Tribochemical Degradation of Polytetrafluoroethylene in Water and Generation of Nanoplastics

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S *Supporting Information*

ABSTRACT: Polytetrafluoroethylene (PTFE) is probably the most extensively used chemically inert and thermally stable polymer. We report the degradation of PTFE in water in the presence of common metals and carbohydrates resulting in polymeric fragments. About 53 mg of solid materials consisting of polymeric fragments and copper was separated from a copper vessel in 15 days when a PTFE pellet of about 920 mg was stirred with 1000 ppm glucose in 70 mL of water at 70 °C. Degradation produced fluorocarbon species in water were detected by high-resolution electrospray ionization mass spectrometry. Triboelectric charging of the PTFE surface during stirring and consequent interaction of the charged surface with the metal ions, brought to solution by carbohydrate-induced corrosion, is attributed to this phenomenon. We show that such a process can be extended to other polymers such as polypropylene. The study suggests important consequences of nanoplastics to environment and health, including impact of such chemistry to cooking.

KEYWORDS: *Tribochemical degradation, Polytetrafluoroethylene, Nanoplastics, Dissolution, Polymer degradation*
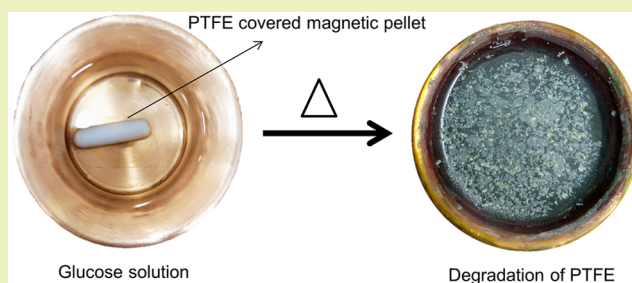
INTRODUCTION

Polytetrafluoroethylene (PTFE), commonly called Teflon, is regarded as the most common chemically inert synthetic polymer known to mankind.[1] Its stability in acids, bases, and at high temperatures has made it one of the most popular materials used to enhance durability of common appliances such as in kitchenware. There are very few reports on the degradation of PTFE due to its high chemical inertness. Kavan et al. degraded PTFE in the presence of highly reactive alkali metals (Li and Na).[2] In this Letter, we present experimental proof of significant degradation of PTFE in water in the presence of common metals and carbohydrates producing nanoplastics in solution. The onset of chemical reactions has also been observed through the detection of short fragments of PTFE in solution.

RESULTS AND DISCUSSION

The experiments performed (as described in the methods section) in which a PFTE covered pellet was stirred in glucose solution (1 mg/mL) of water in the presence of a gold foil, gave a red luminescent polymeric film (Figure 1 and Figure S1A) on the liquid surface after 30 days of reaction. We know that PTFE is not a luminescent material (Figure S2). Chemical analysis of the film by scanning electron microscopy/energy dispersive analysis of X-rays (SEM/EDS) confirmed that it is composed of PTFE with 0.04% Au (Figure S3C). Additional experiments were discussed below to prove that the film was composed of PTFE and gold. Bright red luminescence of the film implied the presence of Au−C bonding as several Au−C compounds exhibit such emission.[3,4] Gradual evolution of Au concentration in the solution (Figure S3B) from 1 ppb on day 3 to 15 ppb on day 30, confirms the glucose-induced dissolution of gold.

Similar degradation of PTFE occurred also with other metals (Cu, Zn, Ag, and Fe) in which a PTFE covered magnetic pellet was stirred in a vessel of metal, containing glucose solution. In every case, these polymeric films were separated and characterized using SEM/EDS, Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). Compositions of the floating films were similar to varying amounts of metals. Fluorine (39.95%) and copper (2.36%) were quantified by EDS mapping of the solid material separated from the copper vessel (Figure S4B). Microscopic localization of copper (1.17%) was observed in the cracks of the materials (Figure S5C). The existence of fluorine (43.09%) and zinc (1.27%) was confirmed by EDS of the zinc vessel-derived material (Figure S6B).

