

Full Length Article

Online lubricant degradation monitoring using contact charging of polymers

Azimet A. Karluk^a, Sunay D. Ekim^{a,b}, Bilge Baytekin^{a,b}, H. Tarik Baytekin^{c,*}^a National Nanotechnology Research Center (UNAM), Bilkent University, Ankara 06800, Turkey^b Department of Chemistry, Bilkent University, 06800, Ankara, Turkey^c Department of Chemistry, Middle East Technical University, 06800, Ankara, Turkey

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ABSTRACT

Lubrication of machine parts is necessary to prevent friction and wear in machine operation. However, oxidation of lubricants upon operation changes their chemical and physical properties and causes lubrication performance to deteriorate. Besides, one liter of wasted/used lubricant oil can contaminate a million liters of water. Current methods for the timely detection of oil deterioration lack practicality. Here we show simple, a triboelectrification-based method for oil degradation monitoring, in which the oxidation can be monitored by the changes in the contact charging (and separation) signals of oil-dipped cellulose and a common polymer tapped to each other. The commercial and base oil samples are oxidized at 100–200 °C for up to 80 h, simultaneously monitored by ATR-FTIR and the triboelectric method. The results show that a 40–90% decrease in the triboelectric open-circuit potentials in the presence of oxidized oil can directly indicate the start of oil oxidation without other accompanying analyses.

1. Introduction

Lubricating oil is an indispensable element in any machine with moving parts. It not only helps to decrease friction (the major contributor of the energy losses in these systems) and therefore minimizes the carbon footprint of the engine but also helps to reduce wear and abrasion of the machine parts. The lubricant market is a major one - the global demand is currently about 45 million tons, and the global market size is projected to reach USD 182.6 billion by 2025.[1] All lubricants have a lifetime, after which the lubrication function significantly deteriorates, and the lubricant has to be changed. If this change is not made timely, it may cause severe wear of the machine parts and even malfunctioning of the machine. On the other hand, lubricant disposal is a severe environmental issue: Lubricants are produced from non-renewable fossil resources, and one drop of oil (lubricant) contaminates 100 L of clean water.[2] Therefore, it is vital to prevent the unnecessary and premature disposal of lubricants. To estimate the end-of-life for their product, the lubricant manufacturers usually provide a 'change time' for the lubricant, which provides only a vague estimate. This estimate is generally inaccurate, especially in varying engine temperatures and speeds, such as urban driving. The more accurate, more economical, and environment-friendly method would be monitoring the

oil condition as the oil is used. For this purpose, a few online (in-situ analysis) and offline (drawing samples for external analysis) methods have been developed using several chemical and physical properties of the lubricants that change upon operation. However, the demand for cost-effective, easy-to-produce, machine-implementable method persists for oil condition monitoring.

This study demonstrates a simple 'oil condition probe' using a common phenomenon also encountered in everyday life - contact charging (aka 'tribocharging' or 'triboelectricity'). Contact-charging is the charge development on surfaces when the two surfaces come into contact and then separate.[3] The triboelectric effect is probably one of the earliest scientific discoveries in human history,[4] and yet, with a complicated mechanism that is far from completely understood.[5,6] However, the effect itself has been used in many technologies such as photocopying,[7] electrostatic separations,[8] and lately in mechanical energy harvesters,[9] and in (bio)chemical sensors.[9] For the latter, there are reports on mercury, pH, glucose, dopamine, and phenol sensors [10–15], all targeted and chemically programmed (functionalized) towards the given analyte. Here we aim to use a similar approach, using the triboelectric effect for sensing oil condition; however, our approach involves monitoring the overall chemical condition of the environment (lubricant) - rather than targeting a given chemical group or molecule.

* Corresponding author.

E-mail address: tarikbay@metu.edu.tr (H. Tarik Baytekin).<https://doi.org/10.1016/j.apsusc.2022.152593>

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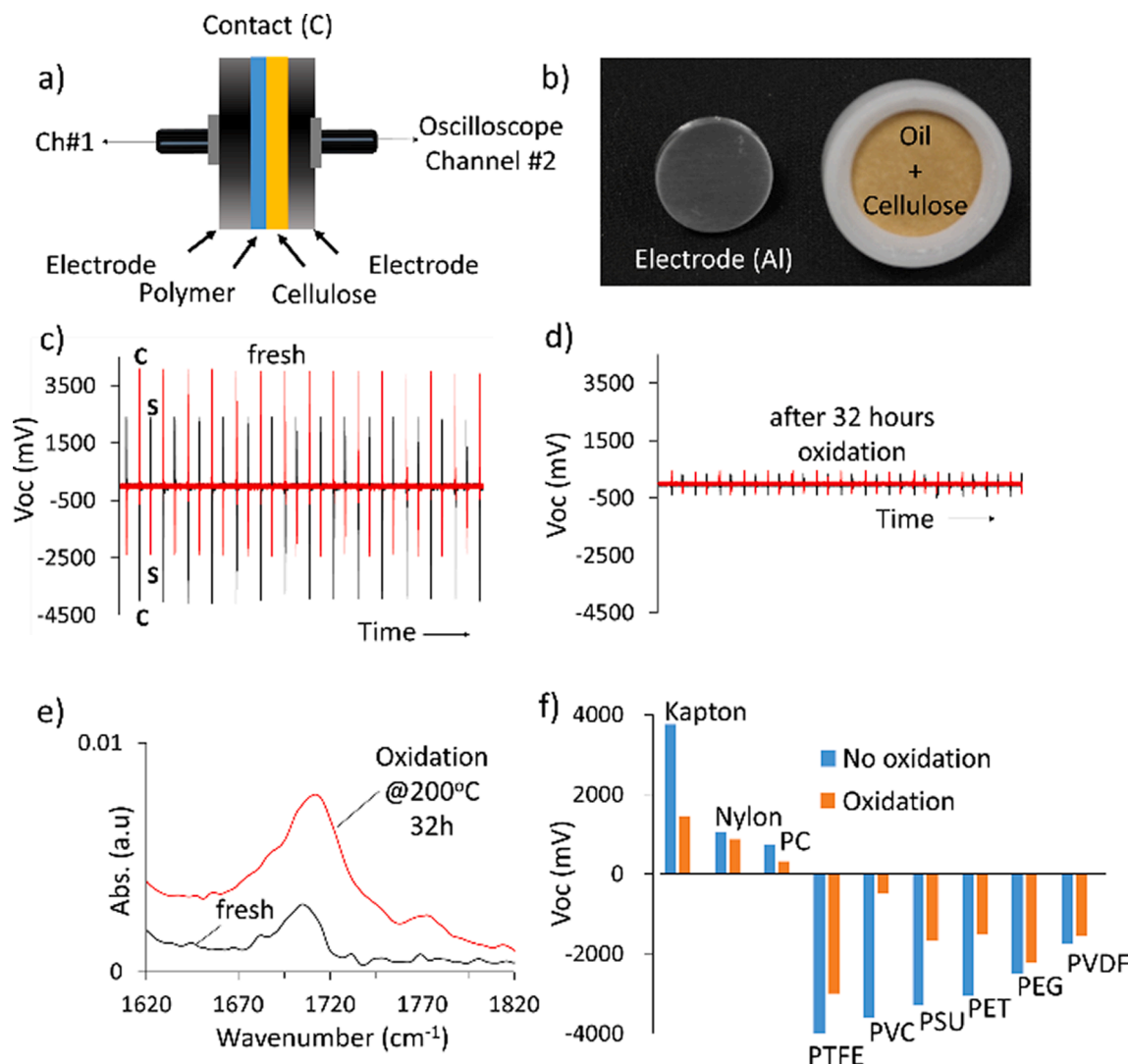


Fig. 1. a) Schematic representation of polymer-cellulose contact for triboelectric oil condition monitoring. b) Photos of the Aluminum counter electrode covered with a thick (0.2–0.5 mm) polymer film (left) and the oil-absorbed cellulose on the electrode (right). c) and d) Triboelectric charges reflected as the contact (C) and separation (S) open-circuit potential, Voc, signals collected for (c) fresh engine oil, and (d) oxidized (at 200 °C for 32 h) engine oil. e) The carbonyl region of ATR-FTIR spectra of the thermally oxidized and fresh engine oils prove the former's oxidation. f) Voc for fresh (blue bars) and thermally oxidized (orange bars) engine oil, generated by using different polymers on the Al electrode.

