Physical and chemical degradation of PTFE magnetic stir bars induced by TiO_2-based materials

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Abstract

Polytetrafluoroethylene (PTFE) magnetic stir bars are widely used in laboratorial, industrial, and biomedical routine activities due to their chemical inertness. Here the physical exfoliation of PTFE magnetic stir bars, previously revealed in specific experimental conditions, was confirmed in the presence of TiO_2 nanoparticles. Moreover, the chemical surface degradation of PTFE magnetic stir bars was revealed for the first time, due to the effect produced by the oxidative activity of a hybrid TiO_2-based material under indirect daylight conditions that might be also combined with the tribocatalytic activity of TiO_2.

Keywords: Polytetrafluoroethylene; Magnetic stir bar; Reactive oxygen species; Titanium dioxide; Physical degradation; Chemical degradation.

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1. Introduction

Polytetrafluoroethylene (PTFE) is a fluorinated polymer that exhibits many interesting properties, such as high chemical and thermal stability, strong surface hydrophobicity, low dielectric constant, and high piezoelectric activity (Puts et al., 2019). Therefore, it is used in various applications ranging from separation and purification processes (Guo et al., 2022; Liu et al., 2024) to biomedicine (Johnson et al., 2022; Ogino, 2019). Due to its high piezoelectric coefficient (Chen et al., 2019), PTFE plays a key role in piezocatalysis (He et al., 2023; S. Zhang et al., 2023), tribocatalysis (Cui et al., 2022; Li et al., 2019, 2023) and contact-electro-catalysis (Z. Wang et al., 2024). These catalytic techniques are based on the direct conversion of mechanical energy into chemical energy, and, recently, their use in the purification of wastewater is increasing (Wang et al., 2022; Wu et al., 2023).

In piezocatalysis, the mechanical stress, generally obtained by high-frequency ultrasounds, induces a polarization of the piezoelectric material, producing a charge separation of the electron- hole pairs. These pairs migrating on the opposite surface of the material, in the presence of water and of dissolved oxygen, can generate reactive oxygen species (ROS), giving rise to the pollutant removal (He et al., 2023; S. Zhang et al., 2023).

In the contact-electro-catalysis, the mechanical stress is obtained by ball milling of tribocatalytic materials producing a contact electrification process. This latter leads to a charge separation at the interface between two different surfaces where ROS are subsequently generated (Z. Wang et al., 2024).

In tribocatalysis, the mechanical stress that generates the charge separation is the friction between a magnetic stir bar, covered with PTFE, and another material (catalyst), which does not necessarily have to exhibit piezoelectricity, such as a metal or semiconductor. The charge separation is supposed to occur through two mechanisms: electron transfer across atoms and electron transition (Z. Wang et al., 2024). In any case, electrons accumulate on the surface of the PTFE magnetic stir bar, which

acts as an electron acceptor in friction, while the catalyst is positively charged (Y. Wang et al., 2024; Wu et al., 2018; Zhao et al., 2020). Tribo-catalytic conversion of H_2O and CO_2 using Co_3O_4 nanoparticles was recently obtained (Jia et al., 2023) as well as the degradation of dyes with ZnO nanorods (Zhao et al., 2020), and organic pollutants by metal sulfide heterojunctions (Y. Wang et al., 2024). When tribocatalysis was coupled with ultrasonic irradiation, the degradation of different chlorophenols (Wu et al., 2023) as well as the unusual exfoliation of PTFE nanoparticles from the surface of magnetic stir bars (Wang et al., 2022) occurred. This discovery could have a wide range of implications concerning the safe use of PTFE in different sectors, such as laboratory, commercial, industrial, and biomedical (Wang et al., 2022). On the other hand, based on recent works (Amato et al., 2024; Pentsak et al., 2019; J. Zhang et al., 2023) the chemical and physical inertness of PTFE should be reconsidered taking into account that water permeation might occur through PTFE nanochannels (Zhang et al., 2023). Microscopic damage of PTFE magnetic stir bars after prolonged use was also reported (Pentsak et al., 2019). The presence of various types of defects favours the accumulation of active components from the reaction mixture, mostly metal species that can be trapped in the above mentioned nanochannels. The impurities trapped in the surface defects cannot be eliminated by washing and cleaning, and may substantially influence reaction outcomes under investigation (Pentsak et al., 2019). The exfoliation of the external layers of PTFE-coated magnetic stir bars was also observed in our recent experimentation dealing with the degradation of microplastics made of linear low-density polyethylene (LLDPE) by a new oxidative process, that does not require any direct energy source (irradiation or heat) and takes place in atmosphere and at room temperature (Amato et al., 2024). Chemical degradation of LLDPE films occurred within 1 month giving alkanes, alcohols and esters and, simultaneously, the surface exfoliation of the PTFE magnetic stir bar was evidenced already after 4 days in the presence of "T-*Abi*". T-*Abi* is an amorphous hybrid material synthesized through a sol-gel route by a trash-to-treasure approach, using a rosin bio-waste,