Similar results were obtained for other metal vessels, too (Figure S7). However, the films were non-luminescent unlike in the case of gold, as expected. Materials with the M−C bond
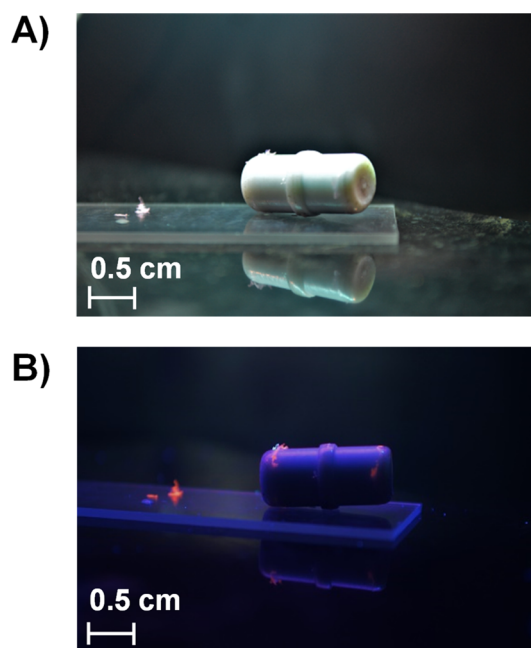
A)

B)

Figure 1. Photographs of the reaction product of PTFE and gold in the presence of glucose under (A) visible light and (B) UV light (mercury vapor lamp). The magnetic pellet pictured here has the reaction product attached on it. The reaction product found floating on the water was kept on the glass slide. The material was red luminescent under UV light.

(Cu−C, Zn−C) are not known to be luminescent under UV light. The thin films from the copper vessel were greenish-blue (Figure S1B) in color suggesting a high amount of Cu

incorporation into PTFE and probably Cu remains in its +2 oxidation state. The dissolution of metals and emergence of the polymeric film are related. The process occurred even at room temperature but upon longer time of reaction. As higher temperature also caused evaporation of water, we conducted the experiment at 60−70 °C as the process was monitored for weeks. Experiments were performed with PTFE samples of different sources (local and Sigma-Aldrich) and shapes (pellet, granules, and sheet) to ensure that these variations did not affect the results.

To get further information on bonding, Raman spectroscopy was performed for the material collected from copper and stainless steel vessels and the spectra were compared with that of pure PTFE. Peaks from the material obtained from copper and stainless steel vessels and pure PTFE are shown in Figure 2Aa,b,c, respectively. Peaks labeled as 1, 2, 3, 4, 5, 6, and 7 represent CF_2 wagging (1), CF_2 twisting (2), CF_3 symmetric deformation (3), CF_2 symmetric stretching (4), CF_2 asymmetric stretching (5), C−C stretching (6), and C−F stretching (7), respectively.[5] A new peak was seen at 472 and 473 cm^{-1} for copper and iron-containing samples, respectively which is absent in pure PTFE. About 1 cm^{-1} Raman shift was observed, which suggested the presence of different metals and chemical environments (Figure S8A). Independent Raman measurements were performed on the separated polymer from copper and stainless steel vessels to check the reproducibility (Figure S9). In a previous report, the Pt−C stretching mode was found in-between 470 and 500 cm^{-1}, depending on the ligand environment[6] which is in agreement with M−C bond formation in the examined materials. Shifts of 2 and 4 cm^{-1} were observed for C−C stretching (peak 6) for copper and
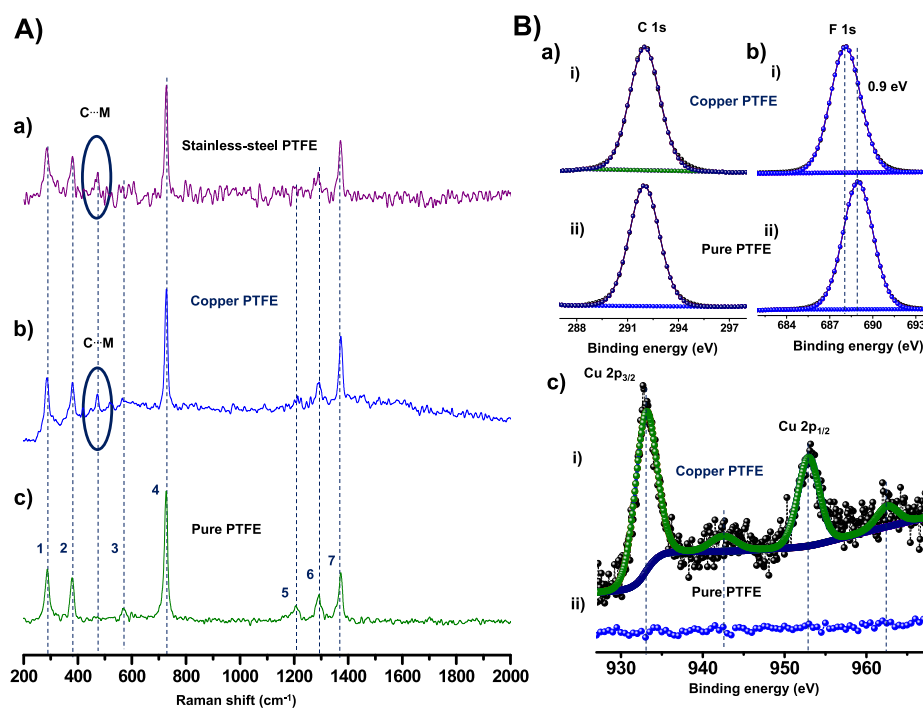

