

Impact of Digestion on Surface Microstructures of Microplastics

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Abstract

Recently, there have been more reports and concerns about microplastics from various media and journals in the world. Except for land and water pollutions, much attention has been given to the impact of microplastics on animal and human health. However, previous studies have shown that digestion could not affect the particles of various microplastics due to their stable behavior. This work focuses on the impact of artificial digestion on the surface microstructures of microplastics from well recognized popular sources such as PP, PE, PET, PS and PVC. SEM and AFM were used to study the impact of artificial digestion on the surface morphologies of microplastics; while ATR-FTIR and XPS were used to investigate the impact of artificial digestion on the chemical properties of the surface of the microplastics. There were no physical differences observed by both SEM and AFM. There were no significant chemical differences detected by both FTIR and XPS after treatment. The slight differences of resolved C1s spectra for PS and PET samples detected by XPS should be further investigated. The study results show that the digestion system could not decompose the microplastics. Generally, plastic particles are widely considered to be inert due to their low chemical reactivity.

1. Introduction

Plastics pollutions are traditionally considered as environmental issues[1]; they are more or less seen as pollution problems [2, 3]. More attention has been given to health issues recently in relation to pollution from microplastics[4, 5]. There have been a lot of news and reports about microplastics from various media and scientific journals recently in the world. The reports show that microplastics cause pollution in the soil [6], air [7], fresh water and sea [8]. For example, the tea made from the popular plastic tea bags in the market contains up to tens of billions of microplastic particles [9], and washing clothes can cause the release of microfibers to water[10], and more than 90% of the 39 different salt brands worldwide contain microplastics [11]. According to media reports, researchers have discovered "traces" of plastic particles in the Arctic and are shocked by the number. Although the Arctic is inaccessible, there are more than 10,000 plastic particles per liter of snow [12]. Recent researches have shown that various food products were contaminated with microplastic particles, indicating a widespread exposure [13–20]. Microplastics can be enriched in food chain and also introduced into foodstuffs through the air, indicating the ubiquitous presence of plastic particles [21, 22].

There is no uniform definition of microplastic size, but a well acceptable size range is between 100 nm and 5 mm. Plastic particles below 100 nm are commonly defined as nano-plastics [23, 24]. The particles below 150 μm in size are considered to be systemically bioavailable to humans, and particles below 4 μm can be taken up by intestinal cells [24, 25]. Hanvey et al [26] have tried initially to standardize analytical methods in order to better estimate human exposure. So far, how microplastics affect human health is still far from being fully understood. Plastic materials are usually considered as very unreactive chemically due to their large molecular sizes. A potential bioreactivity of microplastic particles is therefore more likely to be expected due to their increased surface-to-volume ratio with decreasing particle sizes due to their chemical properties. However, more recently, Stock et al [27, 28] systematically

investigated the impact of the gastrointestinal passage on the physicochemical particle characteristics of the five most produced plastics (PE, PP, PVC, PS and PET). The results showed that all the plastic particles were highly resistant to the artificial digestive juices, and the main stages of the human gastrointestinal tract did not decompose the particles.

In this work, it is hypothesized that artificial digestion may affect only the surface of the microplastics or the whole particles. This work focuses on the surface microstructures and chemical properties of these microplastics, particularly the variations in their atom scale and chemicals. The impact of artificial digestion on the microplastics was studied by SEM, AFM, XPS and ATR-FTIR. This is essential for a reliable future risk assessment of microplastics.

2. Materials And Methods

2.1 Materials

The microplastics, PP-MPs, PE-MPs, PS-MPs and PET-MPs with particles size of about 13 μm , and PVC-MPS with particles size of about 5 μm were obtained from Dongguan Tesulang Chemical Materials, China. The human salivary α -amylase(cat.no.1031), porcine pepsin(cat.no.P7012), pancreatin (cat.no.P7545) and bile(cat.no.B8631) were purchased from sigma-Aldrich. Sodium hydroxide solution (0.5N) was bought from Macklin, while hydrochloric acid standard solution (1N) was obtained from Aladdin. All the inorganic salts were purchased from Kermel, Macklin or Guangzhou Brand. All the chemicals are of analytical pure.