The proposed method, which we show to reflect on the chemical changes, provides information about the oil condition without detailed chemical analysis.

As we all notice in our cars, oil gets darker and thicker as it is used. Therefore, lubricant's color [16] and its viscosity [17–18] can be monitored to determine its end-of-life. In the background of these physical changes in oil lies the changes in its chemical structure. Liquid lubricants are hydrocarbons with long carbon chains. These chains break thermally due to machine heating and mechanochemically [19], because of the shear at the machine parts' surface where the lubricants operate. These thermal and mechanochemical bond-breakages lead to reactive ends, which capture oxygen in the environment, and therefore the oil is 'oxidized'. The oxygen-containing chemical groups (e.g., carboxyl –COOH, carbonyl –C=O, hydroxyl –OH) in oil structure that emerge from oxidation can be monitored, e.g., with infrared spectroscopy, to develop a sensor that follows and reports the end-of-life of the lubricant. The oxidized oil has a higher polarity than the native oil, and therefore, its electrical conductance and capacitance also change compared to the native oil. All these changes can be used to determine the end-of-life for oil and develop methods that prevent early or late oil change. However,

most of these methods cannot be used to develop online sensors since they involve either lengthy analysis of data [20–25] or complex hardware [26–29] that is hard to implement for online operation, which is the ultimate aim in oil condition monitoring. Additionally, the current electrical methods suffer the adverse effects of contamination and the thick film developing on the sensor elements. These methods require sensing under static oil conditions. Here we show, a method based on the triboelectric phenomenon that can be used in simple-to-read and machine-implementable monitoring of the oil condition. To display that the method is working, we first screened the trends in the electrical signal we retrieve from our triboelectric device in parallel with the changes in the oil condition that is spectroscopically monitored. Then we match a 'milestone' chemical change, the complete depletion of an antioxidant additive, with the obtained electrical signal.

2. Experimental section

2.1. Materials

We used the group I base oil SN 150 in our experiment. (Özçınarlar

A.Ş. Oil Manufacturing Company in Kütahya/Turkey). *Engine oil #1* is Castrol Power 14 T-10 W-40 motorcycle oil (BP Petrolleri A.Ş. Oil Manufacturing Company in Bursa/Turkey). *Engine oil #2* is Shell Helix HX7-10 W-40 motorcycle oil (Shell & Turcas A.Ş. Oil Petrol Manufacturing Company in Kocaeli/Turkey).

2.2. Tapping device

We used a tapping device to generate the triboelectric signals for oil condition monitoring, described in our previous work [3]. This tapping device collects and displays the individual electrical potential signals produced upon contact and separation of two surfaces. In this previous study, we confirmed that this setup is sensitive to the changes in electrical signals generated during the contact-charging of the synthetic polymers with cellulose and that the time-resolved signal can be used to analyze the mechanism of contact (and separation) electrification. This study used the identical setup: The two contacting surfaces are directly attached to 100-megaohm (input impedance) oscilloscope probes connected to a two-channel oscilloscope. (OWON SDS7072, 70 MHz, 2 + 1 Channel, 1 GS/s). The oscilloscope measures the open circuit electrical potential at the two channels independently. The magnitude of the open-circuit voltage signal (Voc) is accepted as the triboelectric signal, which we use to probe the oil condition.

2.3. Conductivity measurements

To investigate whether the degradation of Voc signal in the case of oil oxidation time is caused by the decrease in conductivity of oil (vide infra), conductivities of the fresh base oil, and oxidized oil samples (oxidized at 175 °C for 30 min, 4.5, 9, 17, 31, 55 h) were measured using a two-probe method and Keithley 6517 Electrometer. Current versus voltage curves of fresh base oil and oxidized samples were obtained via a probe station (with $w = 5$ mm wide and the distance between copper electrodes $d = 100$ μ m), and the applied voltage was changed from 0 to -50 and 0 to $+50$ V in steps of 10 V, which gave identical results in terms of surface conductivity. The values for surface resistance (R_s) were calculated according to the equation $R_s = (V/I) \cdot (w/d)$ in Ω/sq , using the slope values of the I-V curves. Then, surface resistivities were converted to surface conductivity (σ) using the equation $\sigma = 1/R_s$. Standard deviations of the surface conductivities were calculated from at least five independent measurements.

2.4. Characterization

The cellulose papers' surface morphologies were imaged using an FEI ESEM Quanta 200 – Environmental Scanning Electron Microscope (Thermo Fisher Scientific (USA)). For AFM and surface potential KFM imaging, a Nanosurf AFM microscope was used. FTIR-ATR spectra were taken using a Bruker Alpha FTIR-ATR spectrometer. All samples were