mainly constituted by abietic acid, whose nominal mass content of the bio-waste is significant (43%). On the surface of this hybrid material superoxide radical ions ($O_2^{\bullet-}$) are spontaneously generated, without any energy source, because of two synergic effects, the defective amorphous structure of the material and the ligand to metal charge transfer complex between the organic moiety and the metal, that allow stabilizing a negative charge excess on its surface (Amato et al.).

Here, a specific experimentation is reported to evidence and clarify the role played by T-*Abi* in PTFE exfoliation and degradation, with special attention to ascertain if its extraordinary degradative activity works also towards a very stable material such PTFE.

2. Materials ad methods

The synthesis procedures of materials and the employed characterization methods are thoroughly described in the Supplementary Materials.

Two aqueous suspensions were prepared in a 50 mL beaker of borosilicate glass each of them containing commercial PTFE magnetic stir bar of the same size (3 cm) that had never been used before. The suspension A contained only T-*Abi* (1 mg/mL); the suspension B consisted in T-*Abi* (1 mg/mL) and 12 pieces of LLDPE films (5 mm × 5 mm).

The adopted experimental conditions were the same as the conditions previously optimized for investigating the chemical degradation of LLDPE films, *i.e.* indirect daylight illumination, namely artificial laboratory illumination during the working days and darkness at night, T-*Abi* concentration of 1 mg/mL, room temperature of about 30 °C, stirring rate of 300 rpm, incubation times 4 days and 1 month. These experiments might help to ascertain if the presence of LLDPE can affect the PTFE exfoliation due to its remarkable triboelectric charge density (Zou et al., 2019). Moreover, to further confirm the degradative activity of T-Abi on PTFE, a suspension C, only containing TiO_2 P90 (1 mg/mL) and stirred with a commercial PTFE magnetic stir bar, that had never been used before and whose

size was the same of those used to stir the suspensions A and B, was also prepared. For comparison, a blank sample consisting of a PTFE magnetic stir bar, that had never been used before and whose size was the same of those used to stir the above suspensions, was introduced in a borosilicate glass beaker filled with the same volume of water used for the preparation of the above suspensions and left stirring for 1 month.

The solid residues obtained through centrifugation from the above aqueous suspensions with T-*Abi* were examined by XRD, ATR FT-IR spectroscopy, and XPS, and, hereafter, will be denoted as: A-4d, A-1m, and B-1m, respectively.

3. Results and Discussion

The PTFE exfoliation was already evident after 4 days and became increasingly marked along the time up to one month, as demonstrated by the FTIR and XRD results displayed in Figure 1. The typical absorption bands of PTFE at 1210 cm^{-1} ($\nu_{as\ C-F}$), 1150 cm^{-1} ($\nu_{s\ C-F}$) and 639 cm^{-1} ($\omega_{\ C-F}$) (Yamauchi et al., 2011) are clearly visible on the surface of A-4d, A-1m and B-1m (Figure 1a). Moreover, the analysis of XRD patterns of A-4d, A-1m, and B-1m, showing the most intense XRD peaks of PTFE (Si et al., 2022), confirms the presence of exfoliated PTFE (see Figure 1b).

However, after one month of incubation, an impressive exfoliation of the PTFE magnetic stir bar was observed for the TiO_2 P90, as clearly shown in the photographs of Figures 1c and 1d. The external PTFE layer appears in more points almost completely removed, resulting in the exposure of the metallic part of the stir bar and in the complete covering by PTFE residues of the walls of the glass beaker containing suspension C, as confirmed by the FTIR spectrum of the white precipitate, displayed in Figure 1e, where the absorption bands of PTFE at 1210 cm^{-1}, 1150 cm^{-1} and 639 cm^{-1} are evident.