Figure 2. (A) Raman spectra of the polymeric materials derived from stainless steel (a) and copper (b) vessels compared with pure PTFE (c). Appearance of a new peak at 473 and 472 cm^{-1} were seen for stainless steel and copper-derived materials, respectively in addition to the PTFE features. Peaks 1, 2, 3, 4, 5, 6, and 7 are CF_2 wagging, CF_2 twisting, CF_3 symmetric deformation, CF_2 symmetric stretching, C−C stretching, CF_2 asymmetric stretching, and C−F stretching of PTFE, respectively. (B) XPS data to confirm the presence of carbon (a), fluorine (b), and copper (c) in the copper-derived material. Data for pure PTFE are also shown.
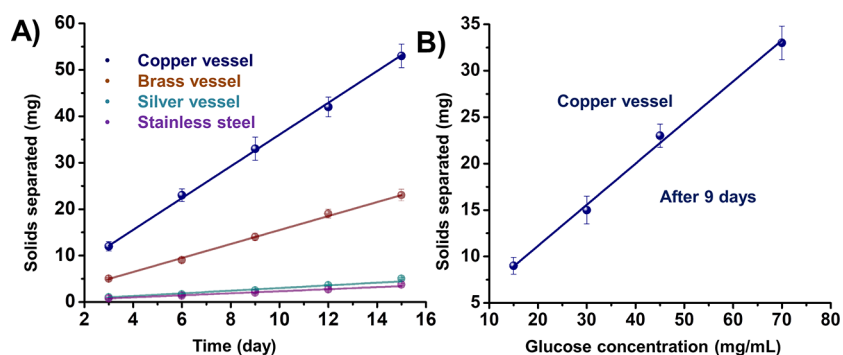
Figure 3. Mass of the solid material separated from different vessels plotted as a function of time (A). Mass of the material separated from the copper vessel as a function of glucose concentration (B).
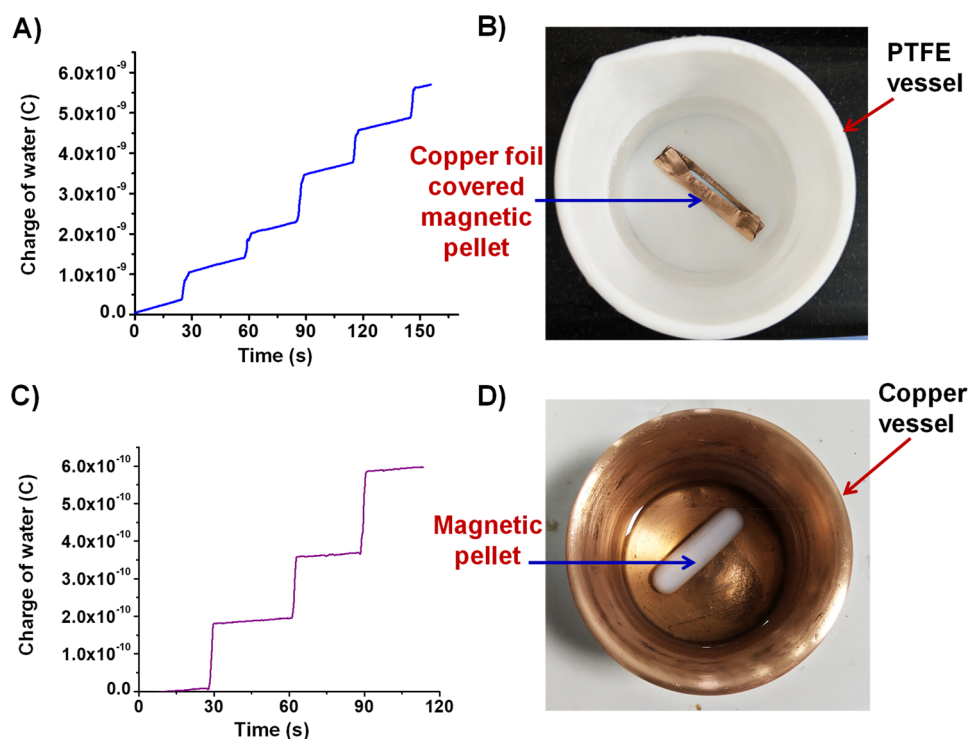

Figure 4. (A) Plot showing the positive charge acquired by the water in a PTFE beaker. (B) Photograph of the PTFE beaker containing 100 mL water with a magnetic pellet covered by a copper foil. (C) Plot showing the positive charge acquired by the water in the copper vessel. (D) Photograph of the copper vessel containing 50 mL water with a magnetic PTFE pellet. Charge was measured by dropping 1 mL of the water into a Faraday cup connected to an electrometer.

iron-containing samples, respectively compared to pure PTFE, as shown in Figure S10A.

