Microplastic Release from E-Beam Sterilized Polymeric Materials Used in Contact with Aqueous Fluids

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ABSTRACT ID 186

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Release of Microplastics in Water and its Implications on Human Health

- Microplastics, tiny plastic particles measuring less than 5 millimeters in size, have emerged as a significant environmental concern worldwide. There are various reports and research papers examining the environmental impact of microplastics from various sources and exploring potential mitigation strategies to address this pressing issue.

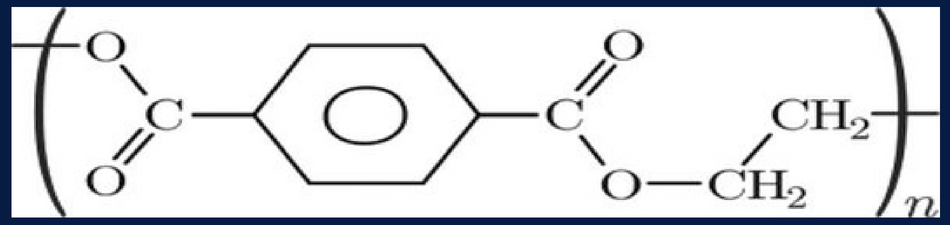
- Microplastics in breast milk samples.
  (Polymers 2022, 14, 2700. https://doi.org/10.3390/polym14132700)

- Microplastics enter the human gastro-intestine by the direct ingestion via, contaminated nourishment or beverages, causing a daily intake of microplastics by the human body.
  (Water Research 188 (2021) 116519)

- Microplastic exposure via ingestion or inhalation affects the human health. (Water Research 155 (2019) 410-422)

Polyethylene Terephthalate (PET)

- Among the various types of microplastics, those derived from polyethylene terephthalate (PET) are of particular interest due to the widespread use of PET-based products in various industries, including packaging, textiles, and consumer goods.
- PET is a thermoplastic polyester synthesized by polycondensation of ethylene glycol and dimethyl terephthalate
- It is crucial in food packaging due to its high-strength barrier and thermoforming abilities
- It's also extensively used in the medical field for its unique physical and biological properties
- PET's properties like resistance, crystallinity, and biostability make it ideal for medical implants



Chemical Formula of $PET(C_{10}H_8O_4)n$

Rationale: Irradiation Effects on Polymeric Materials

Polyethylene Terephthalate (PET)

⬇

Electron Beam Irradiation ➡

01

Destroys microorganism present on the surface of Polymeric PET Material

02

Changes in polymer structure due to crosslinking, chain scission and degradation of functional group leading to deterioration.

03

Causes Changes in the Physical and Chemical properties of the PET.

04

PET/Release of micro plastics in iaqueous fluids which may act as vector.

E-Beam Effects on Polyethylene Terephthalate (PET)

Main Objective: To investigate how damage induced by E-Beam enhances microplastic release and subsequent microbial growth

Two possible approaches:

01

Increase Ebeam Dose

02

Prolonged Exposure of polymer to water

Electron Beam Facility at BRIT Mumbai

Board of Radiation and Isotope Technology (BRIT) Mumbai

Details of Irradiation Parameters
Specifications of Electron Beam Facility

- E-beam Energy: 3.5 MeV
- E-beam Current (Pulse Current): 250mA
- E-Beam Average Current: 1mA
- Pulse Repetition Rate: 10 Pulses/ Second, 10Hz,
- Dose Per Pass: 5kGy Per Pass
- Dose Range: 5 kGy, 25 kGy, 50 kGy, 75 kGy, 100 kGy
- Size of Sample: A4 Size Sheet

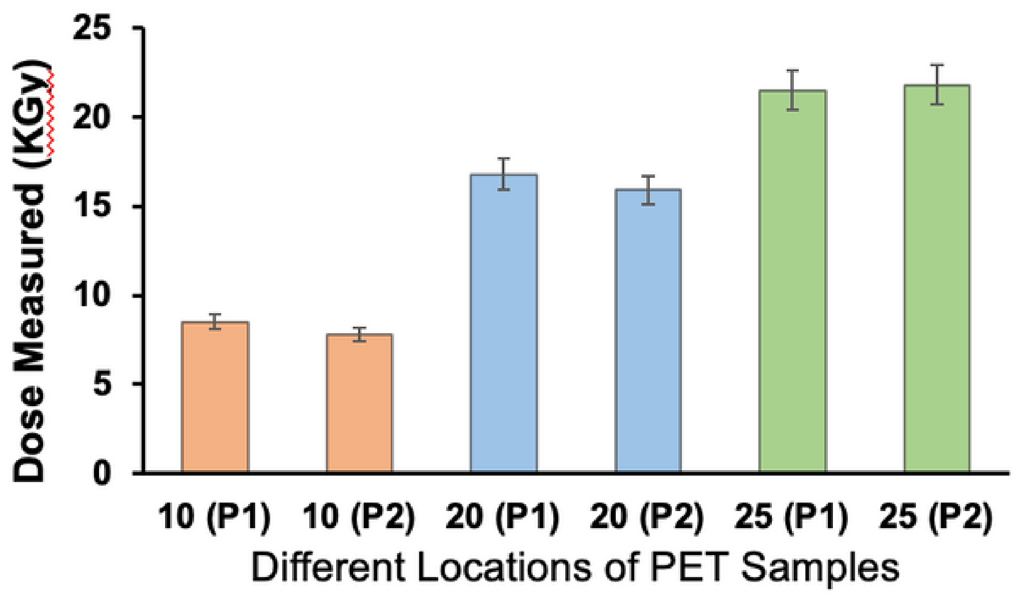
Electron Beam Irradiation of PET Samples

***Electron Beam Facility at BRIT Mumbai**: Board of Radiation and Isotope Technology (BRIT) in Mumbai houses an Electron Beam Facility for research and experimentation.*

Dose Monitoring in E-Beam Irradiation of PET Samples

Variation of Experimentally Monitored Dose using Radiochromic B3 films at top and bottom of the samples at different locations in Tray with Different kGy Sterilization Dose

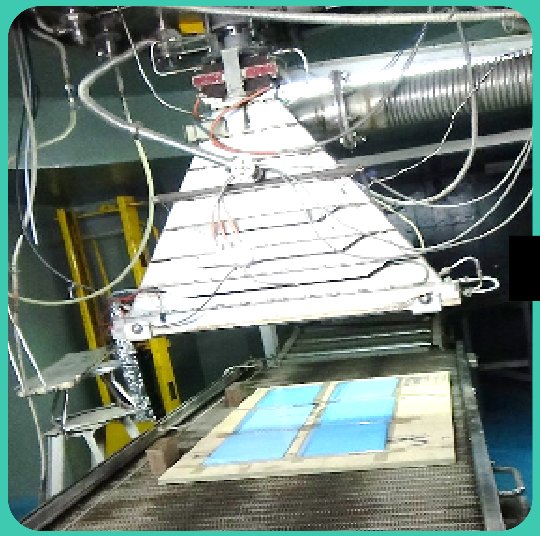
Dose expected (kGy) (position)	Dose measured (kGy)
10 (P1)	8.5
10 (P2)	7.8
20 (P1)	16.8
20 (P2)	15.9
25 (P1)	21.5
25 (P2)	21.8



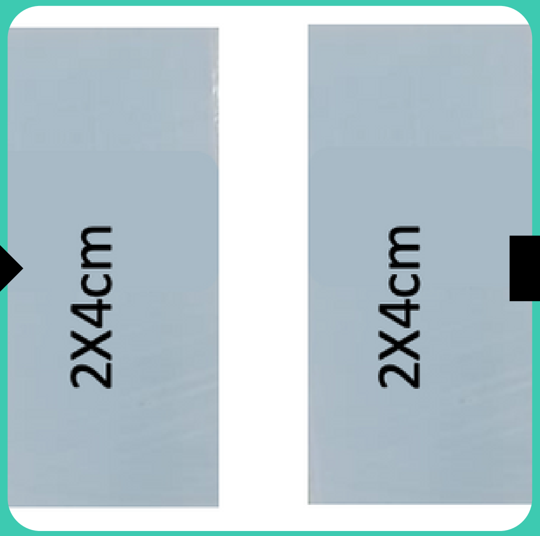
Similar Experiments were done for Irradiation of PET with E-Beam with 50, 75 and 100 kGy of Sterilization Dose.