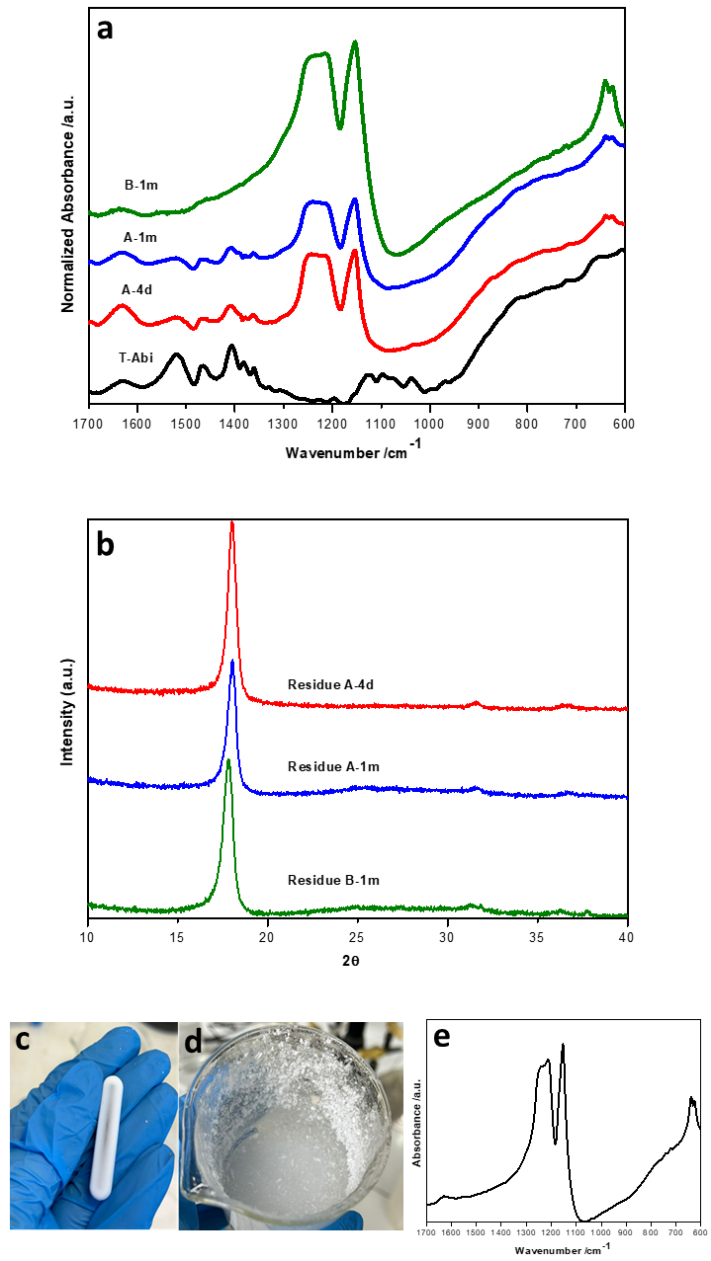
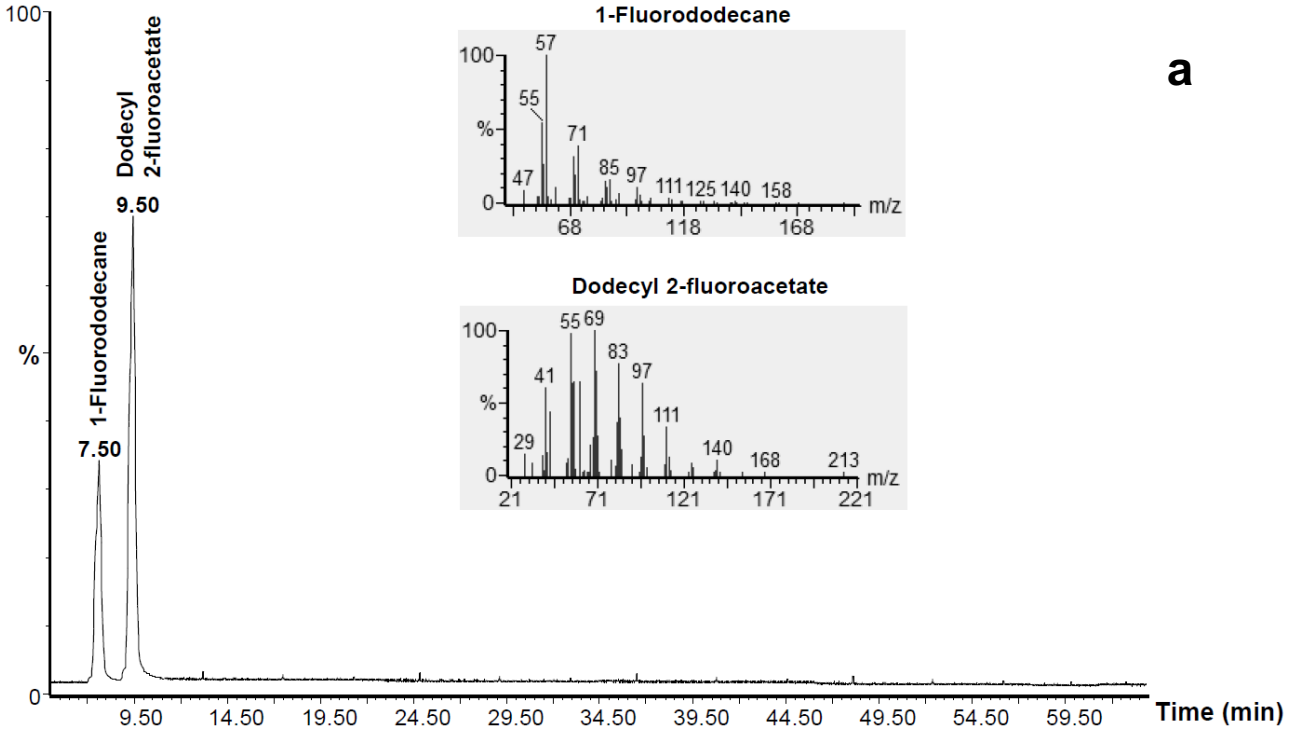


