SurfaceLab 6.3 (ION TOF). The positive ion mass spectra were calibrated using CH_3^+ (15.02 amu), $C_2H_3^+$ (27.02 amu) and $C_2H_5^+$ (29.02 amu), and the negative ion mass spectra were calibrated using C^- (12.00 amu), C_2^- (24.00 amu) and C_2H^- (25.01 amu) with a mass resolution of 5000 or more. The results are presented as regions in the mass spectra around the characteristic peaks

of the deuterated hexadecanol or hexadecanoic acid molecules and around the characteristic peaks of the deuterium and hydrogen molecule. For the comparison of the quantity of molecule ions detected on the various sample surfaces we divided the intensity of each peak by the total intensity of all peaks of secondary ions in acquired spectra. The normalized intensities of the selected peaks are presented. The analysis depth of the SIMS method is about 1 nm.

2.3 XPS

After the ToF-SIMS analysis, the samples were transferred directly to the XPS spectrometer (PHI-TFA XPS, Physical Electronics Inc., Minnesota, USA). The analyses took place in an ultra-high vacuum, which was approximately 10^{-7} Pa during the analysis. A monochromatic X-ray beam from an Al-Kα source (1486.6 eV) was used to illuminate an area with a diameter of 400 μm. The excited photoelectrons were detected using a resolution of 0.6 eV with the pass energy of the analyzer being 29 eV at an emission angle of 45°. The accuracy of the binding energy was ± 0.3 eV. During the analysis, both survey and high-resolution spectra were recorded. In the survey spectrum, the elements that were present were identified and their concentrations were calculated by dividing the peak intensities by the relative sensitivity factors provided by the XPS spectrometer manufacturer [19]. Each sample was analyzed at two different points and the average composition was calculated. In addition to the wide-energy range spectra, the high-energy resolution spectra of the characteristic peaks (C 1s and O 1s) were recorded. Full width at half maximum (FWHM) of measured C 1s and O 1s spectra was (1.3 ±0.1) eV and (1.8 ±0.1) eV, respectively. From the shape and the shift of the energy of the XPS spectra, the chemical bonding of the surface elements was inferred. The XPS spectra were processed with the software MultiPak ver. 9.4. All the components

were referenced according to the C–C/C–H component in the C 1s core level at a binding energy of 284.8 eV. The results are presented as carbon (C 1s) spectra, while the oxygen-to-carbon (O/C) ratios are presented in separate graphs. The XPS method is not sensitive to hydrogen, and the analysis depth of this method is about 3–5 nm.

2.4 Contact Angle

The contact-angle measurements were performed on the same surfaces that were used for the ToF-SIMS and XPS analyses in order to determine the surface-energy density and its polar and dispersion components. The latter two indicate the existence of polar or non-polar structures on the surface, which define the ability of the surface to interact with the surrounding molecules. At the same time, it enables a differentiation of the surfaces containing various amounts and/or types of adsorbed molecules. Two model liquids with well-defined properties were used to measure the contact angles. Demineralized water was used as the polar liquid and diiodomethane was used as the nonpolar liquid. The total surface tensions with their polar and dispersion components for both liquids are presented in Table 2.

The contact-angle measurements were performed using a contact-angle optical goniometer (CAM 101, KSV Instruments, Helsinki, Finland). Each measurement was performed four times so as to enable a statistical evaluation of the results. Some examples of water and diiodomethane droplets on a DLC surface are shown in Fig. 2. The average volumes of the water and diiodomethane droplets ware 5.8 μl ± 0.4 μl and 2.1 μl ± 0.6 μl, respectively. Such

a volume is assumed to be small enough to neglect the effect of the droplet's own weight on the contact angle [20].