- Radio chromic B3 film dosimeters supplied by GEX Corporation were used as dosimeters
- B3 film dosimeters have thickness of 17.8 mm and its response is independent of dose rate
- The useful range of B3 film is in the dose range of 1 to 80 kGy
- B3 Films were annealed at 60°C for 5 min immediately after irradiation
- The Optical Absorbance of B3 film dosimeters was measured at 552 nm with a UV spectrophotometer

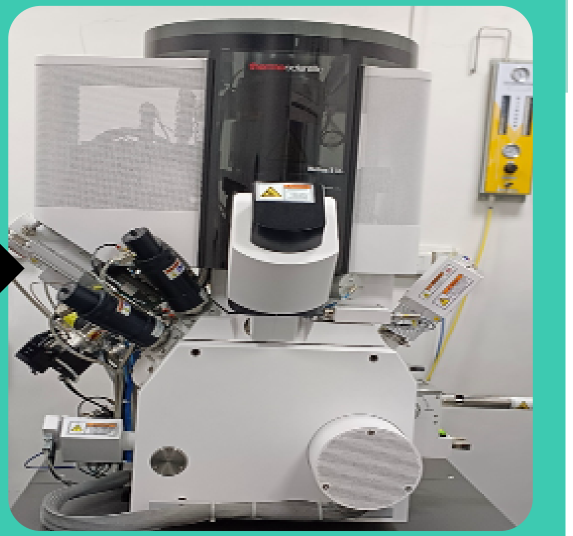
Experimental Setup & Methods



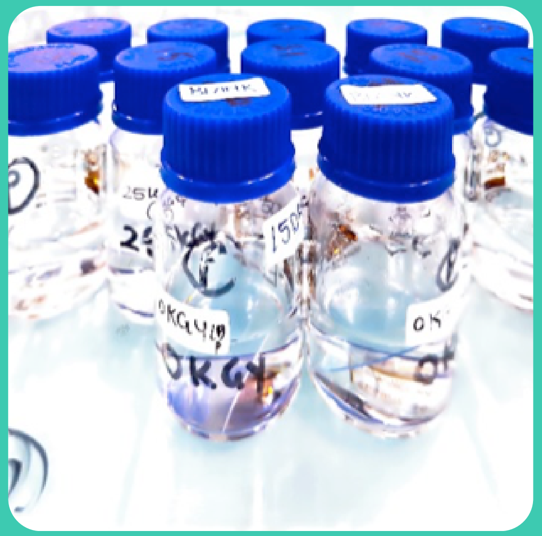
E-Beam Irradiation PET



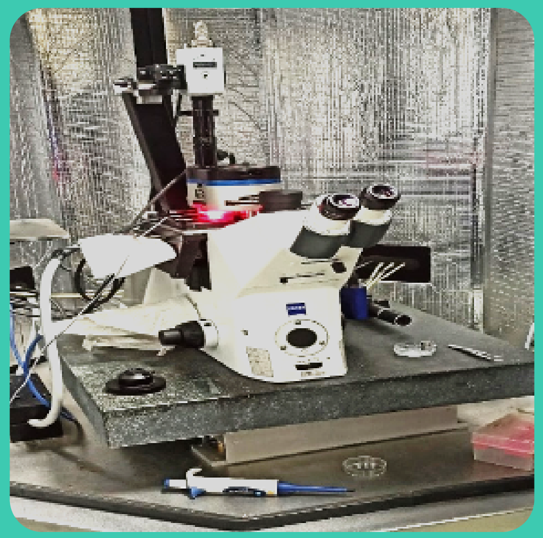
PET Sample size



Focused Ion Beam Scanning Electron Microscope



Water Exposure of PET



Atomic Force Microscope

Microplastics Release in Water from E-Beam Irradiated PET

Steps to Test Microplastics Release:

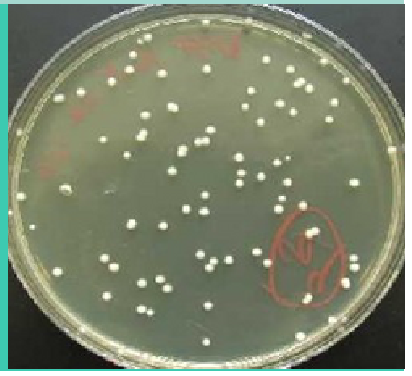
E-Beam Irradiated PET
(2 x 4 cm) at 0, 25, 50, 100 kGy.
Exposed for 10 days in 40 mL water

20 mL water in contact with PET was centrifuged for 15 min

Drops casted on Carbon paste base, and coated with Platinum sputtering (4 nm)

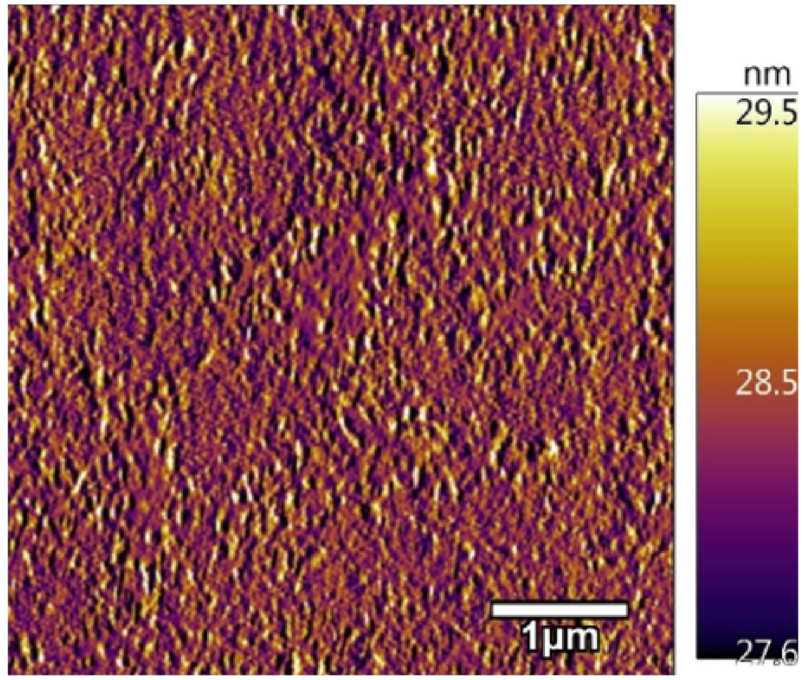
20 mL water in contact with PET was subjected to microbial study