Figure 1. (a) FTIR spectra of: bare T-*Abi* (black line), T-*Abi* incubated 4 days (A-4d, red line) and 1 month (A-1m, blue line) without LLDPE, T-*Abi* incubated 1 month (B-1m, green line) with LLDPE; (b) XRD profiles of: T-*Abi* incubated 4 days (A-4d, red line) and 1 month (A-1m, blue line) without LLDPE, T-*Abi* incubated 1 month with LLDPE (B-1m, green line), bare T-*Abi*; (c) PTFE magnetic stir bar that was used to stir the suspension C after 1 month; (d) the glass beaker that contained the suspension C after 1 month; (e) FTIR spectrum of the white precipitate on the beaker walls of Figure 1 (d).

This result demonstrates that TiO_2 P90 exerts a strong tribological effect, inducing a progressive erosion of surface layers of the PTFE coating and giving a macroscopic exfoliation of the PTFE magnetic stir bar after 1 month of incubation. The exfoliated PTFE fragments, being strongly hydrophobic, tend to adhere to solid surfaces, particularly those with low polarity, such as LLDPE or T-*Abi* (because of the exposed abietate ligands). On the contrary, the PTFE magnetic stir bar that was used to stir the beaker containing only water after 1 month did not reveal any evidence of exfoliation (Figure S1).

The A-1m, B-1m, and C aqueous suspensions were recovered by centrifugation at 10000 rpm for 10 min after incubation to examine the presence of eventual degradation products. The supernatants obtained were filtered (0.45 μm), lyophilized, submitted to extraction by using three different organic solvents (toluene, hexane and chloroform), and finally analysed by means of GC-MS. The analysis of GC-MS spectra performed on suspension C (TiO_2 P90 in water stirred with the PTFE bar) did not reveal any degradation products. In contrast, dodecyl 2-fluoroacetate and 1-fluorododecane were identified in suspension A-1m, while only 1-fluorododecane was found in suspension B-1m (Figure 2).

It should be noted that any compound was identified by GC-MS analysis performed on the blank sample (only water).