2.2 Preparation of stock solutions

In vitro simulating digestion process used in this work was based on Minekua [29] and Andre Brodkorb [30]. The simulated digestion consists of three phases: oral phase, gastric phase and intestinal phase. Electrolyte stock solutions, enzymes and water made up the Simulated Salivary Fluid (SSF), Simulated Gastric Fluid (SGF) and Simulated Intestinal Fluid (SIF). The corresponding electrolyte stock solutions of the digestion fluids are prepared and presented in Table 1 below.

Table 1
Composition of electrolyte stock solutions

Chemicals	SSF (pH 7)	SGF (pH 3)	SIF (pH 7)
Constituent	c[mmol L ⁻¹]	c[mmol L ⁻¹]	c[mmol L ⁻¹]
KCl	15.1	6.9	6.8
KH ₂ PO ₄	3.7	0.9	0.8
NaHCO ₃	13.6	25	85
NaCl	-	47.2	38.4
MgCl ₂ (H ₂ O) ₆	0.15	0.1	0.33
(NH ₄) ₂ CO ₃	0.06	0.5	-
CaCl ₂	1.5	0.15	0.6

2.3 Digestion treatment

All the electrolyte stock solutions (SSF, SGF and SIF) were firstly pre-heated to 37°C to achieve human body temperature. Dispersed 0.5 g of microplastics (PP, PE, PS, PET, and PVC) powder into 5 ml water respectively, then mix microplastics solutions with 5 ml SSF electrolyte stock solution, added salivary amylase into the mixture to reach 75U mL⁻¹ in the final mixture. It was incubated and then mixed in a water bath with integrated shaker at 37°C for 5 minutes. Oral bolus was mixed with 10 ml SGF electrolyte stock solution, then added porcine pepsin to achieve 2000 U/ml in the final digestion mixture. The hydrochloric acid standard solution(1N) was used to adjust the pH to 3.0. It was incubated and mixed at 37 °C for 2 h. Add 20 ml SIF electrolyte stock solution into gastric chyme to achieve a final ratio 1:1(vol/vol). Adjust the pH to 7.0 by adding sodium hydroxide solution (0.5N). Add the bile salt and pancreatin to the SIF/gastric chyme to reach a final concentration of 100 U/mL and 10Mm. Verify the pH and adjust to 7. Incubated and mixed the mixture at 37 °C for 2 h as gastric phases. The mixture was sieved and rinsed with ultrapure water 3 times, then dry the sample for later use.

2.4 Characterization of MPs

2.4.1 Scanning electron microscope (SEM)

The surface morphologies of the microplastic samples were studied by using the scanning electron microscope (Zesis EVO 18, German). The microplastics powders were held by a quadrilateral brass stub using a conductive resin. The samples were coated with Au under high vacuum conditions. The SEM observation was operated at an acceleration voltage of 10 KV and 2000 X, 10000 X magnification.

2.4.2 Atomic force microscopy (AFM)

The surface topography was studied by atomic force microscopy (Bruker-JPK Bio AFM, Germany). Particle solutions were dropped on monocrystalline silicon wafer and dried at room temperature. Then, they were placed on the sample stage. The standard mode for determining the height of the surface structures was applied for surface analysis. AFM imaging was conducted in an area of $30 \times 30 \mu\text{m}^2$.

2.4.3 Fourier transform infrared spectroscopy (FTIR)

FTIR was used to study the molecular structure of the particles and their chemical bonds. Spectrometer FTIR equipped with an attenuated total reflectance (ATR) was used to study the chemical properties of the microplastics. The ATR-FTIR spectra were observed using a Thermo Scientific iS50 ABX, USA. FTIR spectra were obtained at a resolution of 4 cm^{-1} with 64 accumulations in the range of $4000 - 600 \text{ cm}^{-1}$.

2.4.4 X-ray photoelectron spectroscopy (XPS)

The powder samples were placed on non-conductive tape to the sample holder and moved into a spectrometer fast entry lock chamber. The chemical compositions of the samples' surfaces and element oxidation states were determined by using X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD, Kratos, UK). XPS spectra were operated using Al K α radiation ($E = 1486.6 \text{ eV}$). All the binding energies were calibrated with respect to the C 1s peak at 284.8 eV [31].