The most commonly used theoretical methods for the calculation of the surface-energy density from the contact-angle measurements are the Owens-Wendt-Rabel-Kaelble (OWRK) method [21], the van Oss method [22] and the Wu method [23]. Each of these methods is assumed to work best with certain types of surfaces (surfaces with a low surface energy, polar or non-polar surfaces, etc.) [20,24]; however, in the case of DLC surfaces all of these methods give qualitatively similar results that differ only in absolute values [25,26]. In this work the OWRK method was used as it gives the average values of the surface-energy density from among the mentioned methods and it is also the most commonly used method. The polar and dispersive components of the surface-energy density were therefore calculated using the following equation [21]:

$$\gamma_L(1+\cos\vartheta) = \left(\sqrt{\gamma_S^D \gamma_L^D} + \sqrt{\gamma_S^P \gamma_L^P}\right), \quad (4.2)$$

where γ_L is the total surface tension of the model liquid, γ_L^D and γ_L^P are the dispersive and polar components of the surface tension of the liquid, and γ_S^D and γ_S^P are the dispersive and polar components of the surface-energy density. Two model liquids had to be used to calculate both γ_S^D and γ_S^P. By definition, the sum of both components is the total surface energy density: $\gamma_S = \gamma_S^D + \gamma_S^P$.

3 Results

3.1 ToF-SIMS

3.1.1 Negative Ions - Alcohol

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The mass spectra of negative ions of the characteristic peaks related to deuterated hexadecanol for the exposed (D) and the reference (E) DLC surfaces are presented in Fig. 3. The spectrum of the reference surface E, which was immersed into the PAO oil and then rinsed with heptane, showed no peaks at the characteristic masses of deuterated hexadecanol. On the other hand, characteristic peaks appeared in the spectra of all the surfaces exposed to the hexadecanol solutions. These peaks correspond to the molecular weight of deuterated hexadecanol, reduced by the masses of hydrogen, deuterium, carbon or their combination. It is clear from the spectrum of the exposed surface (D) that the peak corresponding to the complete molecule (275.27 amu) was almost absent; however, the peaks at lower masses belonging to the hexadecanol fragments were more pronounced. The most pronounced peak appeared at 270.24 amu, which corresponds to the hexadecanol fragment $C_{16}D_{31}O^-$ (hexadecanol missing one hydrogen and two deuteriums, M-H-2D). This agrees with the assumption of the alkoxide anions being prone to splitting-off two hydrogen atoms from the carbon next to the oxygen [27]. The recombination of such radical anions on the surface was assumed to cause the formation of double and triple bonds in the alkyl chain [28] or even cross-linking of the alkyl chains, i.e., polymerization of the adsorbed layer [29]. The peaks at 273.26 amu, 271.24 amu, 269.23 amu, etc. belong to the molecules containing H in the hydroxyl group. These molecules were most probably adsorbed via strong H-bonds onto the surface oxides/hydroxides. However, the detected molecules without H from the hydroxyl group cannot be classified as physi- or chemisorbed since the missing hydrogen may become detached during surface ionization by the Bi ions. Nevertheless, these peaks indicate the presence of hexadecanol molecules on the DLC surface, despite the rinsing with heptane.

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To reveal the effect of cleaning on the amount of adsorbed molecules the normalized intensities of the selected characteristic peaks of all the exposed and reference surfaces (A–F) were presented on a separate graph, Fig. 4. There are clear characteristic peaks on all of the exposed surfaces (A–D); however, these peaks are absent on both reference samples, i.e., E and F. Each peak had a relatively similar intensity, irrespective of the cleaning procedure. This indicates a relatively strong adsorption of the hexadecanol on the DLC, which was not affected by additional sonication. In other words, the intensities were the same as with rinsing only.

3.1.2 Negative Ions - Acid

The mass spectra of negative ions around the characteristic peaks of deuterated hexadecanoic acid for the exposed (D) and the reference DLC surfaces (E) are presented in Fig. 5. As expected, the reference sample showed no signs of hexadecanoic acid or its fragments on the surface, while the exposed and rinsed sample revealed the characteristic peaks of the acid and its fragments. The most pronounced peak appeared at 286.43 amu, which corresponds to the hexadecanoic acid fragment $C_{16}D_{31}O_2^-$ (hexadecanoic acid without a hydrogen atom). This peak could belong to the chemisorbed acid or to the acid adsorbed via hydrogen bond that lost its carboxylic hydrogen while being bombarded with bismuth clusters during the ToF-SIMS analysis. The peak at 285.42 amu also appeared to be relatively intense, revealing the relatively large amount of hexadecanoic acid molecules missing only one deuterium from the alkyl chain. These molecules could also be adsorbed via hydrogen bond. Another relatively intense peak appeared at 284.41 amu, belonging to a fragment without the carboxylic hydrogen and one deuterium atom of the alkyl chain. These molecules could also be chemisorbed onto the DLC surface. The peaks belonging to the smaller fragments were less pronounced.