Microbial Adherence & Retention

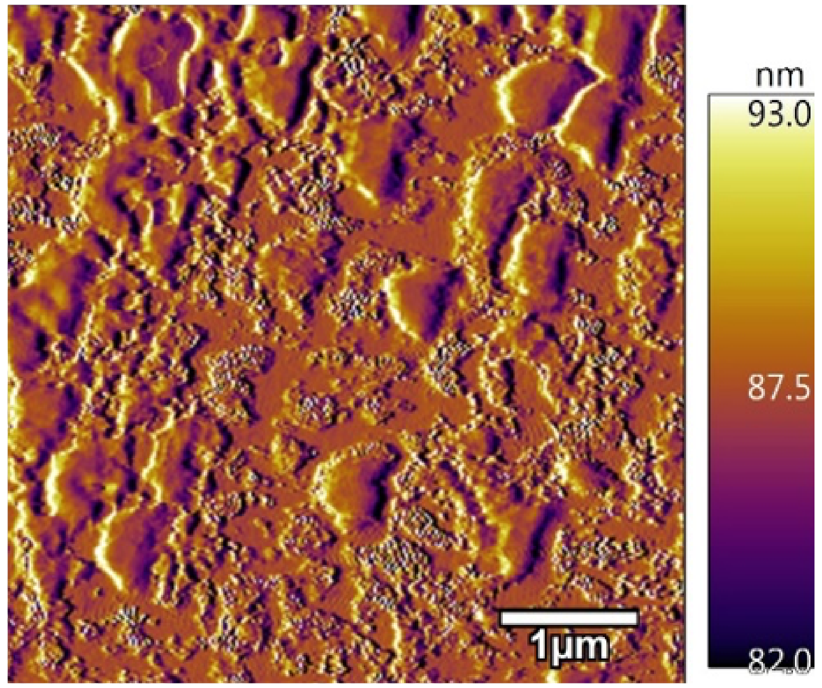


Observation under AFM & FIBSEM

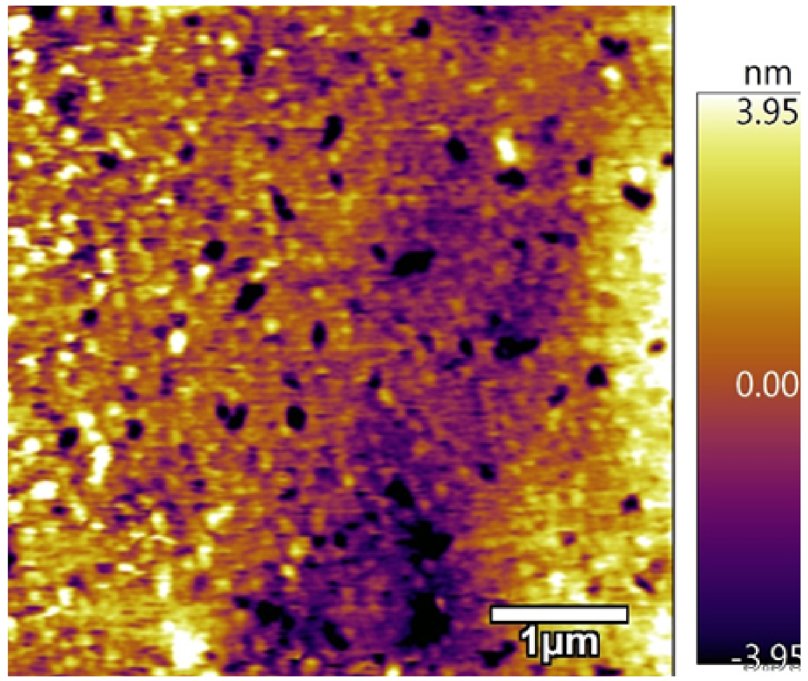
Irradiated PET Atomic Force Microscopic Image Profile



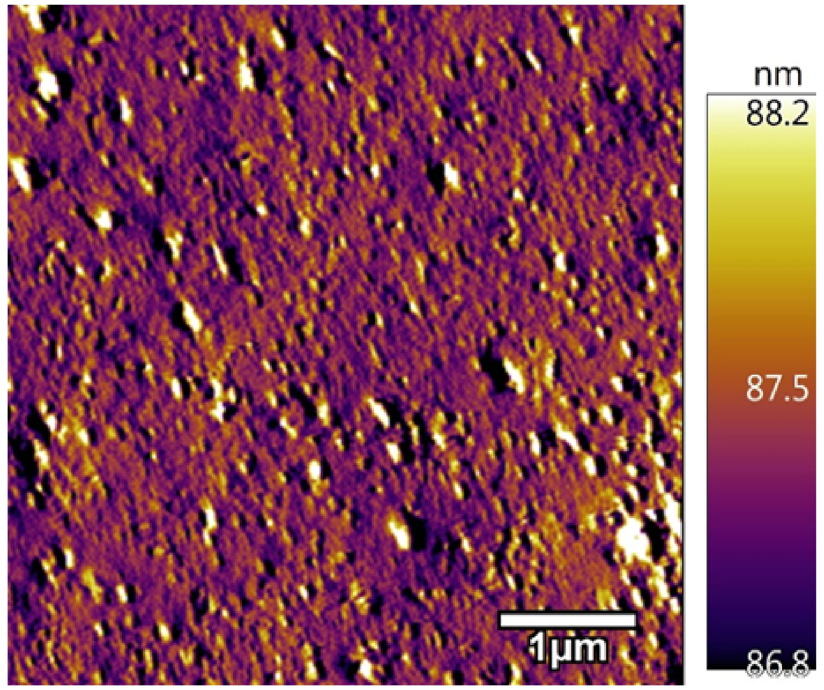
0 kGy



25 kGy



50 kGy

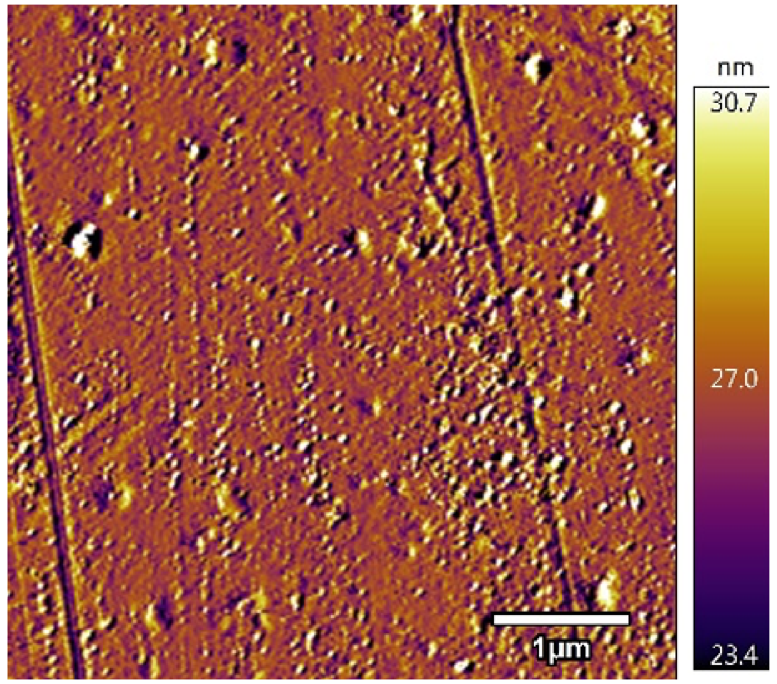


100 kGy

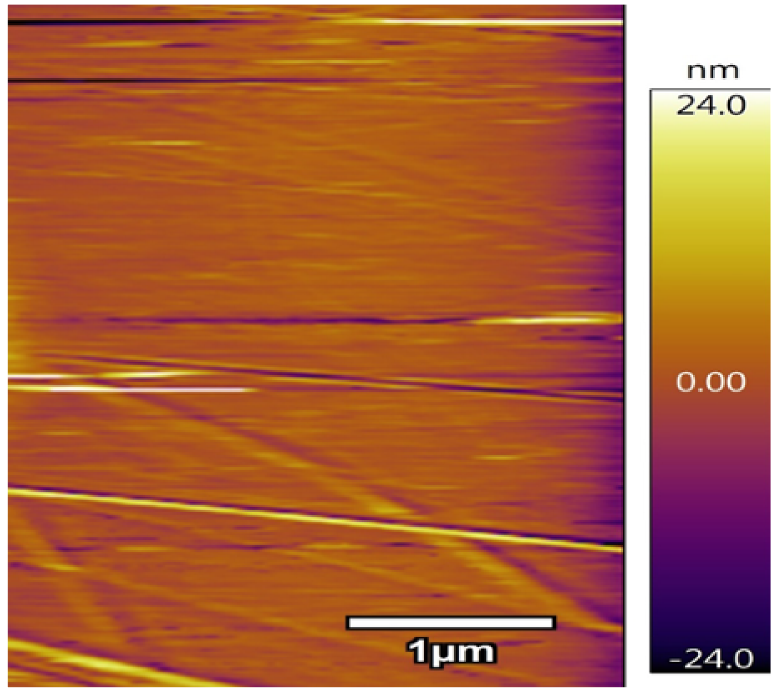
Physical Changes on PET / Morphology: By AFM

- As increase in dose Physical Changes observed and Morphology has changed and become more rough at 25 kGy w.r.t. pristine surface
- On further increasing dose to 50 kGy, crosslinking and PET chain scissions resulted to shrinking of polymer matrix and formation of pores
- At higher dose of 100 kGy, surface matrix again became nanostructuredhomogeneous due to shortening of polymer chains