3. Results And Discussion

3.1 Impact of artificial digestion on the surface morphologies of microplastics

The effect of the artificial digestion on the surface morphologies of the microplastics was studied using SEM and AFM. Figure 1 shows the SEM morphologies of the various microplastics before and after digestive treatment. It is seen that except for the PS microplastics with spherical particles, all the other microplastic materials (PE, PP, PET and PVC) originally had irregular shape particles; their diameters were between 1 and $20 \mu\text{m}$, which were well fed into the microplastic scale. PVC had the smallest particle size and clustered together. PS, PE and PP had reasonable smooth surface, while many deformations and fibers were observed on the surface of PET particles. After artificial digestion, all the microplastic particles kept their original particle size and morphologies. There is no damage phenomenon on the surfaces of the various microplastics, such as hole, fiber, rough surface or corrosion marks.

The surface images of individual PS particles were enlarged to study the impact of artificial digestion on the sample's surfaces in detail. The particles before and after treatment show similar morphologies: reasonable smooth surface with some marks probably from processing. There are no differences or damages observed. All the other microplastics have similar phenomena: there is no morphological difference observed, no holes, deformation stress, fiber, rough surface or corrosion marks was detected. This indicates the artificial digestion could not damage these microplastics.

AFM provides high-resolution images that show the microstructure and surface morphology of molecules directly by measuring the interactive forces between the probe and atom. Fig. 2 shows the typical AFM

images of PET based on a, a+) height retrace image; b, b+) amplitude Retrace image and c, c+) 3D image respectively. AFM revealed the surface characteristics and particle sizes of the samples. The results indicate that the artificial digestion generally did not affect the surface roughness of the samples. There were no significant differences between the surface structure and roughness of the PET microplastics before and after treatment.

The height retrace image was used to present the image in detail. Figure 3 shows the height retrace image of the various microplastics before and after treatment. It is seen that there is no observable difference. There are no damage phenomena such as holes, fiber, rough surface or corrosion marks observed. The results corresponded with SEM observation (see Fig. 1). Both results indicated the artificial digestion could not change the particle sizes and morphologies as well as the surface microstructures of the samples.

3.2 Impact of artificial digestion on the chemical composition of the samples' surface

The impact of artificial digestion on the chemical composition of the samples' surfaces was studied by ATR-FTIR and XPS (see Fig.4). The ATR-FTIR curves provide all the microplastics before and after treatment. The study particularly focused on the ranges of $4000\text{--}600\text{ cm}^{-1}$ wave-lengths. The spectrum of PE particles before and after treatment showed characteristic molecular vibrations at 2950 cm^{-1} , 1460 cm^{-1} and 720 cm^{-1} , representing the C-H bond. The spectrum of PP particles before and after treatment presented peaks at 1460 cm^{-1} and 1378 cm^{-1} referred to $-\text{CH}_2$ bending vibration and $-\text{CH}_3$ bending vibration. The bands at 970 cm^{-1} and 1155 cm^{-1} were assigned to $[\text{CH}_2\text{CH}(\text{CH}_3)_n]$ functional group. The FTIR spectrum of PVC particles before and after treatment displayed characteristic bands at around 2920 cm^{-1} ($-\text{CH}_2$ asymmetric stretching vibration mode), 1430 cm^{-1} ($-\text{CH}$ bending vibrations bond of CH_2), 1250 cm^{-1} (C-H bending vibration near Cl), 1100 cm^{-1} (C-C stretching vibration), and 960 cm^{-1} ($-\text{CH}$ wagging vibration). The peak in the range of $600\text{--}700\text{ cm}^{-1}$ was attributed to the C-Cl stretching vibration. In the FTIR spectrum of the PS particles before and after treatment, the peaks in the range of $2900\text{--}3000\text{ cm}^{-1}$ were related to $-\text{CH}_2$ asymmetric and symmetric stretching vibration; and the bands at 1600 cm^{-1} , 1493 cm^{-1} , 1460 cm^{-1} and 760 cm^{-1} were assigned to aromatic rings. The FTIR spectrum of PET particles before and after treatment showed a characteristic C=O at approximately 1715 cm^{-1} and a typical C-O-C stretching vibration at approximately 1100 cm^{-1} and 1250 cm^{-1} ; the bands at 725 cm^{-1} and 875 cm^{-1} were assigned to aromatic rings. Based on the above results, it is seen that there is no observable difference for all the samples before and after treatment. There are no new peaks, weakened peaks or shift peaks detected, indicating no chemical reaction was detected.