XPS was performed as an alternate analytical technique to obtain elemental information. Peaks at 933.0 and 953.0 eV are attributed to Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively (Figure 2Bci). Presence of the satellite peaks due to configurational interaction at 943.0 and 963.0 eV confirmed the oxidation state of copper (+2). All the spectra were calibrated with C 1s and there was no significant change in the C 1s peak position for copper-derived PTFE compared to pure PTFE (Figure 2Bb). Both of them showed a strong signal for F 1s, further confirming the material to be composed of fragmented PTFE. While F 1s peak appeared at 689.0 eV for pure PTFE, the peak position got shifted to 688.1 eV in copper−PTFE which can be due to the M−C bond formation (Figure 2Bbi). Both Raman spectroscopy and XPS are in good agreement with M−C bond formation in metal-derived PTFE compounds.

Several control experiments were performed to understand the mechanism of such unusual reactivity of PTFE. A linear relation was found between the amounts of solid collected from each vessel with the reaction time (Figure 3A). About 53 mg of solid materials was isolated from the copper vessel after 15 days of reaction. The amount of separated solid materials decreased gradually from copper to stainless steel. A very similar trend was observed for the extracted metal ion concentration in the solution, which is highest for Cu and lowest for Fe (Table S1). A brief summary of the degradation of PTFE with metal ion concentration is provided in Table S1. At higher glucose and hence higher metal ion concentration in solution, the amount of solid precipitate also increased significantly (Figure 3B). Baksi et al. have shown the mechanism of the extraction of silver by glucose.[7] A similar type of degradation was observed when metal ions (Cu^{2+}) were added to the water in the absence of glucose (Figure S11). No

considerable degradation was found in the absence of glucose. The separated materials were colored in nature. These observations confirmed that metal ions play an important role in degrading PTFE and this phenomenon is not because of mechanical abrasions.

The reaction between the PTFE surface and metal ions may be responsible for the generation of M-PTFE products as suggested by the above-mentioned results. We propose that triboelectric charges generated[8] on the rotating PTFE-coated magnetic pellet may lead to reaction with metal ions on its surface to initiate the degradation. The triboelectric phenomenon was proven by measuring the charge accumulated in water as a result of the process of stirring the pellet. The experiment was conducted in two ways: (a) stirring a copper foil-covered magnetic pellet in a PTFE beaker (Figure 4A,B) and (b) stirring a PTFE pellet in a copper vessel (Figure 4C,D), in water. The extent of charge accumulated in water was larger in panel a as the area of the PTFE exposed was larger in it. An increasing positive charge in water was noticed in the course of stirring (Figure 4). From earlier studies, it was proven that when water was passed over a PTFE surface, the former acquires a positive charge and the latter acquires a negative charge.[9−11] The method used is outlined in Supporting Information. The acquired negative charge on the PTFE surface makes the metal ions to interact with it, resulting in degradation. Triboelectric degradation was further supported by the linear dependence of the amount of product on the glucose concentration in solution (Figure 3B), which in turn increased the metal ion concentration. Degradation of PTFE was not noticed without stirring, which also suggested that it is likely to be due to triboelectric phenomenon.

This reaction between the charged surface of PTFE and metal ions, termed as tribochemical reaction, results in metal−$(CF_2)_n$ bonding, which could destabilize certain C−C bonds, leading to their breakage. It is known that triboelectric charges accumulated at dielectric materials may cause reduction[12] or transfer[13] of palladium(II) and copper(II).

To understand the degradation products of PTFE in this process, we performed high-resolution electrospray ionization mass spectrometry (HRESI MS) of the solution derived from a copper vessel, after 15 days of reaction. While scanning the m/z range from 30 to 70, the presence of CF_3^+, C_3F^+, C_2F^+, and CF^+ were detected as shown in Figure 5 along with the isotopic peak of CF_3^+. Calculated and experimental mass spectra for CF_3^+ are given in the inset of Figure 5. These fragments confirm the chemical degradation of PTFE.