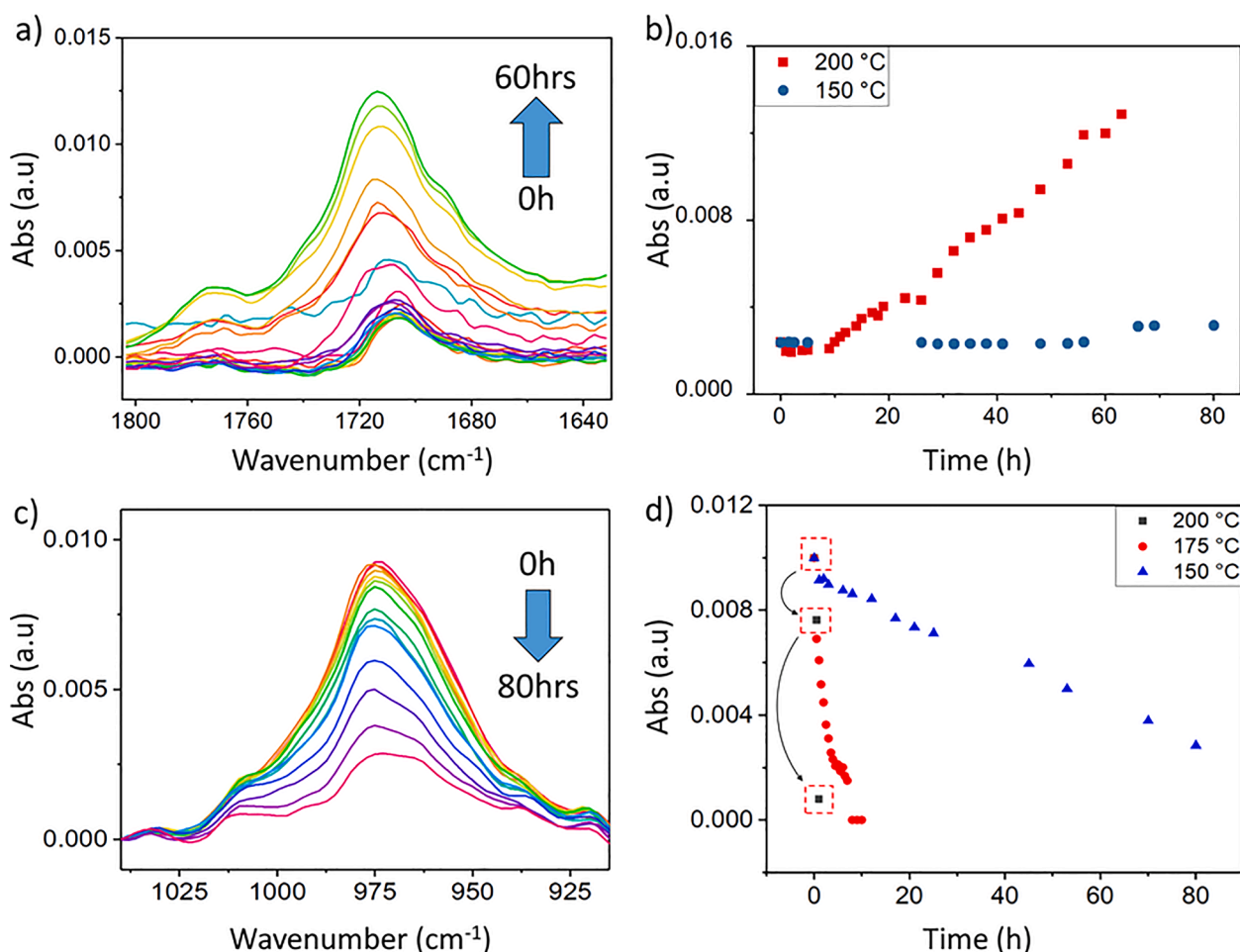


Fig. 2. Chemical changes in the thermally oxidized oil (engine oil #1) monitored by ATR-FTIR spectroscopy of the oil. **a)** The carbonyl region corresponding to the engine oil's oxidized hydrocarbon groups subjected to oxidation at $T = 200$ °C. The intensity of the peak increases with increasing oxidation time (0–60 h). **b)** The increase in the intensity of the ATR-FTIR 'oxidation signal' (carbonyl band centered around 1710 cm^{-1}) shown in (a), at 150 °C and 200 °C, at the corresponding oxidation times. **c)** ATR-FTIR peak corresponding to $\text{P}=\text{O}$ group of the additive material ZDDP monitored at increasing oxidation times (0–80 h) at $T = 150$ °C. **d)** The decrease in the ATR-FTIR 'ZDDP signal' intensity with a maximum at 975 cm^{-1} in (c), 150 °C, 175 °C, and 200 °C, at the marked oxidation times.

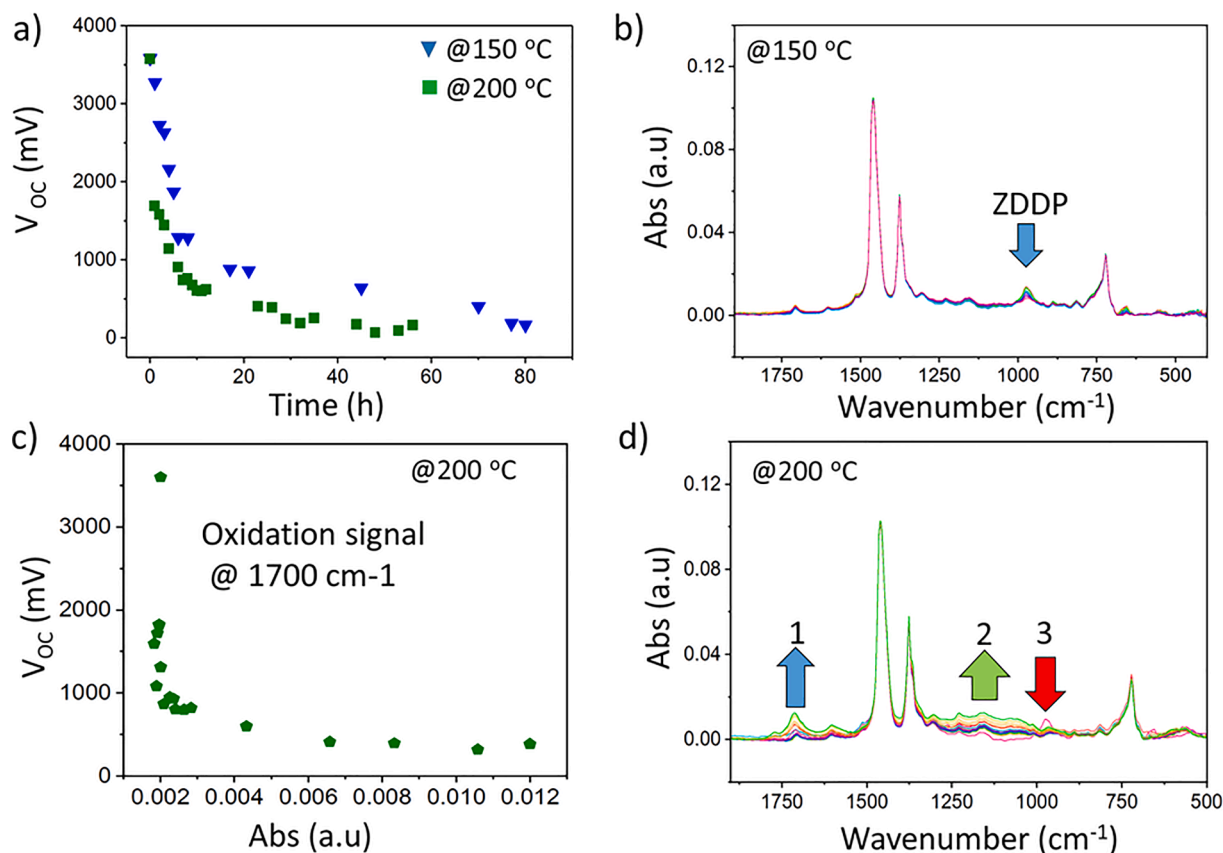


Fig. 3. a) Maximum value of triboelectrification open circuit potential (V_{OC}) vs. oxidation time for engine oil (at 150 °C and 200 °C). b) IR spectra of engine oil that is oxidized at 150 °C. (See also Fig. 2c for the changes in ZDDP P=O band in detail). c) The maximum value of triboelectrification V_{OC} vs. absorbance at 1710 cm^{-1} (carbonyl region) (oil oxidized at 200 °C). d) IR spectra of engine oil that is oxidized at 200 °C. Band 1 shows the carbonyl region (hydrocarbon oxidation), Band 2 depicts other chemical groups in other oxidation products, and Band 3 corresponds to the ZDDP P=O group.

analyzed with a spectral width of 4,000–400 cm^{-1} and 64 scans at a resolution of 4 cm^{-1} . The spectra were baseline corrected, and absorbance was normalized at the 2850 cm^{-1} signal (aliphatic C-H stretching). The viscosities of the oil samples were obtained using a Physica MCR 301 Rheometer (Anton Paar).