As organic polymers, carbon and oxygen were used to present the variation of the chemical impact by XPS. Both carbon and oxygen elements can be clearly detected for all samples. There are no new peaks, weakened peaks or shift peaks detected, indicating no chemical reaction was detected. Table 2 lists the detailed data. It is seen that the atomic percentages of carbon to oxygen on the various microplastics

display no remark difference before and after artificial digestion treatment. The results corresponded with ATR-FTIR results.

Table 2
XPS results of atomic concentration

Samples	%C	%O	%Cl
PE	94.01	5.99	–
Treated PE	93.71	6.29	–
PP	96.16	3.84	–
Treated PP	92.44	7.56	–
PVC	86.41	4.15	9.24
Treated PVC	84.47	4.74	10.79
PS	79.54	20.46	–
Treated PS	78.78	21.22	–
PET	83.28	16.72	–
Treated PET	83.23	16.45	–

As carbon-based materials, the carbon peaks C1s of these samples were deconvoluted according to their binding energy to study the impact in detail [32–34]. Figure 5 shows the deconvoluted carbon peaks detected by XPS for the various microplastics. The peak C1s for the microplastics were deconvoluted into 2 or 3 peaks at corresponding binding energy, which represents different chemical bonds of the carbon element. C1s spectra were deconvoluted at the peaks of 284.8 eV (C–C/ C–H), 286 eV (C–O), 289 eV (C=O) and 287 eV (C–Cl) respectively. It is seen that there are no obvious changes in the position of binding energies, peak number and shape of the deconvoluted carbon spectra for each microplastic before and after treatment. There is no prominent change of the intensity for the C–C, C–O bonds in PE, PVC and PP microplastics, which confirmed that artificial digestion has no impact on the microplastics. The results correspond with ATR-FTIR analysis. It is observed that the peak areas of C=O for PS and PET samples are slightly different after treatment. The peak area of C–O for PET also decreased. The fluctuation of the proportions of C=O and C–O bonds can be attributed to the additives in the polymer or the partial oxidation of the surface of the microplastic PET [35]. It could also be the error of measurement or divided processing and calculation since XPS is a quality other than quantity technology in many cases. The details will be investigated in our future work.

Table 3
High resolution carbon XPS analysis of the various microplastics before and after artificial digestion treatment

	CC/CH	C-O	C=O	C-Cl
PE	91.2	8.8	–	–
Treated PE	91.5	8.5	–	–
PP	96.2	3.8	–	–
Treated PP	93.9	6.1	–	–
PVC	57.1	–	–	42.9
Treated PVC	59.1	–	–	40.9
PS	72.4	18.6	9.0	–
Treated PS	67.6	25	7.4	–
PET	72.3	19.2	8.5	–
Treated PET	83.2	10.9	5.9	–

4. Discussion

Based on the above results, it can be concluded that there are no observable differences or damage phenomena observed by both SEM and AFM, such as holes, deformation strength, fiber, rough surface or corrosion marks for all of the microplastics used in this work. Regarding the surface chemistry, there are no new peaks, weakened peaks or shift peaks detected by ATR-FTIR or XPS, indicating no chemical reaction was detected. The results indicate that artificial digestion could not affect these microplastics.