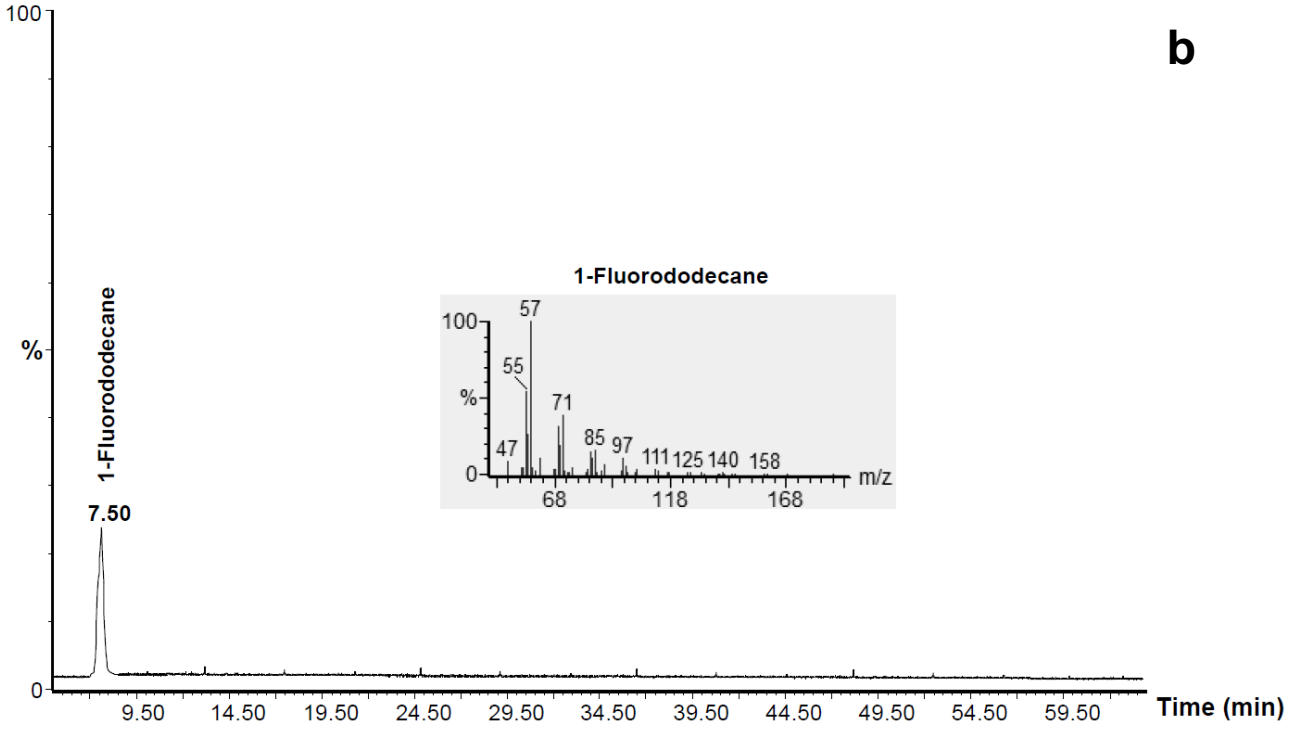


Figure 2. Total chromatogram of the degradation by-products obtained analysing the supernatants of a) suspension A-1m, b) suspension B-1m, and standard mass spectrum of each compound identified.

To the best of our knowledge, the degradation by-products originating from a PTFE magnetic stir bar are here identified for the first time. We assume that these products are originated by the degradation of organic fluorinated additives, such as per- or poly-fluoroalkyl compounds, used in the manufacturing of PTFE stir bars (Meng et al., 2021).

The PTFE exfoliation was confirmed through XPS analyses of A-4d, A-1m and B-1m samples. The XPS survey spectra can be found in Figure 3.