3. Results and discussions

3.1. Oxidation of oil can be followed by triboelectric signal

As is stated above, our ultimate aim is to develop a method for the online monitoring of oil degradation in an engine. To achieve this goal, in this study, we first started with 'an offline analysis' setup that will display the proof-of-principle of oil condition monitoring through the changes in the V_{OC} signal. In our experiments, circular cellulose disks that are previously immersed in the oil sample to be analyzed are tapped at 1 Hz with synthetic polymer sample disks of (12.3 mm diameter, 0.2–0.5 mm thick) polytetrafluoroethylene (PTFE), polyvinyl chloride (PVC), Kapton, polyethyleneglycol (PEG), polyethylene terephthalate (PET), polysulfone (PSU), Nylon, polyvinylidene fluoride (PVDF), polycarbonate (PC) (Fig. 1a and b). The tapping produces almost equal but oppositely charged individual contact (C) and separation (S) V_{OC} signals (Fig. 1c) on each electrode. To probe the possible effect of oil amount on the final V_{OC} signal and determine the amount of oil-soaked, 5 different samples were let to soak oil for 1 min – 3 hrs. The samples were then let to drip, contacting a filter paper vertically. The final oil amount on the papers after tapping did not show a significant variation (36–38 mg on cellulose paper), which shows that the dipping time (after letting the oil drip) does not affect the results obtained in electrification. In the first set of experiments, cellulose disks were immersed in fresh commercial

engine oil #1. The disks were then mounted on one of the tapping device's electrodes and tapped with a PVC disk fixed on the other electrode. (Fig. 1b). Both surfaces' tribocharging produces open-circuit potentials (V_{OC}) with maxima around ± 4 V at each electrode (Fig. 1c). It is shown before that in contact electrification of insulators, prolonged contact/separation cycles result in material transfer between the surfaces, affecting the V_{OC} signal intensities. After polymer and oil-soaked cellulose contact and separate, the polymer can be wet with residual oil. We performed 54,000 contact-separations (for 3 hrs) to monitor the possible loss of accuracy because of this residual oil. There was no attenuation/increase in signal intensity. We should add that, in another design showing on-site detection, the contact-separation events take place in oil (Fig. 7), showing that complete wetting of the surfaces does not change the qualitative outcome.

We then used cellulose disks soaked in thermally oxidized oil in the tapping experiment and tapped them against PVC. The V_{OC} signals decreased to ± 0.3 V (Fig. 1d) when the thermally oxidized oil instead of fresh oil was used. The oxidized oil soaked into cellulose disks was previously prepared by a thermal process in a temperature-controlled reactor (heating for 32 h, at 200 °C), simulating the lubricant oil's oxidation process. The oxidation of thermally oxidized oil was confirmed by the increase in the carbonyl peak intensity with a maximum at 1710 cm^{-1} in the Attenuated Total Reflectance FTIR spectrum (ATR-FTIR) of the oil, Fig. 1e. The decrease in the V_{OC} signal maxima was observed with some other polymers (listed above) used as the counter electrode surface, as shown in Fig. 1f, proving that the V_{OC} decrease is (qualitatively) independent of the nature of the counter electrode material.

Although the persistent differences between the V_{OC} signals of the fresh and oxidized oil samples are excitingly high (40–90% decrease in

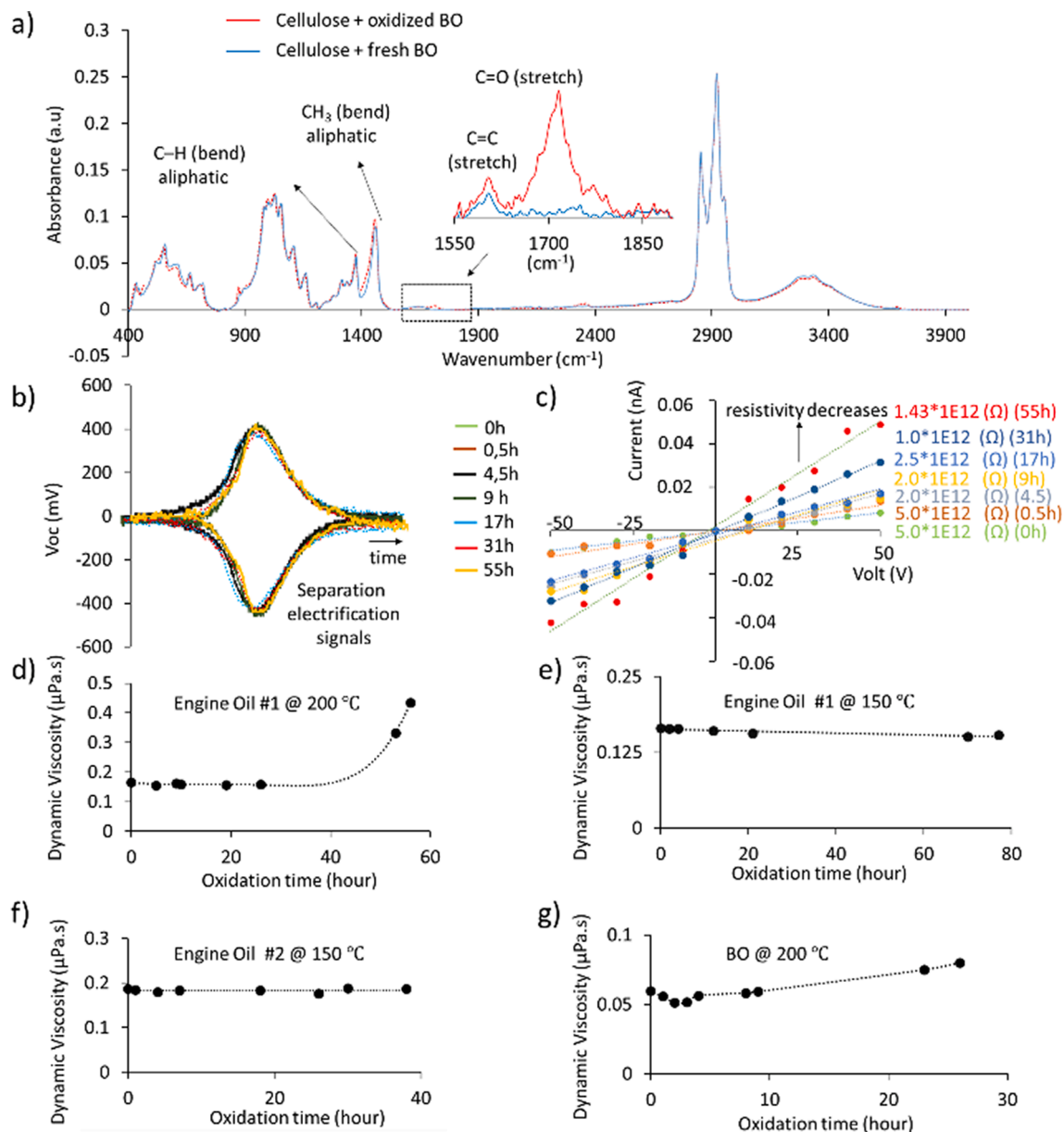


Fig. 4. a) The ATR-IR spectra of the fresh and oxidized (at 200 °C, 24 h) base oil samples indicate that there is no substantial change in the absorption intensity of the OH stretching of water (at 3300 cm^{-1}) in oil. b) Normalized triboelectric Voc separation signals (marked with 'S' in Fig. 1) generated with the tapping of oil-soaked cellulose on PTFE for different oxidation times of the oil (0 to 55 h). The signals are normalized and overlapped to compare the decay of the separation electrification signals in time. The decay profiles are almost identical. c) I-V curves of the fresh and oxidized base oil samples measured in (b). Oxidation was performed at 175 °C. Dynamic viscosities of d-g) the engine oil #1 up to 60 h of heating at 200 °C (d), the engine oil #1 up to 80 h of heating at 150 °C (e), the engine oil #2 up to 80 h of heating at 150 °C (f), the SN150 base oil (BO) up to 26 h of heating at 200 °C (g).