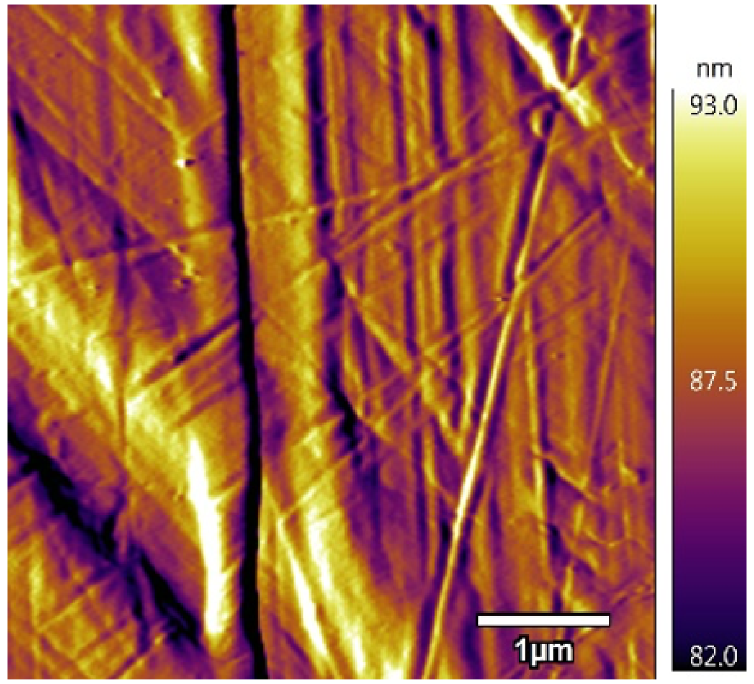
Irradiated & Water Exposed PET AFM Image Profile



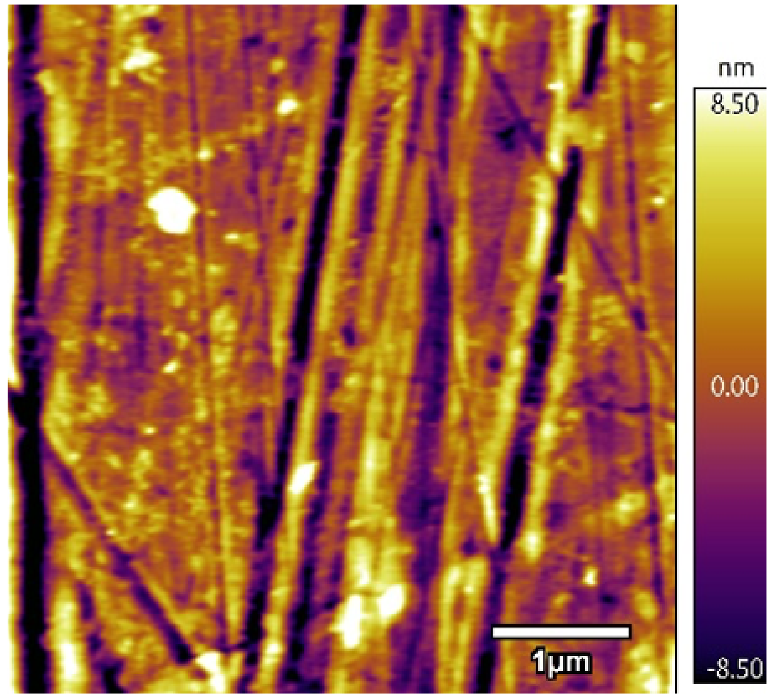
0 kGy



25 kGy



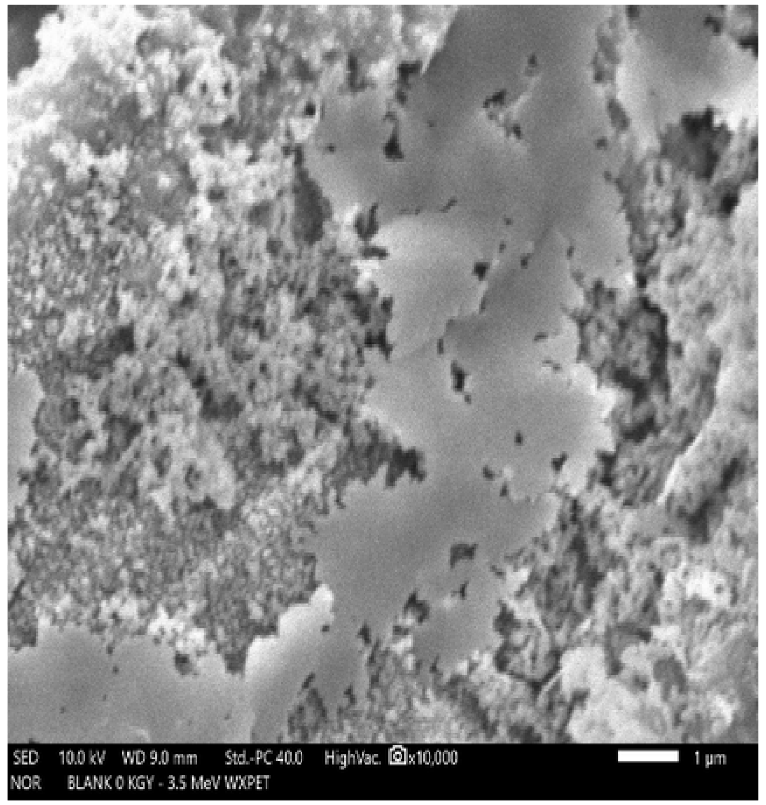
50 kGy



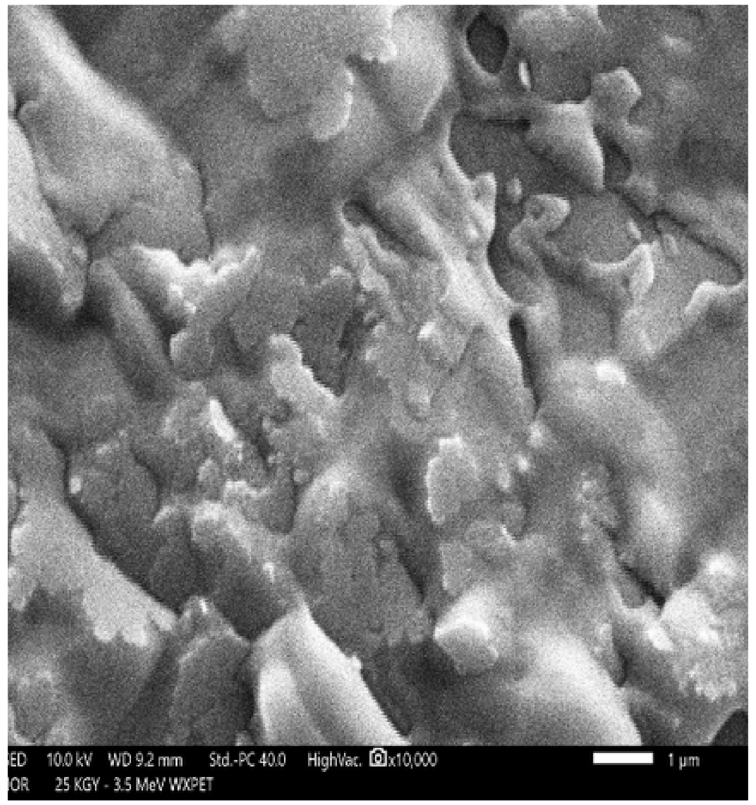
100 kGy

- After immersion of PET samples in water, the surfaces were changed significantly suggesting loss of materials in the form of microplastics in equilibrating water
- The change of surface morphology was minimum in pristine sample

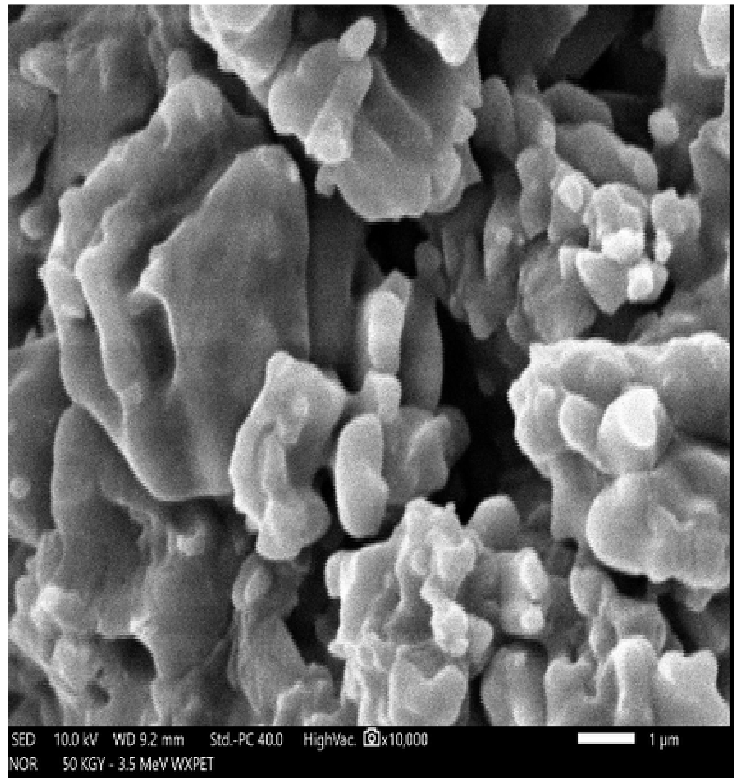
The Focused Ion Beam Scanning Electron Microscope (FIBSEM)