Similar results have been observed for a brass vessel (Figure S12). Fluorocarbon species were also obtained from a copper vessel in the presence of dissolved Cu^{2+} from $CuCl_2$ without glucose (Figure S13), confirming the need for metal ions and not sugar for the reaction.

As the concentration of these soluble fluorocarbon fragments were very less in the solution, other spectroscopic studies in solution such as nuclear magnetic resonance (NMR) were impossible. Similar results were obtained for other types of carbohydrates like cyclodextrins (Figure S14 and Figure S15).

Degradation of PTFE in the presence of metals generated nanoplastics in water. We observed 4−10 μm and 200−400 nm pieces of polymer particles in the solution. Transmission electron microscopy (TEM) images of the nanoplastics are shown in Figure S16. We have analyzed the TEM grid by SEM also. SEM image and EDS mapping information is provided in
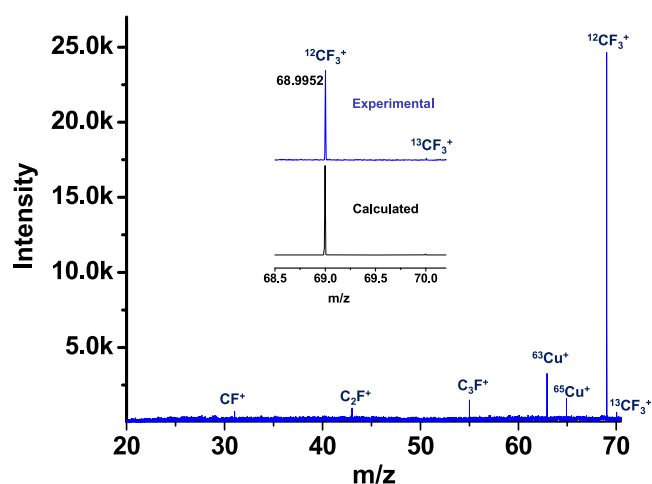

Figure 5. HRESI MS of the solution derived from a copper vessel. Presence of various fluorocarbon species in solution was identified by mass spectrometry. Inset of Figure 5 shows the calculated and experimental mass spectra of CF_3^+.

Figure S17. Presence of fluorine and copper were confirmed by EDS mapping.

Degradation of polypropylene was also noticed after reaction with glucose solution in a copper vessel (Figure S18). Raman (Figures S19 and S20) and SEM (Figure S21) studies confirmed the formation of plastic particles of polypropylene in solution.

Nowadays, PTFE is utilized as a coating for different cooking appliances. Presence of different metal ions in foodstuff and carbohydrates-induced dissolution of metals from the container could lead to fluorocarbon fragmentation, which may bring plastics into the solution.

As the process requires no high temperature, hard chemicals or additional activation, we believe that this method offers a new and greener strategy for polymer degradation.

■ CONCLUSION

In summary, we have investigated an unusual reaction between PTFE and various metal ions derived from bulk such as gold, copper, zinc, silver, and iron (stainless steel) in an aqueous solution of carbohydrates like glucose and cyclodextrins, leading to the degradation of the polymer. A red luminescent product was obtained by the reaction between gold and PTFE, and non-luminescent products were obtained for other metals. Presence of the M−C bond in such products was confirmed by Raman spectroscopy and XPS. Tribochemical reactions and interaction of metal ions with charged PTFE surfaces are proposed to be the possible pathways for the degradation of PTFE. HRESI MS confirmed the presence of small fragmented fluorocarbon species in water. We have detected nanoplastics in water that may lead to toxicity. The method presented was extended to polypropylene. We postulate that the method opens up greener strategies for polymer degradation. The impact of such chemistry on food through cooking practices points to the need for additional studies. We note that many of the non-stick cookware is coated with PTFE these days. High-temperature processing of foodstuffs containing metal ions could initiate such degradation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssusche-meng.9b03573.

> Materials and methods section, instrumentation employed, photograph of PTFE degradation, SEM/EDS of the PTFE−metal polymeric film, reactions of PTFE with metal ions, HRESI MS of the solution, TEM images of the nanoplastics after reaction, SEM/EDS of the plastics particles after reaction, reaction of polypropylene, Raman spectra of polypropylene, SEM/EDS of the copper-derived polypropylene polymeric film (PDF)

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Author Contributions
A.N. designed and conducted all experiments. A.B. supervised some of the experiments. J.G. carried out the XPS measurements. A.N. and V.K. carried out the charge measurements. S.B. carried out Raman measurements. B.M. carried out the TEM measurements. T.P. proposed and supervised the whole project.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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