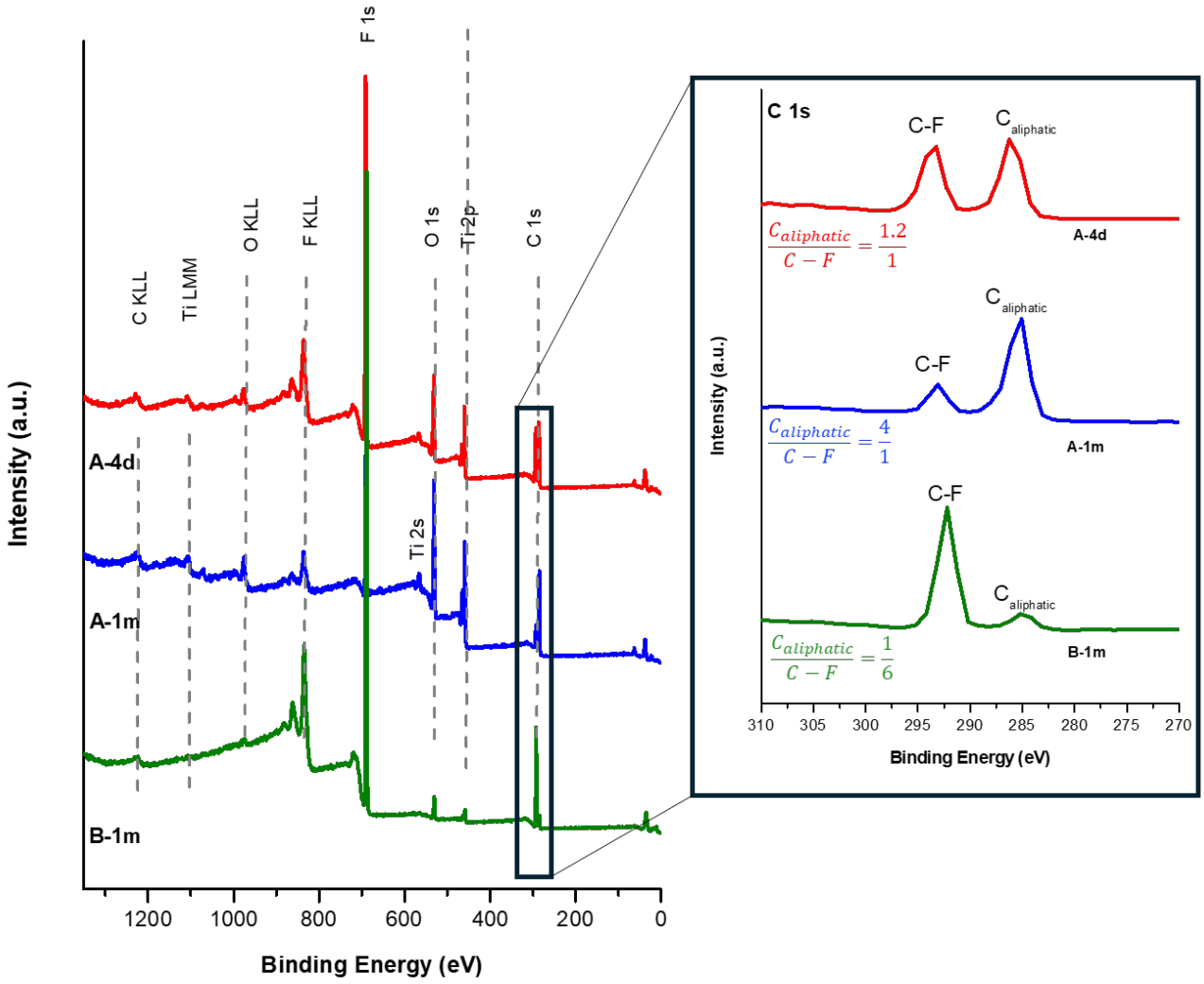
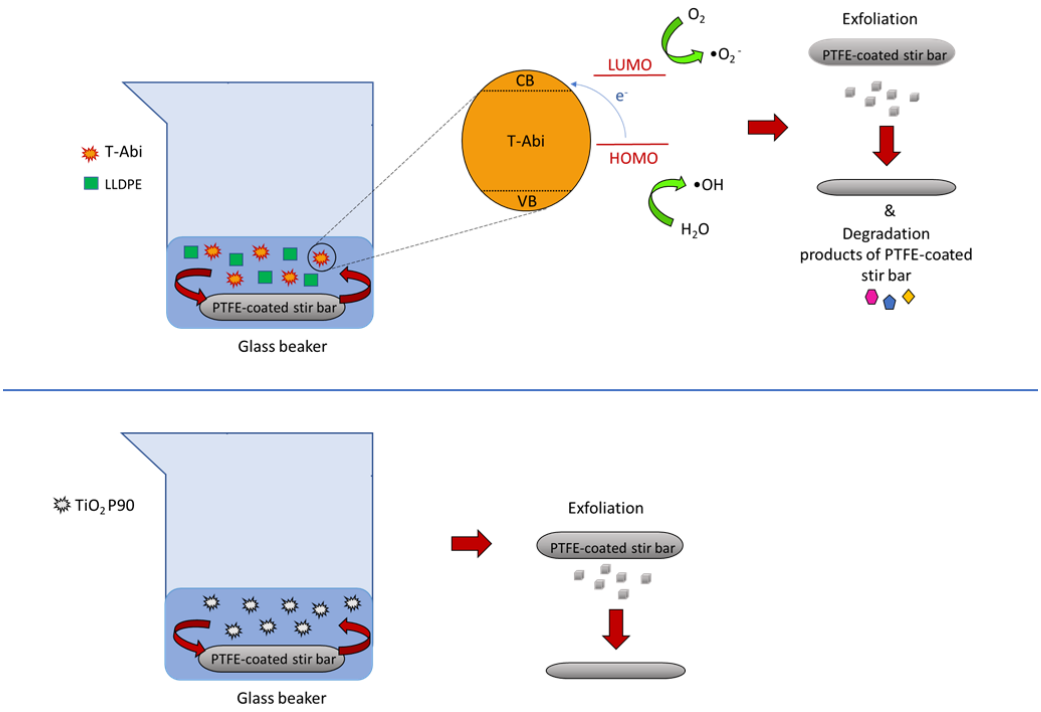


Figure 3. XPS survey spectra of the analysed samples. In the inset, a magnification of the C 1s region is shown, and the $R_C = C_{aliphatic}/C\text{-}F$ ratios are reported. X-ray source: Al kα.