Voc obtained with the oxidation of the oil), the link between the oxidation and the Voc decrease should be chemically clarified before getting into the next step. Commercial motor oil has many chemicals ingredients; each may affect the observed triboelectric Voc displayed in Fig. 1c and 1d. The main preventer of the oxidation in these motor oils is zinc dialkyl dithiophosphate (ZDDP), usually doped at ca. 0.1% concentrations. Therefore, to prove that the decrease in the triboelectric signal is mainly due to the oil's oxidation, we then prepared oxidized oil samples of SN 150 Base oil (highly refined mineral oil), free of ZDDP. We first monitored the chemical changes in the base oil and the commercial engine oil (engine oil #1) upon the identical thermal oxidation processes by following the changes in the intensity of the peaks at the carbonyl region (1660 and 1800 cm^{-1}) of their ATR- FTIR spectra. The 150 °C –200 °C interval is taken to match ZDDP depletion kinetics, which helps generate and use a calibration curve data, monitoring the oil oxidation.

As expected, the base and the engine oil are oxidized at elevated temperatures and with prolonged oxidation times, as evident from the increase in the intensity of the carbonyl absorption due to the formation of the oxidized products, such as the carboxylic acid species peaking at 1710 cm^{-1} (Fig. 2a). If this signal is followed as an indication of oxidation, the antioxidant additive prevents the oxidation for days at lower temperatures (up to 150 °C) for the engine oil. At elevated temperatures (around 200 °C), the engine oil is oxidized rapidly in a few hours (Fig. 2b). This rapid oxidation can be straightforwardly linked to the ZDDP additive's chemical degradation (consumption) - if one follows the IR signal of ZDDP P=O stretching at 975 cm^{-1} . This signal decreases (Fig. 2c) in parallel to the increase in the carbonyl signal of the oxidation products (Fig. 2a); e.g., as shown in Fig. 2d, the intensity of the ZDDP signal decreased to half after 80 h of heating at 150 °C, and disappeared after 10 h of heating at 175 °C. At that time, the intensity of the

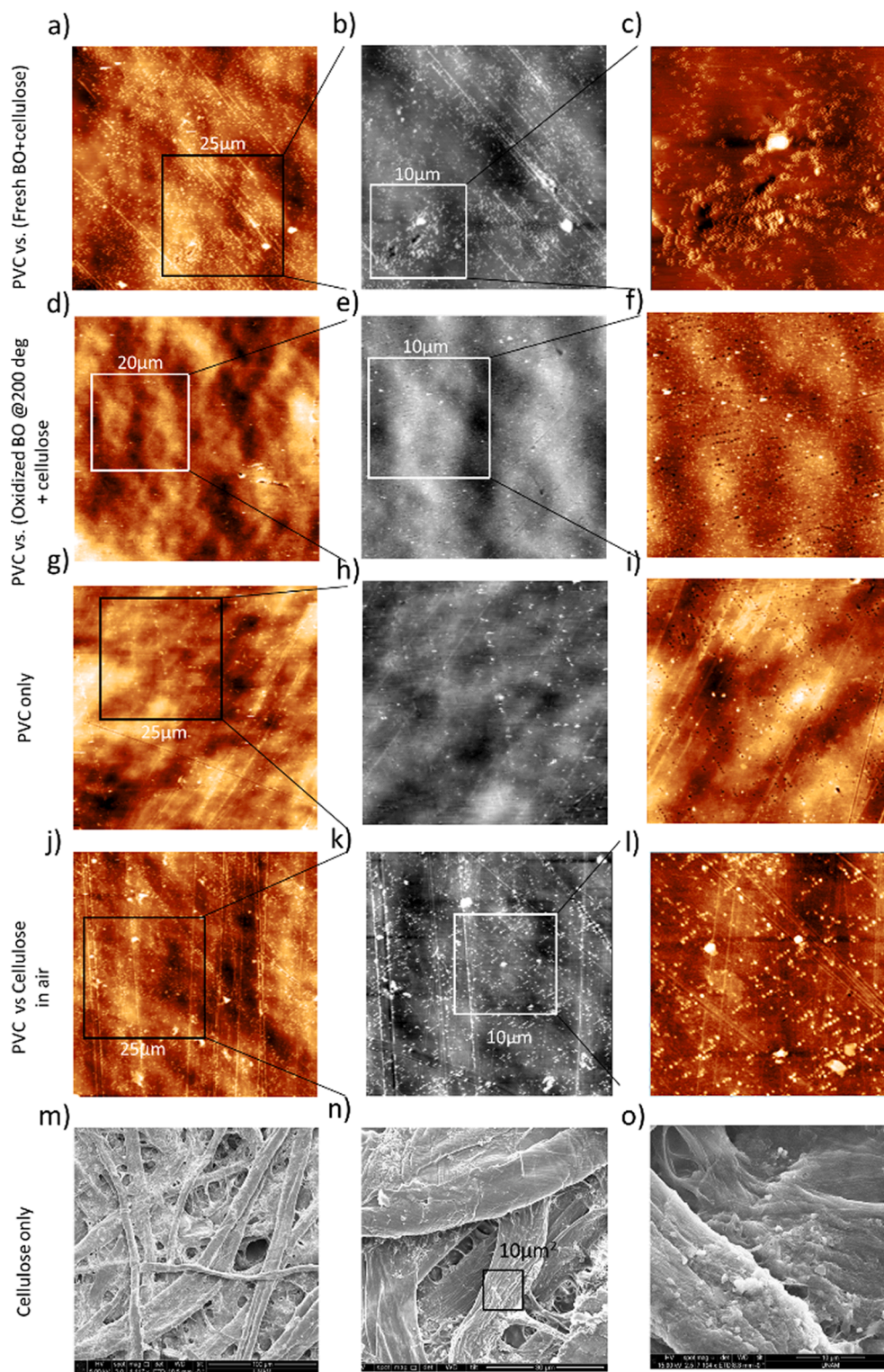


Fig. 5. AFM height image of **a–c)** the PVC film after tapping to fresh oil-soaked cellulose, **d–f)** the PVC film after tapping to oxidized oil-soaked cellulose, **g–i)** the PVC film before contact, **j–l)** the PVC film after tapping to cellulose in air. Oxidation of oil was performed at 200 °C for 24 h. The tapping frequency is set to 1 Hz, and surfaces were contacted and separated 600 times. **m–o)** SEM images of the cellulose surface at different magnifications.

carbonyl signal started to increase rapidly. At 200 °C, the ZDDP was consumed entirely after only 30 min of heating. As expected, the oxidation of the oil speeds up as the ZDDP is consumed: Heating the oil samples (engine oil #1) for 80 h at 100 °C, we observed no oxidation no ZDDP consumption. At 150 °C and 175 °C, there was a slow ZDDP consumption but no oxidation (owing to the remaining ZDDP). Finally,

at 200 °C, ZDDP was consumed rapidly, causing fast oxidation of the oil sample (Fig. 2d).