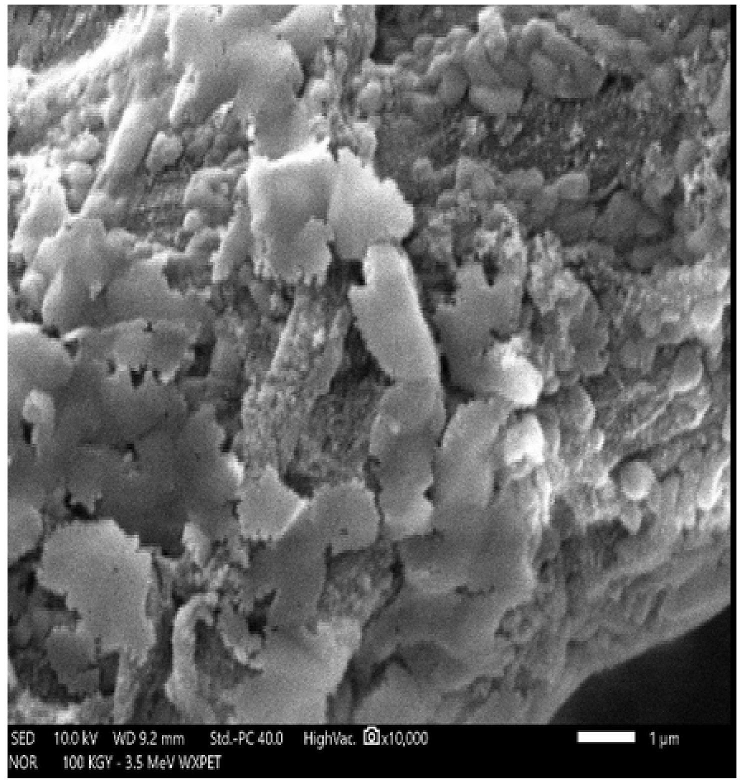
Blank PET



25 kGy Water Exposed PET



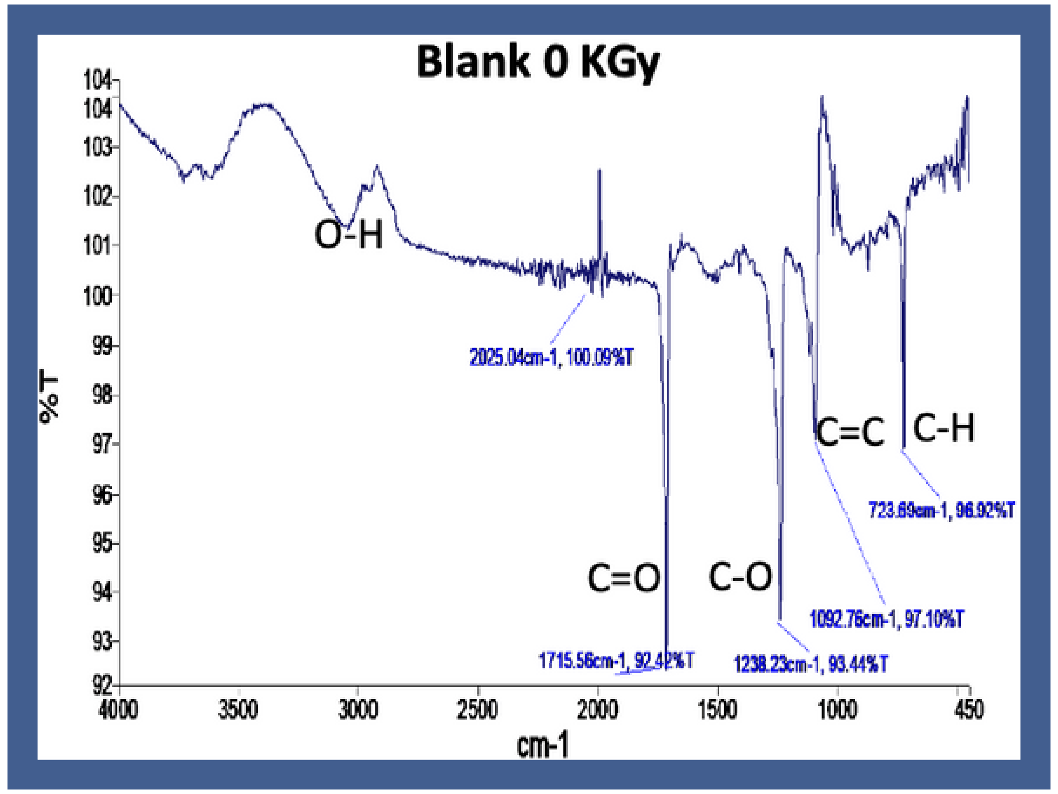
50 kGy Water Exposed PET

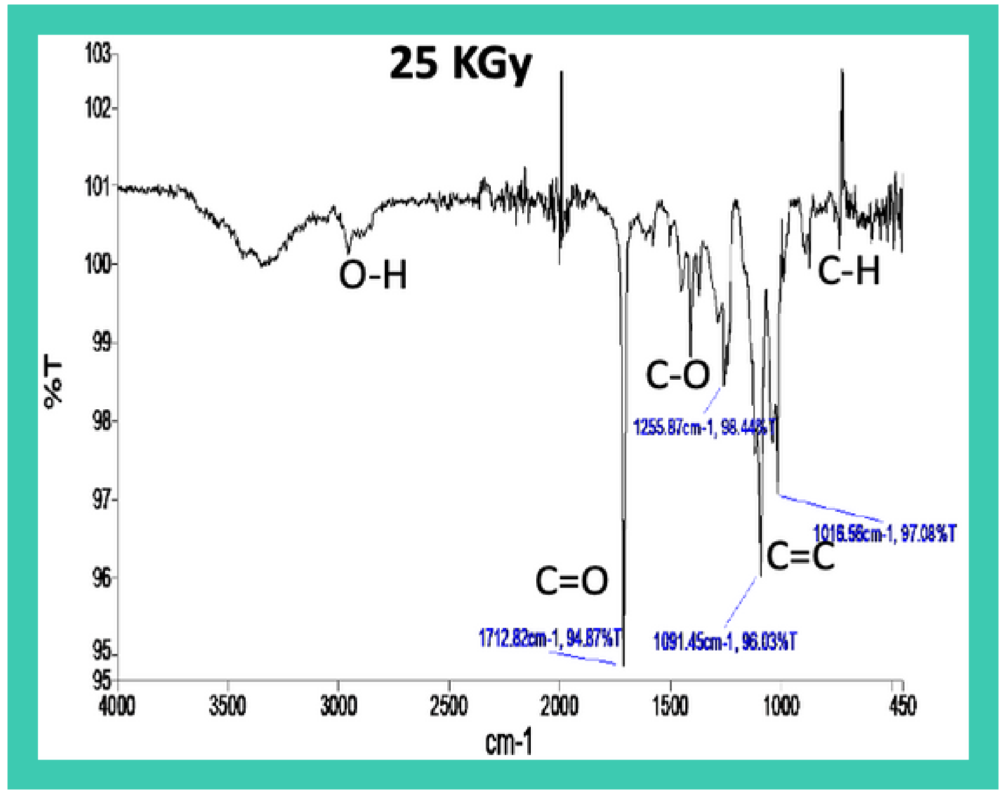


100 kGy Water Exposed PET

- The Focused Ion Beam Scanning Electron Microscope (FIBSEM) Images corroborated observations made in AFM studies
- To observe the changes in the morphology with electron beam dose depending upon extent of crosslinking and chain breakings