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The intensities of the selected peaks of the characteristic negative ions for variously cleaned surfaces are presented in Fig. 5. As expected, the characteristic peaks were completely absent on both reference surfaces. The normalized intensities of the selected peaks on the exposed surfaces appeared to be almost the same for the various cleaning procedures. This again shows that additional ultrasonic cleaning has no particular effect on the amount of adsorbed molecules, if we compare it with rinsing alone. A comparison of the selected characteristic peaks in the cases of the alcohol and the acid (Figs. 4 and 6) shows substantially larger intensities of molecular fragments in the case of the acid. This indicates that the acid is adsorbed onto the surface of the a-C:H to a substantially greater extent in comparison to the equivalent alcohol.

3.1.3 Positive Ions - Alcohol

A part of the mass spectrum of positive ions around the masses of deuterium and molecular hydrogen in the case of the DLC exposed to d-hexadecanol and the reference samples is presented in Fig. 7a. Molecular hydrogen H_2^+ was detected on all the surfaces. However, in contrast to both reference surfaces, the exposed surfaces also showed a deuterium peak, Fig 7a. Its absence on the reference samples was expected due to the negligible amount of naturally occurring deuterium (0.016 at. % compared to H) [30-32]. The presence of deuterium on the exposed sample therefore confirms the existence of adsorbed, deuterated, hexadecanol molecules on the a-C:H surface. The normalized intensities of the deuterium and the hydrogen peaks are presented in Fig. 7b. The similar intensity of the H_2^+ peak on all the tested surfaces (exposed and reference) indicates that most of the detected hydrogen

originates from the coating itself. The deuterium was indeed absent on both reference samples, but it was present in similar amounts on all the exposed surfaces. In addition to deuterium we also detected the presence of fragments related to molecule alkyl tail: $C_2D_5^+$ (34.07 amu), $C_3D_5^+$ (46.07 amu), $C_3D_7^+$ (50.10 amu). This further confirms successful adsorption of alcohol molecules on DLC.

3.1.4 Positive Ions - Acid

Fig. 8a shows parts of the mass spectra of the positive ions around the deuterium peak for the surfaces exposed to the acid and for the reference surfaces. Again, deuterium only appeared on the surfaces exposed to the deuterated acid, while there was no deuterium on the reference samples. The result shows that the deuterium originates from the adsorbed, deuterated acid molecules. The normalized intensities of the D^+ and H_2^+ peaks for the case of the acid are shown in Fig. 8b. It is clear that the amount of deuterium detected was independent of the cleaning procedure used. The ratio of D^+ to H_2^+ was close for all the exposed surfaces ($D^+/H_2^+ \approx 0.2$). This indicates the relatively similar amounts of deuterated molecules on all the surfaces, confirming once again that sonication does not affect the quantity of acid molecules adsorbed onto the a-C:H coating. Similar as for the alcohol we detected also fragments related to molecule alkyl tail: $C_2D_5^+$ (34.07 amu), $C_3D_5^+$ (46.07 amu), $C_3D_7^+$ (50.10 amu). This further confirms successful adsorption of acid molecules on DLC.