Plastic materials are usually considered as chemically unreactive due to their large molecules even in micro-size particles. The results demonstrated a high resistance of all the plastic particles to the artificial digestive juices, and the main stages of the human gastrointestinal tract did not decompose the particles. Previous articles that report the adverse effect of digestive juice on microplastics are limited, and the research of consequent toxicity is in its infancy as well. Stock et al [28] showed that human gastrointestinal tract did not have adverse effect on particle sizes and shapes of microplastics. They revealed that the uptake of microparticles by intestinal epithelial cell line is dependent on the material and size of particles; it is only when exposed to high concentrations that is more than dietary exposure, microplastics would lead to cytotoxic effects. The cellular uptake of small amounts of PS microplastics, and PS particles do not pose health risk to mammals under the corresponding experimental conditions.

It is expected that the nanoparticles from plastics could be harmful to man's health since the nanoparticles can penetrate into cells [36]. Recently, Wang et al [37] investigated that nano-size polystyrene which was transformed by artificial gastric fluid greatly damaged hepatocytes. Actually, all materials can be in nano-size naturally and their effect on human health are complex and not understood. Hence, the present study did not discuss the impact of nano-particles on man's health.

Finally, it should be pointed out that all the microplastics used in this work are artificially made through granulating virgin materials as done in most previous reports. Practically, it is hard to collect the real microplastics from nature and identify their years. It is expected that the actual microplastics in nature may have different molecular weight and molecular weight distribution; they might even have slightly different chemicals, such as less plasticizer content or contain some by products through decomposition. The future work should consider this factor.

5. Conclusion

Both SEM and AFM studies show that the artificial digestion could not change the particle size and morphologies as well as surface microstructures of all the microplastics PE, PP, PVC, PS and PET used in this work. There is no observable difference or damage phenomenon observed, such as holes, deformation strength, fiber, rough surface or corrosion marks. The results indicate that artificial digestion could not change these microplastics. The impact of artificial digestion on the chemical composition of the samples' surface was investigated by ATR-FTIR and XPS. The results showed that there are no new peaks, weakened peaks or shift peaks detected, indicating no chemical reaction was detected. The results indicate that there is no chemical reaction or damages from the treatment. It is observed that the intensity of C = O peak detected by XPS was slightly weakened for PS and PET. The contents of C-O of PET also decreased. The fluctuation of the proportions of C = O and C-O bonds can be attributed to the additives in the polymer or the partial oxidation of surface of PET and PS microplastics particles. These results should be further investigated.

Declarations

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Data availability: The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Code availability: Not applicable

Authors' contributions: Conceptualization, Methodology, Writing-original draft, Supervision, Formal analysis and Writing-review & editing: LY. Conceptualization, Investigation, Methodology, Data curation, Formal analysis, and Writing-original draft: HC. Funding acquisition, Project administration, and Supervision: HSL. Investigation: FYC. Investigation: ZYZ. Investigation: ZJL. Supervision: LC.