So far, with the initial experiments, we have shown that the magnitude of the Voc obtained using the triboelectric device working in the presence of the oil-wet cellulose disk changes as the condition of the oil changes upon thermal oxidation (Fig. 1). Then, we separately

monitored the basic chemical changes, and the emergence of the oxidation products as the ZDDP antioxidant is depleted (Fig. 2). Next, we investigated the correlation between the extent of oil oxidation, the ZDDP depletion, and whether the Voc signal timely reflects these changes. As shown in Fig. 2b, the oxidation of the oil can easily be followed spectroscopically by the sharp increase in the intensity of the carbonyl absorption (at 1710 cm^{-1}) in the ATR-FTIR spectra of the oil samples thermally oxidized for increasing oxidation times. Subjecting all these samples to the triboelectric device (letting the cellulose disks absorb the oil samples and then tapping the disks at the triboelectric device at 1 Hz with PVC counter electrode), we collected the Voc signal vs. oxidation time data (Fig. 3a). Comparing the decrease in the Voc signal with time and the oxidation/ZDDP depletion signals in the ATR-FTIR spectra at the corresponding times, it can be concluded that the reduction of the Voc signal timely follows the oxidation of the oil.

Chemical changes that affect the triboelectric signals

It is also essential to know which chemical changes affect the Voc signal predominantly: is it the emergence of the oxidized products, or is it the depletion of the ZDDP? To answer this and get an insight into the chemical mechanism that results in the Voc signal changes, we performed oxidations at temperatures of 150 and 200 °C. The main difference between these two oxidations performed at different temperatures is in the rate of the chemical oxidation processes (the depletion of the ZDDP and the oxidation of hydrocarbons). At 150 °C, the oxidation is much slower than that at 200 °C. This slow oxidation results in the slower depletion of ZDDP (P=O absorption band centered at 975 cm^{-1} decreases slowly), which leads to almost no carbonyl oxidation product even at 80 h (Fig. 3b). Therefore, the decrease in the corresponding triboelectric output (Fig. 3a) can be assigned to the ZDDP consumption and the emergence of the ZDDP degradation products. This result is especially valuable since it shows that our method of triboelectric sensing of oil degradation is probing the oil oxidation at the ZDDP depletion stage even before the “damaging oxidation” (formation of the oxidized hydrocarbons) starts to take place. At 200 °C, the oxidation is faster, leading to an increase in the oxidation products followed at the ATR-FTIR carbonyl region (marked as band 1) and at the broad region of 1000 and 1300 cm^{-1} (marked as band 2). This fast oxidation also results in rapid depletion of ZDDP followed at the 975 cm^{-1} (marked as band 3) in Fig. 3d. Therefore, all these chemical changes at elevated temperatures may decrease the triboelectric output signal, e.g., as displayed in Fig. 3a for oxidation at 200 °C. Nevertheless, suppose only the carbonyl region is monitored as the “basic” indicator of oxidation. In that case, one can finely correlate the increase in the intensity of the carbonyl peak and the corresponding sharp decrease in the obtained Voc signal (Fig. 3c).

The mechanism of oil oxidation sensing with the triboelectric sensor

Besides the chemical changes, there surely can be other physical alterations in the oil, leading to the observed decrease in the Voc signal upon oil oxidation. One possible scenario is; the water content may increase as the oil is oxidized since the oxidation is done under ambient conditions, which affects the triboelectric signals due to increasing conductivity. Such an increase would, e.g., cause fast discharging of tribocharges on the surfaces. However, the ATR-FTIR spectra showed no substantial increase in the absorption signals corresponding to water (Fig. 4a). Secondly, the decay profile of the separation signals generated with the tapping of oil-soaked cellulose on PTFE for different oxidation times of the oil (0 to 55 h) are almost identical (Fig. 4b). In addition, the measurement of the oxidized and fresh base oil conductivities shows both are non-conductive (with resistivity values higher than $1 \times 10^9\text{ ohm}$), implying that the change in the Voc signal is not conductivity-driven (Fig. 4c). Finally, the decrease in the Voc signal might be due to the change in viscosity upon oxidation. The viscosity of the engine oil samples #1 and #2 did not change up to 40 h of heating at 150 °C and 200 °C, respectively. This result implies that the Voc change is not due to a change in the viscosity (Fig. 4d-g).

To get more insight into the mechanism of sensing oxidized oil by the

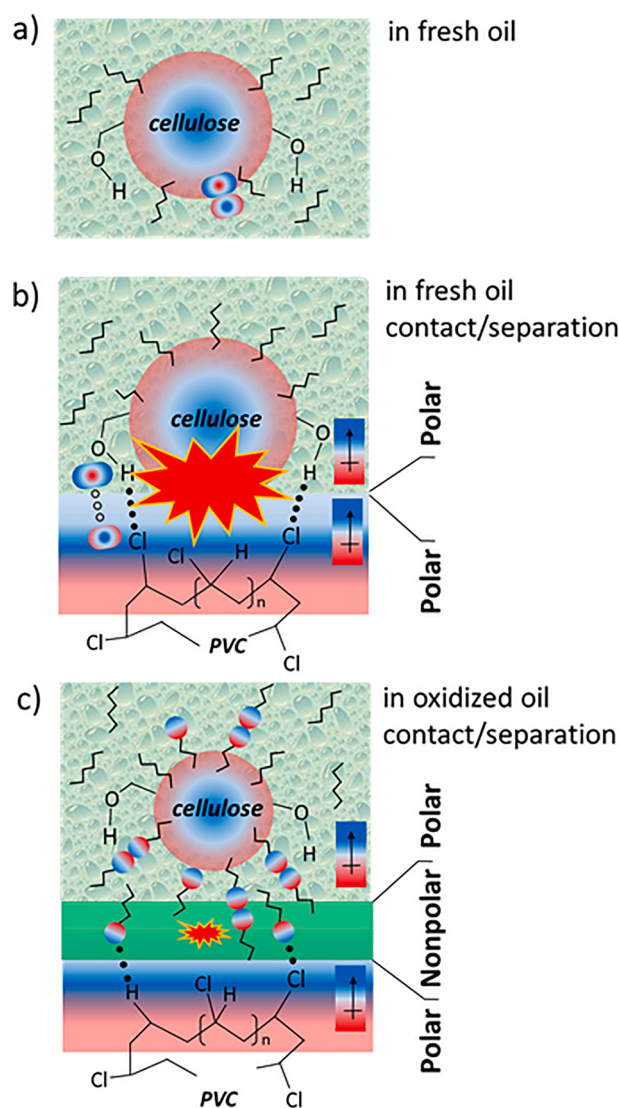


Fig. 6. Schematic representation of the possible attractive weak interactions between the interfaces (••• = H-bonding, $\leftrightarrow$ polar-polar, and (oppositely colored circles) = dipole-dipole dispersion interactions at the polymer-oil-cellulose interfaces. a) Between cellulose and fresh oil, b) between cellulose and PVC in the presence of fresh oil, c) between cellulose and PVC in the presence of oxidized oil. Note in (c), polar groups of the oxidized oil molecules may form a bilayer between the polar cellulose and polar PVC through weak interactions.

triboelectric sensor, we probed the possible events on the contacting surface. Previously, other groups and we showed that upon contact and separation tapping, static charges and thus the Voc potentials are developed in a series of events initiated by mechanochemical processes at the surfaces [3,4,30] that also cause a change in surface topography. [31] Here, analyzing the surfaces using AFM, before and after tapping, we detected surface deformations on the polymer surface tapped with cellulose that is wet with either fresh or oxidized engine oil (Fig. 5). SEM images of the cellulose used in this study were shown in Fig. 5m-o.