3.2 XPS

The main information about the chemical bonds on the surface was available from the carbon C 1s spectra. Figure 9 shows C 1s spectra from reference samples and samples after exposure to hexadecanol (Fig. 9a) and hexadecanol acid (Fig. 9b) and cleaned after that for different

periods. These spectra are normalized so that the intensity at the binding energy of 284.8 eV, which corresponds to the C-C and C-H bonds, equals unity. A binding energy of around 286.4 eV corresponds to C-O/C-OH bonds; 287.3 eV, to a C=O bond; and 289.3 eV, to an O-C=O bond. From Figure 9 it is possible to see that the main variations in C 1s spectra are around the position of the C-O/C-OH peak at 286.4 eV. Therefore, we deconvoluted some representative C 1s spectra to show more precisely the evolution of this type of bond. Fig. 10a and 10b show deconvoluted C 1s spectra of the non-treated DLC and DLC immersed in PAO oil, respectively. On both reference samples, the main peak at 284.8 eV, which is about 92 % of total C 1s area, is attributed to C-C/C-H bonds from the DLC structure. The carbon-oxygen C-O/C-OH bonds were identified on both reference samples as peaks at 286.4 eV with a relative intensity of about 6 % of total C 1s area. This shows that the reference DLC surfaces consisted mostly of carbon and hydrogen with some amount of surface (hydro-)oxides. The origin of this surface (hydro-)oxide layer may be atmospheric surface oxidation and hydroxylation of DLC or due to the preparation process of the DLC coating. Such layer was often observed and reported in the literature [33,34]

Figure 11 shows the oxygen O 1s spectrum from the reference DLC sample deconvoluted into three components. The peaks at 531.5 eV and 532.5 eV are assigned to surface (hydro-)oxide layer (C-OH bonds), and the small peak at 533.6 eV may be due to H_2O or CO_2 adsorbed molecules [19]. Oxygen (O 1s) spectra on other surfaces did not show significant differences in spectrum shape except the intensity. Therefore, we used the O 1s intensities to calculate oxygen-to-carbon (O/C) ratios and presented them in a graph in Fig. 12.

3.2.1 Alcohol

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Fig. 10c shows C 1s spectrum from surfaces exposed to hexadecanol and then sonicated for 30s in heptane. The samples exposed to hexadecanol (Fig. 9a and 10c), however, showed larger C-O/C-OH peak at 286.4 eV (14 % of total C 1s area) in comparison to reference samples (6 %, Fig. 10a and 10b). We explain this increase of the relative concentration of C-O/C-OH bonds as a chemisorption of hexadecanol molecules to the surface (hydro-)oxide layer, which was present on the native DLC coating. All C 1s spectra after exposure to hexadecanol molecules (Fig. 9a) and cleaning for different periods present similar relative intensity of the C-O bonds of about 14 % showing that amount of hexadecanol molecules was not affected by the intensity of the cleaning procedure. In addition to previous mentioned ToF-SIMS results this confirms the chemisorption of hexadecanol molecules on DLC surface.

3.2.2 Acid

All the spectra of the surfaces exposed to the acid (Fig. 9b) showed increased C-O/C-OH peak at 286.4 eV besides the main carbon peak. Fig. 10d shows deconvoluted C 1s spectrum of the DLC surfaces in the case of the exposure to the hexadecanoic acid and sonication for 30 s. The relative concentration of C-O/C-OH bonds is about 10 % of total C 1s area, what is larger than that of the reference DLC samples and shows that some new C-O/C-OH bonds are present (Fig. 10d). Similar to the case of hexadecanol, we assign the increase of the C-O/C-OH bonds to the chemisorption of acid molecules to the native surface (hydro)-oxides, which serve as the binding sites for chemisorption of the alcohol and fatty-acid molecules. The fact that the observed C-O/C-OH peak was generally less intense in the case of the acid than in the case of the alcohol may be related to the larger surface coverage in the case of the acid molecules, i.e., the latter covered a larger amount of the surface oxides and hydroxides and

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thus attenuated more of the C-O signal compared to the alcohol. The shielding of the surface C-O bonds also had a substantial effect on the wetting properties of the exposed surfaces, as presented later in the text.