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Figures

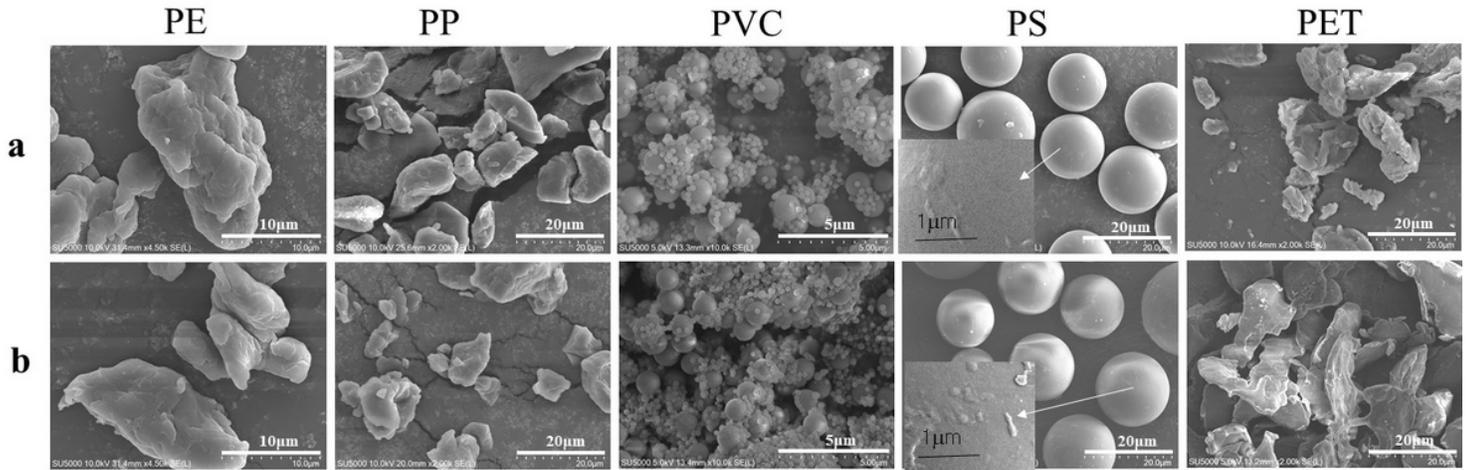


Figure 1

SEM morphologies of the various microplastics before (a) and after treatment (b)



Figure 2

Typical AFM images of PET microplastics before (a, b, c) and after (a+, b+, c+) artificial digestion treatment: height retrace image (a, a+), amplitude Retrace image (b, b+) and 3D images (c, c+)

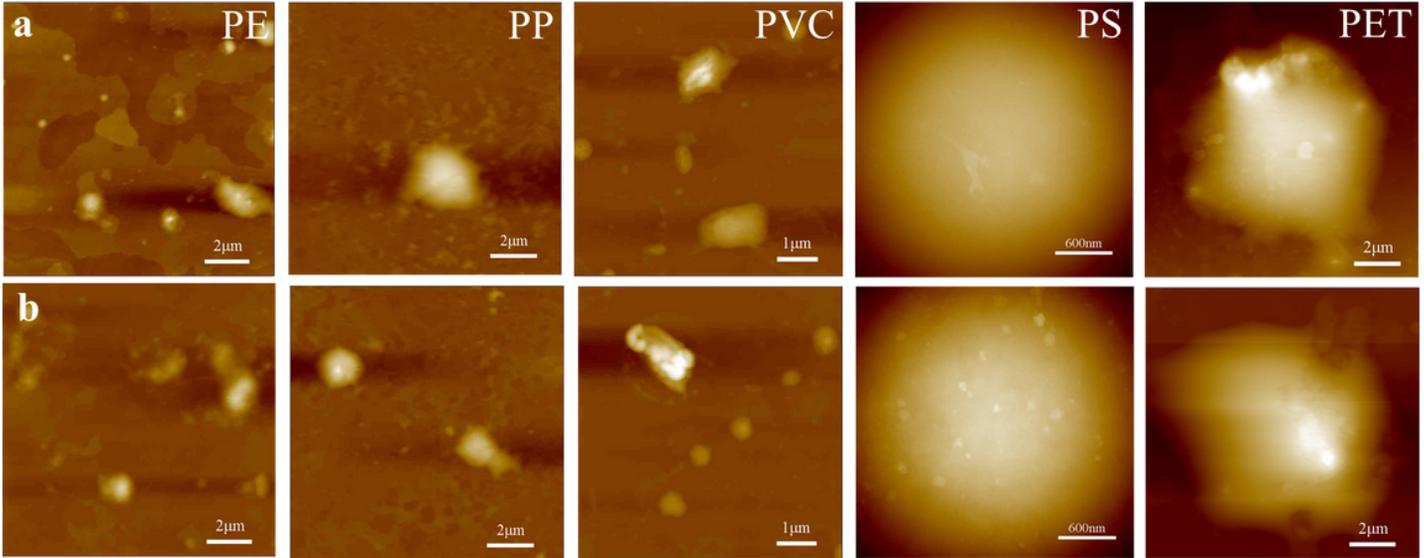


Figure 3

AFM images of the various microplastics before (a) after (b) artificial digestion treatment