As shown above, oxidized samples produced decreased Voc signals upon tapping, meaning less surface charging with these samples. We believe that this decrease is due to the stronger secondary interactions between the oxidized (thus more polar) oil and the polar C-Cl bonds in PVC and polar cellulose surfaces. (Fig. 6). These stronger interactions between the oxidized oil, PVC, and cellulose surfaces weaken the interactions between the PVC and cellulose upon their contact, leading to less surface deformation (see AFM images in Fig. 5d-f), less bond-

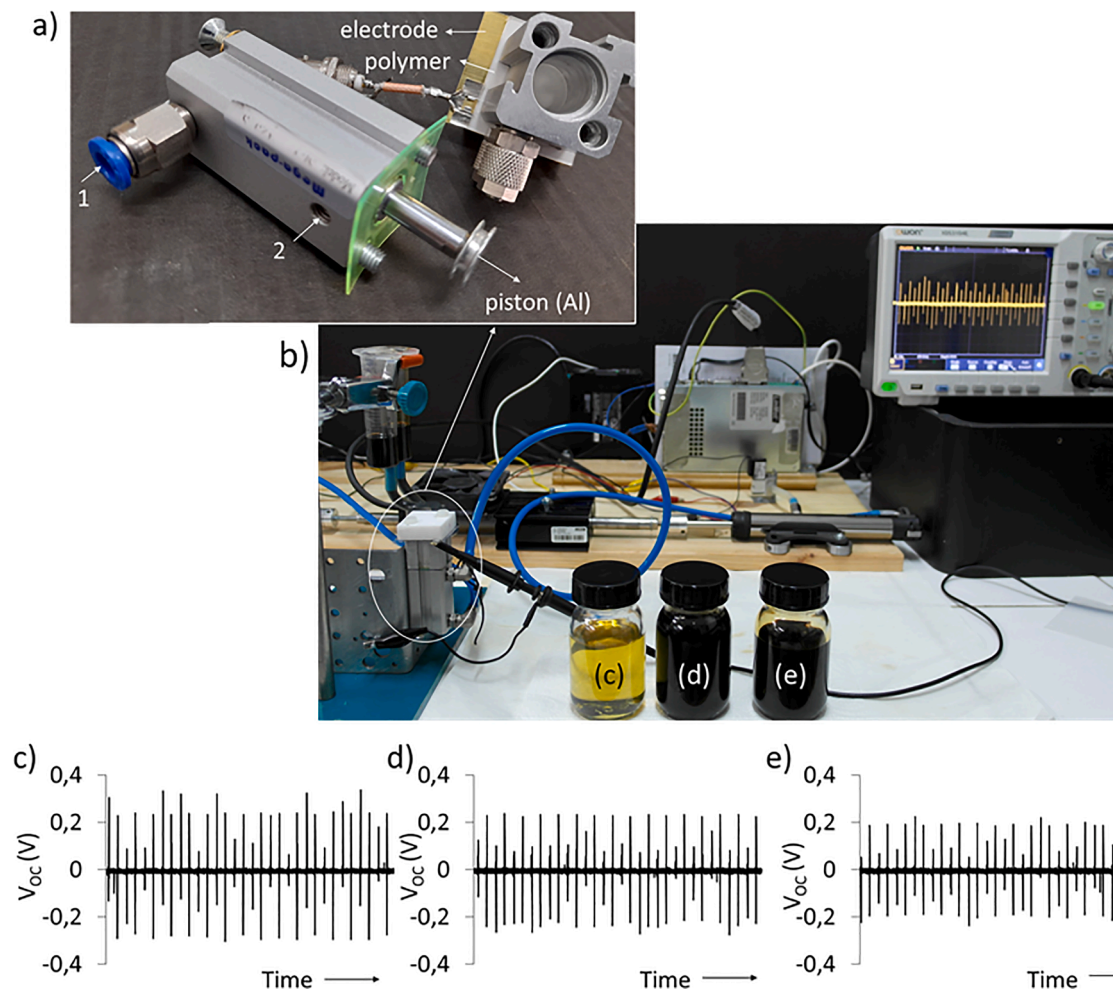


Fig. 7. A pneumatically driven online triboelectric oil oxidation sensor. a) The triboelectric sensor unit showing the tapping compartment. b) The overall photo of the sensor system and the oil samples. Open-circuit electrical signals (V_{oc}) given for c) fresh base oil, e) for 24-hour-oxidized base oil, and d) 1:1 mixture of (c) and (e).

breaking, and less charging on surfaces. If the generated V_{oc} signals are carefully monitored by high-resolution data acquisition, the contact and the separation signals are resolved.[3] Both the contact and the separation V_{oc} signals decrease upon tapping polymers with oxidized oil-soaked cellulose (Fig. 1c and d), implying that these secondary interactions are prominent in contact and separation electrification.

3.2. Online monitoring of oil condition by a triboelectric sensor without the need for other analysis

Finally, we built an on-site oil condition triboelectric sensor using a pneumatic actuator. The lubricant oil can continuously flow throughout the sensor's compartment, where the triboelectric charge is generated (Fig. 7) by tapping a flat PVC surface and Aluminum disc. The generated signals were collected by a brass electrode (2.5cmx2.5 cm) attached to the backside of the PVC polymer, as shown in Fig. 7a. At the beginning of the operation, a stable V_{oc} signal (about 10 contact-separation cycles, taking about a few seconds) was achieved. Since the oil oxidation would take a long time (days to months, e.g., in engine operation) we operated the sensor with fresh and oxidized oils separately at room temperature to show the change in the V_{oc} signal. Indeed, in operation, the continuous detection would not be ultimately necessary – checking, e.g., once in a month could be practical. The results in the presence of fresh base oil and oxidized (at 200 °C and 24 hr) base oil samples are shown in Fig. 5c and 5e. The average signal intensity decreases (21%) in the presence of oxidized base oil. The difference is even larger for the separation signals

(47%). Additionally, both contact and separation signals were measured to be much irregular in the presence of fresh base oil. This irregularity is presumably because of a larger adhesion force between Aluminum and PVC surfaces in the presence of fresh (unoxidized) base oil because of fresh oil's more nonpolar character.

4. Conclusion

This study shows that the oxidation of engine oils can be tracked by the changes in the triboelectric signals produced by tapping the oil-wet cellulose to common synthetic polymers. As the time of oil oxidation increases, the V_{oc} signal decreases. With the engine oils having the antioxidant ZDDP, the change can be probed before the damaging oxidation levels are reached; since the depletion of ZDDP decreases the V_{oc} signal. The AFM analyses of the contacting surfaces showed that the decrease in the V_{oc} signal is associated with the fewer deformations observed with the polymer surfaces in contact with oxidized oil since the plastic deformations (bond-breakings) are less pronounced on the polymer surface. It can be surmised that fewer bond-breaking results from stronger secondary bonding interactions between the oxidized oil and the surfaces, which prevents the efficient contact and charging of the contacting surfaces. We then used our results in the offline analysis to build an example of a portable online triboelectric oil oxidation sensor. We believe that this new online oil oxidation monitoring method can help prevent economic losses and help protect the environment.