The trend of the ratio (R_C) between the peak area of aliphatic carbon ($C_{aliphatic}$) and that of carbon linked to fluorine ($C_{C\text{-}F}$) provides intriguing indications. When LLDPE is absent, increasing the incubation time leads to an increase in R_C, confirming the progress of PTFE exfoliation and its subsequent deposition on the surface of T-*Abi*. However, at the same incubation time (1 month), in the presence of LLDPE, the R_C is much lower than that for T-*Abi*, indicating that the deposition of exfoliated PTFE on the surface of T-*Abi* is favored and, consequently, its degradation is disfavored in agreement with the GC-MS data as we have already shown (Amato et al., 2024).

In view of the above results, a mechanism for the physical exfoliation and related degradation phenomena is proposed, as illustrated in Scheme 1. The role of water may be crucial in both processes. The permeation of water and ions through nanochannels in the PTFE coating may weaken its structure, facilitating the surface erosion and consequent exfoliation (Pentsak et al., 2019; J. Zhang et al., 2023). The nanochannels and other structural defects formed in the PTFE coating may also allow the transport of reactive oxygen species (ROS) generated in aqueous solution to the inner layers of the material and the contact with ROS may assist the release and partial degradation of fluorinated organic components of the PTFE-coated stir bar. The redox-active species could derive from two main sources: the activity of T-*Abi* under indirect daylight conditions and a tribocatalytic effect. Specifically, T-*Abi* has a hybrid structure with Ti-abietate charge transfer complexes that promote the adsorption of O_2, its reduction to superoxide radical, $O_2^{\bullet-}$, and the stabilization of the latter at surface sites, as previously proven for similar hybrid TiO_2 systems by experimental and computational methods (Imparato et al., 2024; Ritacco et al., 2021). In water medium, hydroxyl radicals, $OH^{\bullet}$, are generated from $O_2^{\bullet-}$ and these species concur to oxidative processes without continuous light irradiation (Amato et al., 2024; Pirozzi et al., 2020). The same mechanism is expected to occur in this case, under the same conditions that allowed the surface chemical degradation of LLDPE.



Scheme 1. Schematic drawing of the physical and chemical degradation of PTFE in the presence of T-Abi (upper panel) and of the physical degradation of PTFE in the presence of TiO_2 P90 (lower panel).

Additionally, a semiconductor such as TiO_2 may act as a tribocatalyst, exploiting mechanical energy to separate electron/hole pairs (Cui et al., 2022; Mao et al., 2024), and a tribocatalytic activity was reported even for bare PTFE particles derived from stir bars (Wang et al., 2022) due to its high triboelectric charge density (Z. Wang et al., 2024; Zou et al., 2019). Here, the friction between PTFE bars, TiO_2 particles and the glass beaker results in PTFE exfoliation and the chemical degradation of fluorinated compounds can be ruled out. On the contrary, in the presence of the hybrid TiO_2 material, T-Abi, the ROS are stabilized, and they are responsible for the presence of fluorinated by-products in solution.

4. Conclusions

The exfoliation of the PTFE magnetic stir bars, a phenomenon that has recently gained attention in the literature, is now better elucidated. In this study this phenomenon is observed to be driven by a

strong tribological effect of TiO_2. Moreover, the evidence of the formation of degradation by-products originating from components of a PTFE-coated magnetic stir bar in the presence of a TiO_2-based hybrid material, T-*Abi*, is here provided. This discovery can be attributed to the strong oxidative activity of T-*Abi*, which is a result of the existence of superoxide radicals stably adsorbed on its surface, in conjunction with the intrinsic tribological activity of TiO_2. This study sheds some light on the stability of PTFE-coated stir bars used in contact with metal oxide particles in a water medium, suggesting the need of further investigations concerning the interactions between semiconducting solids, reactive oxygen species and fluorinated polymer materials.