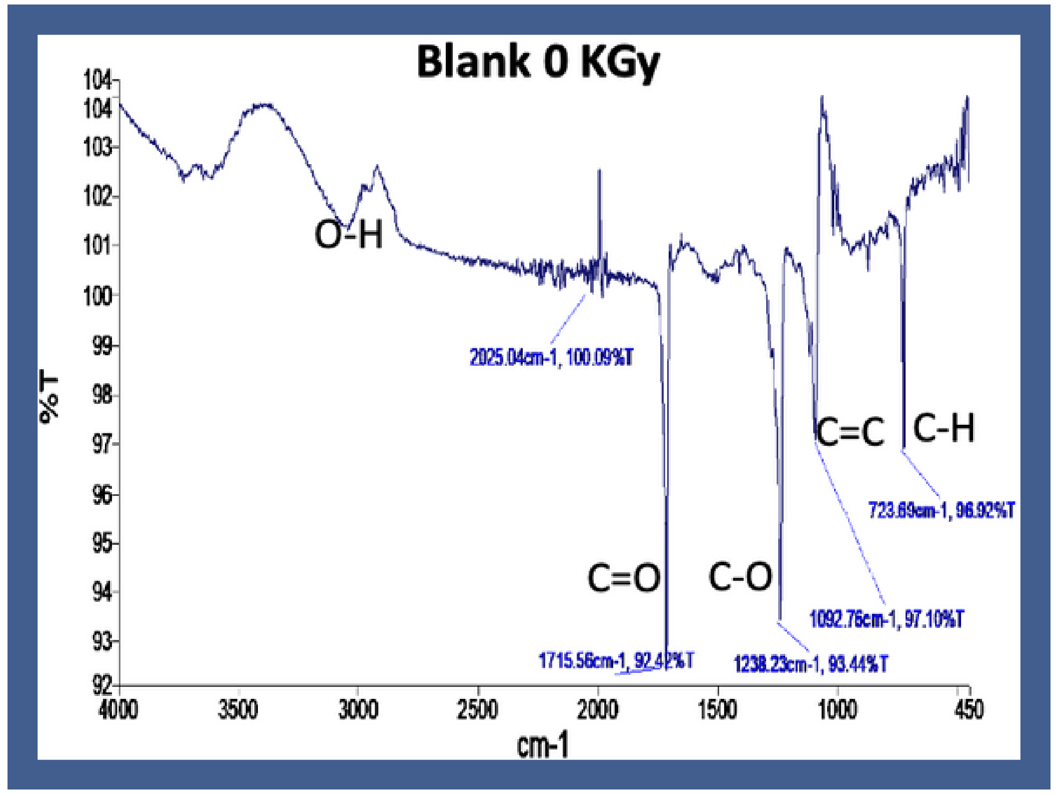
Chemical Changes by Attenuated Total Reflection – Fourier Transform Infra Red (ATRFTIR) Spectroscopy

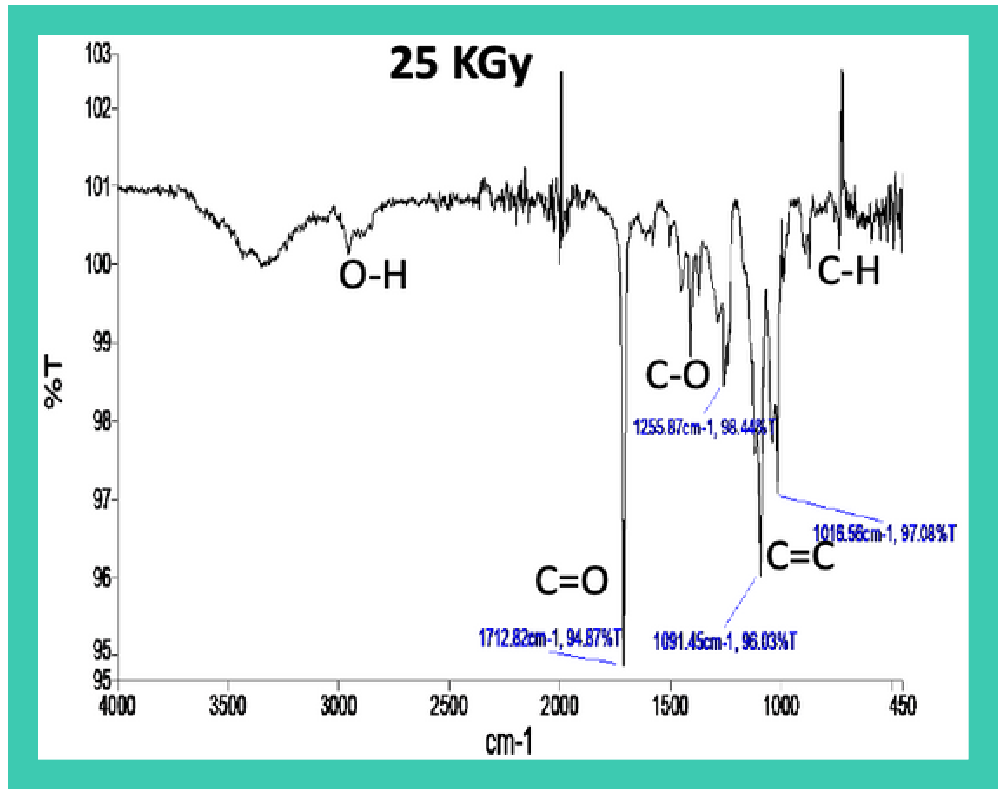




- No Bulk Changes in Chemical Structure: - Overall, there were no significant alterations observed in the bulk chemical structure of PET
- However, changes in transmittance were noted at peaks corresponding to C-C bonds, suggesting PET chain breaking upon irradiation
- Breaking of Ester Bond: - Peak splitting in the C-O bond region was observed, indicating the breaking of ester bonds during irradiation. Formation of New -OH Groups: - Changes in the O-H bond peaks were detected, indicating the formation of new hydroxyl (-OH) groups.

Chemical Changes by Attenuated Total Reflection – Fourier Transform Infra Red (ATRFTIR) Spectroscopy





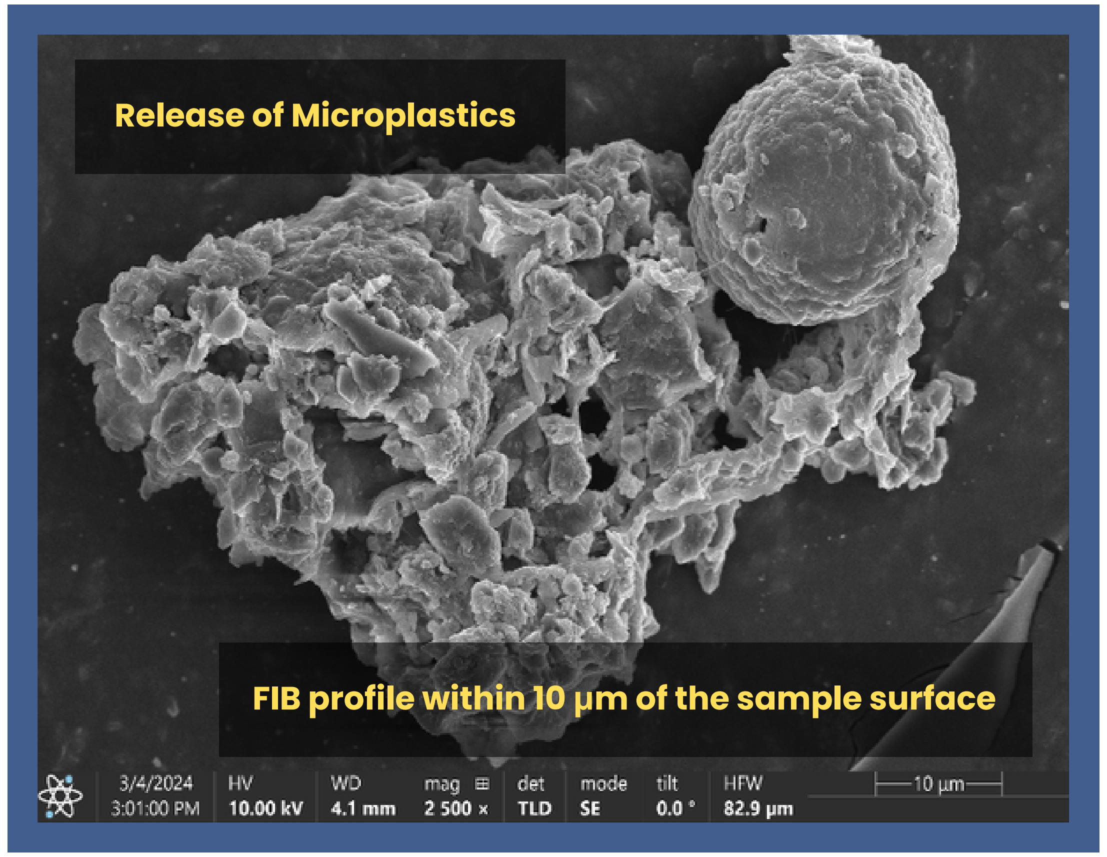
- Characteristic bands of the pristine PET were observed at :
  -2956 cm -1 (C-H stretching of the CH2 groups)
  -1715 cm -1 (C=O stretching of carboxylic ester group)
  -1238 and 1092 cm -1 (C-C-O stretching of ester group)
  723 cm -1 (in-plane C-H stretching and out-of-plane C-H bending of aromatic ring)