3.2.3 O/C Ratio

The oxygen O 1s spectra revealed no significant differences between the samples. However, the O/C ratio showed that there was relatively more oxygen detected on the samples exposed to the alcohol than to the acid: the O/C ratio was around 0.30 ± 0.04 in the case of the alcohol, 0.23 ± 0.03 in the case of the acid and 0.27 ± 0.03 for the reference samples, Fig. 12. These results support a better adsorption ability in the case of the acid, where greater adsorption onto surface oxygen atoms causes a greater attenuation of the signal from the surface oxide layer.

3.3 Contact Angle

The average measured contact angles with water and diiodomethane for all the tested surfaces are presented in Table 3. Despite some minor variances between the variously cleaned surfaces, the contact angles were in general larger on the DLC surfaces that were exposed to the acid compared to the ones exposed to the alcohol. In the case of wetting with polar liquids like water, a larger contact angle means poorer wetting and, therefore, a lower polar component of the surface energy. It means that the surface contains a small amount of polar structures on the surface. This was the case with the fatty acids adsorbed on the DLC, where a generally higher contact angle with water indicates less polar structures on the surface, as in the case of the adsorbed alcohol. On the other hand, larger contact angles with a nonpolar liquid like diiodomethane indicate a lower dispersive component of the surface energy.

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The measured contact angles were used to determine the components of the surface energy, which are presented in Fig. 13. The results showed that the surfaces with adsorbed fatty acid had lower dispersive and polar components. However, the relative difference between the surfaces exposed to the alcohol and the fatty acid is much larger in the case of the polar component, which was 7.2 mJ/mm^2 for the DLC with alcohol and 4.7 mJ/mm^2 for the DLC with the fatty acid. It is clear that the adsorption of the fatty acid makes the surface less polar than the adsorption of the alcohol. This agrees with the assumption that polar molecules adsorb onto polar oxide/hydroxide groups on the surface, where alkyl groups create a nonpolar shield that makes the surface less polar. Of course, the polar structures crucially determine the surface properties and have a substantial effect on the tribological behavior [35].

3.4 Discussion

In this study we used several techniques to confirm and compare the adsorption ability of two organic polar molecules onto an a-C:H coating and to analyze the resistance of the adsorbed film to external influences like solvent cleaning. Although ToF-SIMS cannot, in general, provide quantitative information regarding the exact quantity of molecules on the surface due to possible unequal probabilities for the ionization and detection of different molecules, it does enable a relative comparison of the hexadecanol and hexadecanoic acid molecules, because of their similar size and structure. Therefore, higher intensities in the mass spectra of the characteristic negative ions for the acid (Figs. 3-6) represent a greater quantity of adsorbed acid molecules compared to the alcohol. On the other hand, the larger quantity of deuterium that was detected in the case of the alcohol (Figs. 7 and 8) does not represent a

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larger quantity of adsorbed polar molecules, but it is assumed to originate from the high probability that the alcohol molecules will split-off hydrogen (or deuterium) atoms next to the hydroxyl group when exposed to ionizing particles, which was referred to in the literature previously [27]. This can be confirmed by the characteristic peaks in the spectra of negative ions, Figs 3 and 4, i.e., the highest peak in the case of the alcohol appeared at the masses of hexadecanol missing a hydrogen from the hydroxyl group as well as two deuterium atoms from the alkyl group. In contrast, for the acid, the highest peak appeared at the mass corresponding to the whole molecule missing one hydrogen atom only. All the results obtained with the ToF-SIMS, therefore, show that fatty acid adsorbs onto the a-C:H surface in larger amounts than the corresponding alcohol.

This result agrees with all our previous findings. We showed in our previous studies with tribotests that increasing the concentration of hexadecanol or hexadecanoic acid in PAO decreases the wear of the a-C:H coatings in boundary-lubricating conditions, Fig. 14 [36]. Although both molecules enabled a similar decrease in the wear at high concentrations, the fatty acid proved to be more efficient at lower concentrations, which was assumed to be the effect of a better adsorption ability. In addition, we showed using AFM that the surface coverage with polar molecules increases with the concentration and is consistently larger in the case of the acid compared to the alcohol [36]. To further confirm these findings we performed neutron reflectometry analyses to determine the thickness and the density of the adsorbed layers on the a-C:H directly in the PAO oil. Again, we proved the better adsorption ability for the case of the acid, which is schematically shown in Fig 15. In this case, the fatty acid enabled the formation of an approximately 1-nm-thick adsorbed layer with a 50% bulk density, whereas the layer formed by the alcohol appeared to be too thin to be clearly