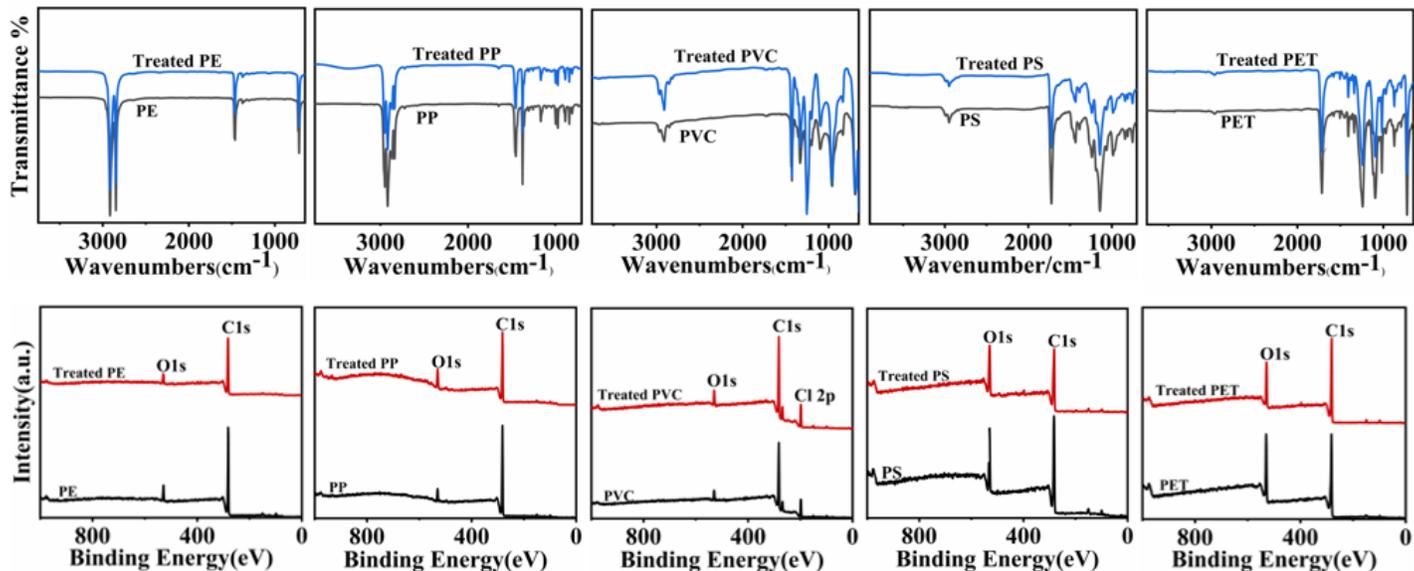


Figure 4

ATR-FTIR (top) and XPS (bottom) curves of the various microplastics before and after artificial digestion treatment

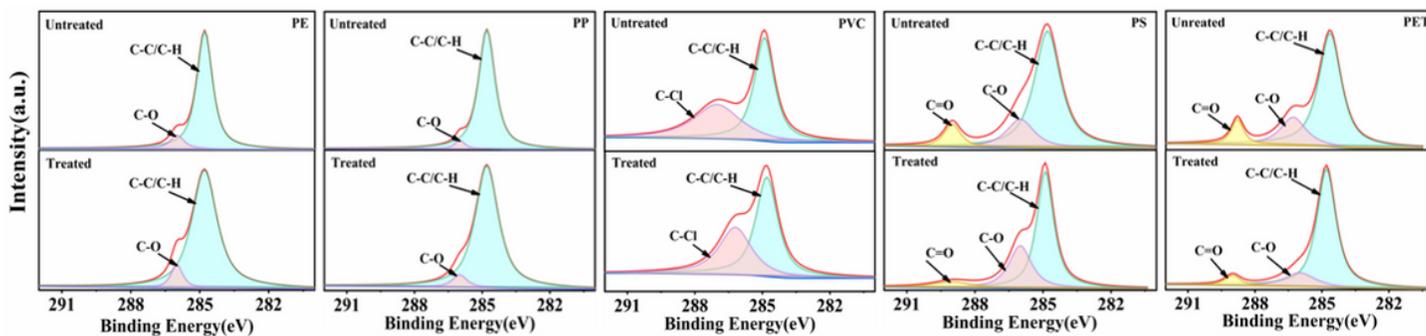


Figure 5

Deconvoluted carbon peaks detected by XPS for the various microplastics before and after artificial digestion treatment