- Characteristic bands of irradiated PET were observed at:
  -2895 cm -1 (C-H stretching of the CH2 groups)
  -1712 cm -1 (C=O stretching of carboxylic ester group)
  -1255 and 1091 cm -1 (C-C-O stretching of ester group)
  1018 and 723 cm -1 (in-plane C-H stretching and out-of-plane C-H bending of aromatic ring)

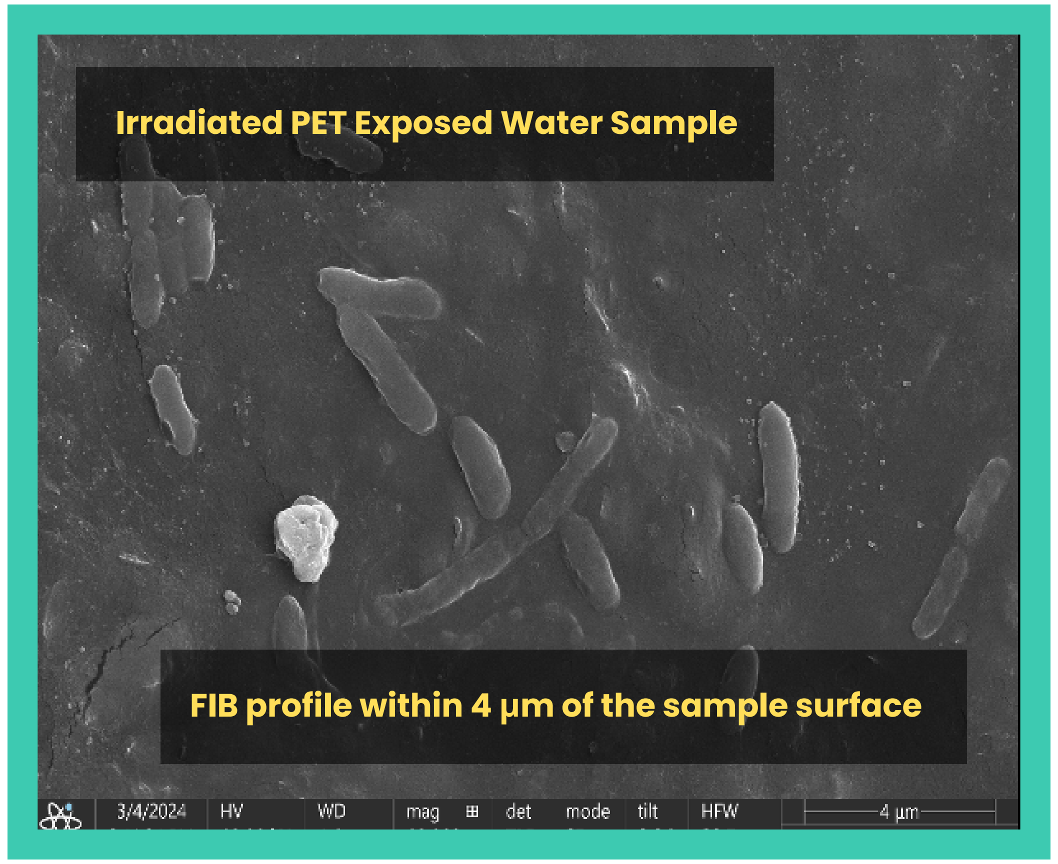
If OH (inter molecular hydrogen bonding), and more C-H appear that means the degradation of PET has occurred.

Visual Images by Focused IonBeam Scanning Electron Microscope (FIBSEM)

Water Sample in Contact with Irradiated PET

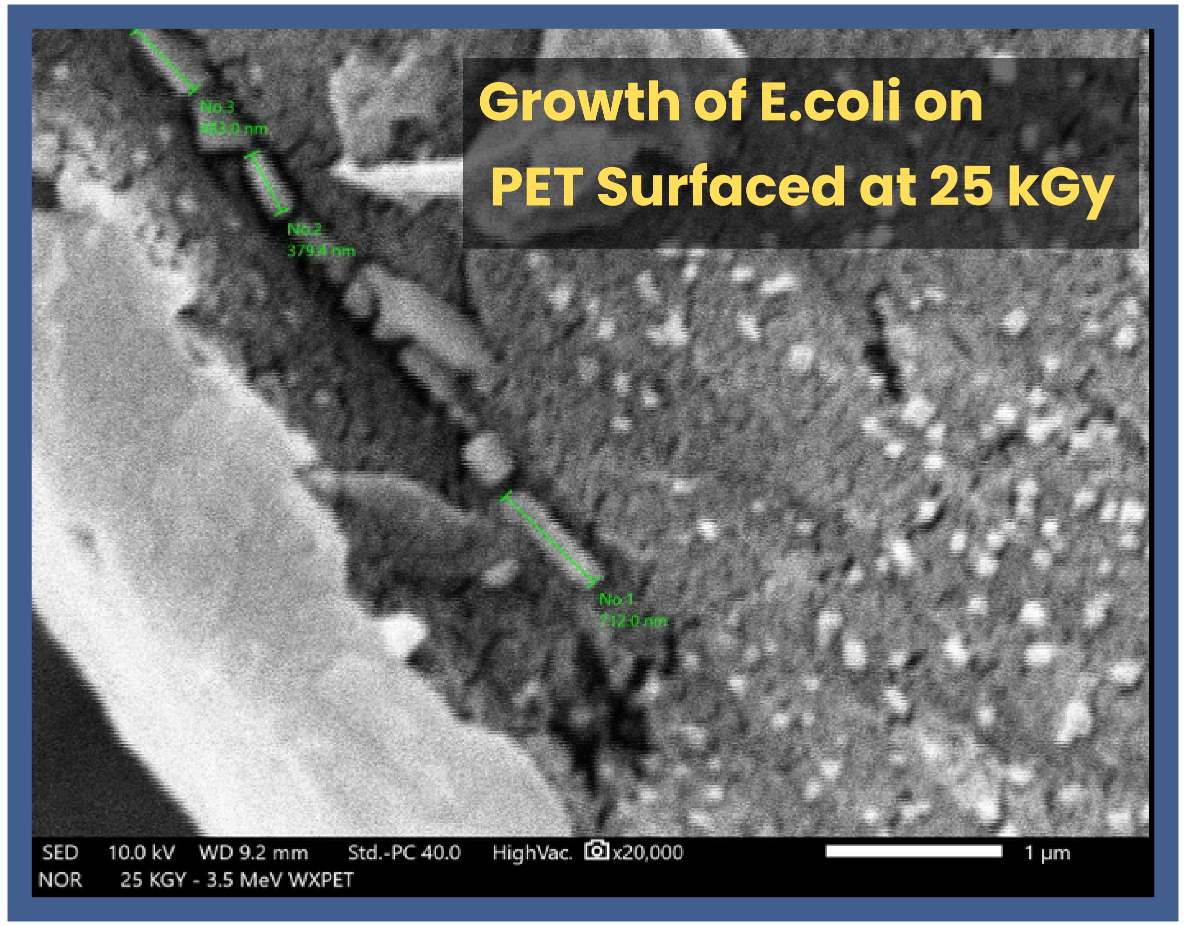


Growth of E. coli on PET surface



- The E-beam exposure of PET :
  - causes changes in surface morphology above 25kGy.
  - the formations of cracks so formed, enhances the sticking of pathogens on the surface of the PET and promotes growth of their colonies at higher doses.