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detected by the neutron reflectometry [16,17]. Nevertheless, all these experimental results are also supported by *ab-initio* calculations using DFT, where it was shown that the energetically most-favorable binding takes place via the molecule's oxygen atom, where the binding of the COOH group was found to be more stable than the binding of the OH group [18].

What is more, and was shown in this study, is that the relative intensities of the characteristic peaks and therefore the amount of adsorbed molecules on the surface are independent of the different cleaning procedures that were used in this work. This not only shows the relatively good adsorption ability of these molecules, but provides useful information for future experimental work regarding the cleaning and preparation of samples for chemical analyses.

The ToF-SIMS results, and all the previous results, indeed show a better adsorption ability of the acid compared to the alcohol. The XPS analyses showed that the oxide/hydroxide layer is present already on the native DLC coating. This layer can be due to atmospheric surface oxidation and hydroxylation or due to preparation process of the DLC coating. This layer is recognized through the C-O/C-OH bonds in the XPS spectrum C 1s and as oxide/hydroxide peaks in oxygen O 1s spectrum. Polar hexadecanol or hexadecanoic acid molecules dissolved in the PAO oil adsorb to this oxide/hydroxide through the formation of C-O-C bonds by the removal of H_2O molecule or through the hydrogen bonds. These bonds were also recognized in XPS spectrum C 1s as an increase of C-O/C-OH peak at 286.4 eV. XPS results show slightly higher concentration of the C-O/C-OH bonds (16 %) on the hexadecanol treated DLC than on the hexadecanoic acid treated DLC (10 %). The C-O bonds in C 1s spectra originate from two contributions: C-OH bonds in oxide layer and C-O bonds from the chemisorbed molecules. The lower C-O peak in the case of the acid compared to the alcohol could thus be

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caused by larger amount of adsorbed acid molecules, of which hydrocarbon tails screen more of the surface C-O bonds compared to the alcohol. This was verified by the wetting analysis in this study, where we showed that the adsorbed fatty acid enables a lower polar component of the surface energy than the alcohol. Namely, nonpolar hydrocarbon tails cover the polar adsorption sites (surface oxides/hydroxides), making the surface less polar and thus less prone to interactions with polar fluids. Moreover, it has been shown in previous reports that the polar component of the surface energy, which is determined by the polar surface structures, substantially affects the friction as well as other functional properties of the surfaces [35].

5 Conclusions

In this study the adsorption ability and the adsorption mechanisms of long-chain alcohol and fatty-acid molecules onto hydrogenated (a-C:H) DLC coatings were investigated to explain the previously reported positive effect of these molecules in the sliding contacts of the DLC coatings. By using ToF-SIMS, XPS and contact-angle analyses, as well as different surface cleaning procedures, the results allow us to draw the following conclusions:

1. Polar molecules of hexadecanol and hexadecanoic acid can adsorb relatively strongly onto the a-C:H coatings by bonding to the native surface oxides and hydroxides.

2. The nonpolar hydrocarbon tails of the adsorbed molecules cause shielding of the polar oxide and hydroxide structures on the surface. This makes the surface less polar, resulting in a smaller polar component of the surface energy, which was reported previously to have a significant effect on the tribological and functional properties of the surfaces.

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3. Of the two examined molecules, the acid showed a greater adsorption ability with respect to the a-C:H than the alcohol, which explains the previously reported better tribological properties when the acid is used as an additive in PAO oil compared to the alcohol.

4. Ultrasonic cleaning in heptane has no significant effect on the quantity of adsorbed molecules, their chemical state, or on their surface properties, like the surface energy. This not only proves the relatively strong adsorption of these molecules, but provides useful information for future experimental work regarding sample preparation and cleaning.

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