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Supporting Information

Physical and chemical degradation of PTFE magnetic stir bars induced by TiO_2-based materials

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Materials and Methods

Materials

TiO_2 P90 (Evonik, CAS-No. 13463-67-7), titanium (IV) n-butoxide ($Ti(OBu)_4$, 97+ %, Sigma-Aldrich, and ethanol (EtOH, 99.8+%, Sigma-Aldrich) were used as received without further purification. As bio-waste commercial rosin was used. Films of linear low-density polyethylene (LLDPE) 150 µm thick (Flexirene FG 20 F) were supplied by Blu Plast s.r.l.

Synthesis of T-Abi hybrid material

The hybrid TiO_2-based material was obtained by a hydrolytic sol-gel route previously described (Amato et al., 2024). In a typical experiment, a solution containing 5 mL of $Ti(OBu)_4$, 20 mL of EtOH and 0.88 g of rosin (acting as a complexing ligand) was mixed with a solution containing distilled water and EtOH obtaining the following molar ratio Ti : rosin: ethanol: water = 1: 0.2: 24: 4. The final solution was stirred for 2 h and after ageing at room temperature for 24 h, it was centrifuged obtaining a light-yellow particulate gel, named T-*Abi* as abietic acid was the major component of the rosin, that was dried at 50 °C.

Structural characterization

The structural characterization was performed by Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and X-Ray Diffraction (XRD) experiments.

FTIR spectra were recorded in the 4000–400 cm^{-1} range (resolution of 2 cm^{-1}) both on pressed disks of powders, that had been previously diluted in KBr (1 wt%), using a Nicolet Instrument Nexus model (Thermo Scientific, Waltham, MA, USA) equipped with a DTGS KBr (deuterated triglycine sulfate with potassium bromide windows) detector.

X-Ray Diffraction (XRD) experiments were carried out with a Malvern Panalytical diffractometer (Malvern, UK) with a nickel filter and Cu Kα radiation.

X-ray photoelectron spectroscopy measurements were carried out using a Theta Probe spectrometer (Thermo Fisher Scientific, Walman, US) equipped with a monochromatic Al kα X-ray source ($h\nu$ = 1486.6 eV). The linearity of the binding energy scale of the spectrometer was periodically checked according to ISO 15472:2010. The samples were analyzed as pellet on copper biadhesive tape. Only the survey spectra were acquired for each sample, setting the pass energy to 200 eV. Under these conditions, the full width at the half maximum height of Ag $3d_{5/2}$ peak acquired during the spectrometer calibration, was found to be 1.5± 0.1 eV (energy resolution).

To compensate for sample charging a flood gun was used and the binding energy values were referenced to C1s of aliphatic carbon at 285.0 eV.

The spectra were processed with CasaXPS software (version 2.3.25PR1.0) (Fairley et al., 2021) and the quantitative analysis was performed starting from the Shirley-Sherwood background-subtracted areas of the peaks detected on the survey spectra, according to the first principle method, assuming samples' homogeneity. The details on the correction parameters applied to the experimental areas for the quantification are provided in (Berrettoni et al., 2015).

Identification of degradation by-products from LLDPE by GC-MS

The identification of degradation by-products was obtained by Gas Chromatography-Mass Spectrometry (GC-MS) according to the standard spectra of the NIST 1.7 library data.

GC-MS instrument used was a Perkin Elmer AutoSystemTMXLGC, equipped with a Programmed Temperature Split/Splitless injector, a Restek Rtx-5MS capillary column (5 % diphenyl-95 % dimethylpolysiloxane, 30 m × 0.25 mm, 0.25 µm) and, a Perkin-Elmer Turbo Mass Goldmass-spectrometer.

The following experimental conditions were adopted: the initial temperature of the column oven was held at 40 ◦C for 5 min, and then heated up to 285 ◦C at a ramping rate of 5 ◦C/min; helium was used as carrier gas; the mass spectrometric detection was performed using the 70 eV electron impact (EI) mode with an ionization current of 50 µA and an ion source temperature of 250 ◦C.

The qualitative analysis was conducted by recording the mass spectra in a full scan mode (m/z 50–1000).

Results

The external PTFE layer of magnetic stir bar used for 1 month in the suspension C (TiO_2 P90 in water, Figure S1a) appears in more points almost completely removed, whereas that used to stir the blank sample appears completely undamaged (Figure S1b).

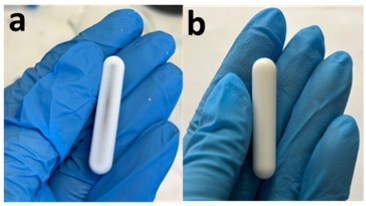

Figure S1. Comparison between PTFE magnetic stir bars that were used to stir for 1 month the suspension C (a) and the blank sample (b).

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