Microbial Growth on Irradiated PET Surface



Sr. No	Water Exposed PET Samples	Bacterial Retention (%) of E. coli ATCC 6538	Percent increase of E. coli ATCC 6538
1	10 kGy 3.5 MeV WXPET	100	Not significant
2	20 kGy 3.5 MeV WXPET	100	Not significant
3	25 kGy 3.5 MeV WXPET	100	43.67%
4	50 kGy 3.5 MeV WXPET	100	36.73%
5	100 kGy 3.5 MeV WXPET	100	33.67%

- Adherence found but marginal decrease in growth of microbes on surface with higher dose of E-Beam Irradiations

Study of Microbial Growth in Water Samples.

- Sample Size: 30 ml
- Test: Assessment of % Bacterial adherence/ retention by In-House method
- Plate Count Agar, E. coli Inoculum Size : 1.5 - 3.0 x 10^5 CFU/mL
- Incubation Conditions: 37°C for 24-48 hrs

Sr. No	Water Samples	Percent increase of E. coli ATCC 6538
1	10 kGy-3.5 MeV PET XW	Not significant
2	20 kGy-3.5 MeV PET XW	Not significant
3	25 kGy-3.5 MeV PET XW	21.24%
4	50 kGy-3.5 MeV PET XW	414.29 %
5	100 kGy-3.5 MeV PET XW	1043 %

The microbial studies have been carried out by planting appropriate ISO protocols.

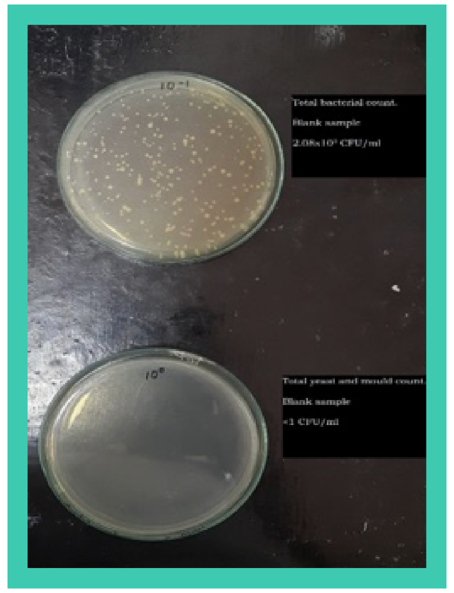
Procedure: Sample was inoculated with 0.1 ml of bacterial culture of E. coli and incubated at suitable conditions. After 24 hours, the bacterial count was calculated by serial dilution followed by pour plate method. The same as compared against count obtained at '0 hour' and percentage of bacteria retained on the sample were calculated.

Observation:
Microbial growth enhanced due to higher release of microplastics with higher dose of E-beam.

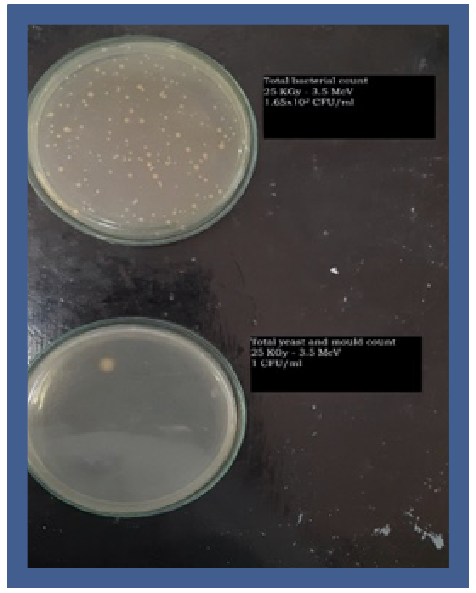
Bacterial Growth on Post Irradiated PET Exposed Water

	E-Beam Irradiations			
	Blank (0kGy)	25kGy	50kGy	100kGy
Total Bacterial Count Incubation Conditions: 30-35˚C, 3-5 days Media: Soyabean Casein Digest Agar	2.08×10^{3} CFU/mL	1.44×10^{2} CFU/mL	2.17×10^{2} CFU/mL	2.93×10^{2} CFU/mL
Total Yeast and Mould Count Incubation Conditions: 20-25˚C, 5-7 days Media: Sabouraud Chloramphenicol Agar	1 CFU/mL	1 CFU/mL	1 CFU/mL	1 CFU/mL

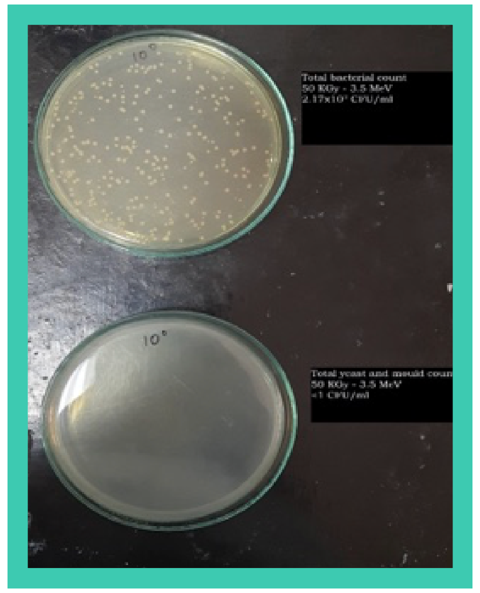
Colony Forming Representation of PET Exposed Water Samples



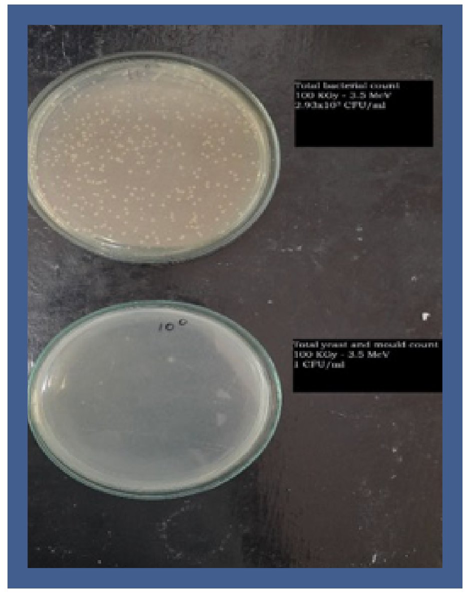
Blank



25 kGy
Bacterial Growth



50 kGy



100kGy
Yeast & Mould Count

Conclusions

- Study of microplastic release from PET to equilibrating water as a function of E-beam dose:
  - The E-beam exposure of PET causes changes in surface morphology above 25kGy as supported by ATR-FTIR.
  - Higher doses of E-Beam induce greater damage to the PET structure, leading to enhanced release of microplastics and nanoplastics.
  - The formations of cracks so formed, enhances the sticking of pathogens on the surface of the irradiated PET.
  - However, microbial growth on Irradiated PET surfaces decreases as a function of Dose

- Enhancement of microbial growth was observed in water due to release of micro plastics as indicated by AFM and FIBSEM.

- Release of Microplastics in E-beam Irradiated PET Exposed water samples:
  - Promoted Total Bacterial Count in the samples irradiated with higher dose of E-beam.
  - Whereas, Yeast and Mold hardly show any growth.

Conclusions

- Higher doses of electron beam irradiation results in increased degradation of the PET matrix.
  Higher doses may also lead to structural changes in the PET material, altering its physical and chemical properties, which could impact its performance and interactions with surrounding environments
  With increased microplastic release, there's a potential for accelerated bioconcentration of toxic elements on PET microplastics in aquatic environments due to the higher surface area available for adsorption.
  The release of a higher volume of microplastics and potential alterations to PET structure due to higher doses of E-Beam irradiation may have significant environmental implications, including increased pollution and potential risks to aquatic ecosystems and organisms.

Future Plans

In comparison other Pathogen and Fungus will be studied.

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Studies on Sorption and Preconcentration of Radionuclides/Toxic Metal Ions on PET Microplastics.

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Microplastic Remediation in water combined with ionizing radiation and subsequent mineralization will be studied.

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