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CRediT authorship contribution statement

Azimet A. Karluk: Data curation, Software, Investigation, Writing – original draft. **Sunay D. Ekim:** Methodology, Software, Investigation, Writing. **Bilge Baytekin:** Writing – review & editing. **H. Tarik Baytekin:** Supervision, Validation, Methodology, Writing – original draft. Azimet A.Karluk and Sunay D. Ekim contributed equally to this study.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] Markets and markets, Market Research Report, <https://www.marketsandmarkets.com/Market-Reports/lubricants-market-182046896.html> (2021).
- [2] T. Mang, *Used Oil Disposal and Collection*. Encyclopedia of Lubricants and Lubrication, (Springer-Verlag, Berlin, Heidelberg, 2014, pp. 2205–2206).
- [3] U.G. Musa, S.D. Cezan, B. Baytekin, H.T. Baytekin, The Charging Events in Contact Separation Electrification, *Sci. Rep.* 8 (2018) 2472.
- [4] H.T. Baytekin, A. Patashinski, M. Branicki, B. Baytekin, S. Soh, B.A. Grzybowski, The Mosaic of Surface Charge in Contact Electrification, *Science* 333 (2011) 308–312.
- [5] D.J. Lacks, R.M. Sankaran, Contact Electrification of Insulating Materials, *J. Phys. D: Appl. Phys.* 44 (2011), 453001.
- [6] S.D. Cezan, A.A. Nalbant, M. Buyuktemiz, Y. Dede, H.T. Baytekin, B. Baytekin, Control of Triboelectric charges on Common Polymers by Photoexcitation of Organic Dyes, *Nat Commun.* 10 (2019) 276.
- [7] D.K. Davies, Charge Generation on Dielectric Surfaces, *J. Phys. D: Appl. Phys.* 2 (11) (1969) 1533–1537.
- [8] A. Tilmatine, K. Medles, S.E. Bendimerad, F. Boukholda, L. Dascalescu, Electrostatic Separators of Particles: Application to Plastic/metal, Metal/metal and Plastic/plastic mixtures. *Waste Manage.* 29 (2009) 228–232.
- [9] Z.L. Wang, Triboelectric Nanogenerators as New Energy Technology for Self-powered Systems and as Active Mechanical and Chemical Sensors, *ACS Nano* 7 (11) (2013) 9533–9557.
- [10] B.D. Chen, W. Tang, C. He, T. Jiang, L. Xu, L.P. Zhu, G.Q. Gu, J. Chen, J.J. Shao, J. Luo, Z.L. Wang, Ultrafine Capillary-Tube Triboelectric Nanogenerator as Active Sensor for Microfluidic Biological and Chemical Sensing, *Adv. Mater. Technol.* 3 (2018) 1700229.
- [11] Z.H. Lin, G. Zhu, Y.S. Zhou, Y. Yang, P. Bai, J. Chen, Z.L. Wang, A Self-Powered Triboelectric Nanosensor for Mercury Ion Detection, *Angew. Chem. Int. Ed.* 52 (2013) 1–6.
- [12] Y. Wu, Y. Su, J. Bai, G. Zhu, X. Zhang, Z. Li, Y.i. Xiang, J. Shi, A Self-Powered Triboelectric Nanosensor for pH Detection, *J. Nanomater.* 2016 (2016) 1–6.
- [13] H.L. Zhang, Y. Yang, T.C. Hou, Y.J. Su, C.G. Hu, Z.L. Wang, Triboelectric Nanogenerator Built Inside Clothes for Self-powered Glucose Biosensors, *Nano Energy* 2 (2013) 1019–1024.
- [14] Y. Jie, N. Wang, X. Cao, Y. Xu, T. Li, X.J. Zhang, Z.L. Wang, Self-Powered Triboelectric Nanosensor with Poly(tetrafluoroethylene) Nanoparticle Arrays for Dopamine Detection, *ACS Nano* 9 (2015) 8376–8383.
- [15] Z. Li, J. Chen, J. Yang, Y. Su, X. Fan, Y. Wu, C. Yu, Z.L. Wang, β -Cyclodextrin Enhanced Triboelectrification for Self-Powered Phenol Detection and Electrochemical Degradation, *Energy Environ. Sci.* 8 (2015) 887–896.
- [16] E. Maguire, Monitoring of Lubricant Degradation with RULER and MPC, (Linköping University, 2010).
- [17] A. Agoston, C. Otsch, B. Jakoby, Viscosity Sensors for Engine Oil Condition Monitoring Application and Interpretation of Results, *Sens. Actuator A Phys.* 121 (2005) 327–332.
- [18] B. Jakoby, M. Scherer, M. Buskies, H. Eisenschmid, An Automotive Engine Oil Viscosity Sensor, *IEEE Sens. J.* 3 (2003) 562–568.
- [19] I. Minami, Molecular Science of Lubricant Additives, *Appl. Sci.* 7 (2017) 445.
- [20] P. Lopez, J. Mabe, G. Miró, L. Etxeberria, Low cost Photonic Sensor for In-line Oil Quality Monitoring: Methodological development process towards uncertainty mitigation, *Sensors* 18 (7) (2015) 2015, <https://doi.org/10.3390/s18072015>.
- [21] L. Guan, X.L. Feng, G. Xiong, J.A. Xie, Application of Dielectric Spectroscopy for Engine Lubricating Oil Degradation Monitoring, *Sens. Actuator A Phys.* 168 (2011) 22–29.
- [22] J. Zhu, J.M. Yoon, D. He, Y.Z. Qu, E. Bechhoefer, Lubrication Oil Condition Monitoring and Remaining Useful Life Prediction with Particle Filtering, *Int. J. of Progn. Health Manag.* 4 (2013) 124–138.
- [23] Jagannathan, S.; Raju, G. V. S. Remaining Useful Life Prediction of Automotive Engine Oils Using MEMS Technologies. In *Proceedings of the 2000 American Control Conference* 3511–3512 (ACC, Chicago, 2000).
- [24] Jagannathan, S.; Schricker, D. R.; Simpson, T. *Method for Determining the Condition of Engine Oil Based on Soot Modeling*, 1999, US Patent No. 5.914.890.
- [25] Jagannathan, S. Method and Apparatus for Predicting a Fault Condition. 1999, US Patent No 5.987.976.
- [26] N. Gracia, S. Thomas, P. Bazin, L. Duponchel, F. Thibault-Starzyk, O. Lerasle, Combination of mid-infrared spectroscopy and chemometric factorization tools to study the oxidation of lubricating base oils, *Catal. Today* 155 (2010) 255–260.
- [27] K. Maier, in: *Vibration and Wear in High Speed Rotating Machinery*, Springer Netherlands, Dordrecht, 1990, pp. 75–85, https://doi.org/10.1007/978-94-009-1914-3_6.
- [28] Z. Han, Y. Wang, X. Qing, Characteristics Study of In-Situ Capacitive Sensor for Monitoring Lubrication Oil Debris, *Sensors*. 17 (2017) 2851.
- [29] X.L. Zhu, C. Zhong, J. Zhe, Lubricating Oil Conditioning Sensors for Online Machine Health Monitoring—A Review, *Tribol. Int.* 109 (2017) 473–484.
- [30] M. Özel, F. Demir, A. Aikebaier, J.K. Yiğitbasi, H.T. Baytekin, B. Baytekin, Why Does Wood Not Get Contact Charged? *Chem. Mater.* 32 (2020) 7438–7444.
- [31] H.T. Baytekin, B. Baytekin, J.T. Incorvati, B.A. Grzybowski, Material Transfer and Polarity Reversal in Contact Charging, *Angew. Chem. Int. Ed.* 51 (2012) 4843–4847.