Vol. 37 / 3
October, 2025

ISRAPS Bulletin

ONE-DAY DISCUSSION MEETING:

NEW FRONTIERS OF RADIATION PROCESSES IN POLYMERS, PAINTS, AND NANOCOMPOSITES

Guest Editor
Dr. N. K. Goel

A Publication of
Indian Society for Radiation and Photochemical Sciences

Message from the President and Secretary, ISRAPS

Dear ISRAPS members,

On behalf of the Executive Council of ISRAPS, we extend our gratitude to all ISRAPS Life Members and researchers for their continued support and active participation in the Society's activities across the country throughout the year.

ISRAPS remains steadfast in its commitment to advancing knowledge and promoting research in radiation and photochemistry and its interdisciplinary applications. As part of its outreach initiatives, ISRAPS, in collaboration with the Department of Polymer & Surface Engineering, ICT Mumbai, organized a one-day discussion meeting on "New Frontiers of Radiation Processes in Polymers, Paints, and Nanocomposites" on 19th July 2025 at ICT Mumbai, which was inaugurated by Prof. Anirudh Pandit, Vice-Chancellor, ICT Mumbai. The meeting featured seven invited talks by experts from research institutions and industry, highlighting recent advances in radiation-based synthesis, functionalization, and characterization of polymers, paints, and nanocomposites, as well as the evaluation of their performance for diverse applications. We sincerely thank all participants and extend special appreciation to Prof. Anagha Sabnis (ICT) and Dr. Narender K. Goel (BARC) for their pivotal roles in ensuring the success of the meeting.

This bulletin presents a collection of articles based on the topics discussed at the meeting. We gratefully acknowledge the contributions of all authors and express our special thanks to Dr. Narender K. Goel for serving as Guest Editor for this issue.

The ISRAPS Executive Council earnestly invites all member scientists and students to actively participate in and contribute to initiatives that promote the growth and dissemination of radiation and photochemical sciences among young researchers across the country. The Society remains committed to providing full logistical support for such endeavours.

We also look forward to welcoming you to the 18th Trombay Symposium on Radiation and Photochemistry (TSRP-2026), to be held from January 6–10, 2026, at the DAE Convention Centre, Anushaktinagar, Bhabha Atomic Research Centre, Mumbai.

We once again extend sincere thanks to all Life Members for their unwavering support and encouragement and looks forward to your valuable suggestions and active participation in future events.

Wishing you all an inspiring and productive year ahead!

Dr. A.C. Bhasikuttan
President, ISRAPS

Dr. P. Mathi
Secretary, ISRAPS

ISRAPS Bulletin

A Publication of
Indian Society for Radiation and Photochemical Sciences

Editor's Desk...

It is our privilege to present the current issue of the ISRAPS Bulletin, dedicated to the theme of the ISRAPS Discussion Meeting on "New Frontiers of Radiation Processes in Polymers, Paints, and Nanocomposites," held on 19th July 2025 at the Institute of Chemical Technology (ICT), Matunga. Upholding the rich legacy of ISRAPS in advancing the frontiers of radiation and photochemical research, this thematic meeting was convened to facilitate scholarly interaction and the exchange of ideas among students, researchers and professionals. The deliberations underscored the growing significance of radiation processing as a versatile and sustainable approach for the development of advanced materials, encompassing high-performance polymers, eco-friendly coatings, and functional nanocomposites.

This bulletin features six articles based on the topics covered in the meeting. The first article, by Dr. Apurav Guleria, discusses the potential of ionizing radiation in the synthesis of silicon nanocomposites, which have applications in sensing and biomedicine. The second article, by Dr. Juby Ajish, explores the role of radiation in the synthesis and functionalization of biopolymers and polymeric composites. Dr. Mondal discusses the use of high-energy radiation as an additive-free tool for modifying polymeric materials for the detection of volatile organic compounds. While the aforementioned articles describe the advantages of radiation-assisted synthesis of functionalized polymers and nanocomposites, the article by Dr. A. S. Sabnis and her group discusses the use of radiation for the depolymerization of polymeric waste. This issue also includes an article by Dr. R. S. Parmar, Asian Paints Ltd., which reviews advancements in radiation and photochemical sciences relevant to the paints and coatings industry. Overall, each article in the bulletin offers insights that point toward promising directions for future research with societal impact. We trust that the contributions compiled in this issue will not only showcase the breadth of expertise in the field but also spark further curiosity, dialogue, and collaboration across disciplines.

On behalf of ISRAPS, I extend my heartfelt gratitude to all the contributors for their valuable inputs and to the readers for their continued interest and support. I am thankful to ISRAPS for the opportunity to serve in this editorial role.

Dr. N. K. Goel is a Scientific Officer at the Bhabha Atomic Research Centre (BARC), Mumbai, and currently heads the Advanced Materials Section of the Radiation Technology Development Division. He obtained his M.Sc. in Organic Chemistry from M.D. University, Rohtak (Gold Medalist) and earned his Ph.D. from Homi Bhabha National Institute (HBNI) in 2014. His research focuses on polymer surface modification using high-energy radiation (gamma and electron beam) for environmental, industrial, and healthcare applications. Dr. Goel has authored several national and international publications and has been recognized with multiple honors, including Best Poster Awards and two DAE Group Achievement Awards for his significant contributions to radiation technology development.

INDIAN SOCIETY FOR RADIATION AND PHOTOCHEMICAL SCIENCES (ISRAPS)

EXECUTIVE COUNCIL (2024-2026)

President

Dr. A. C. Bhasikuttan

Vice-Presidents

Prof. Anindya Dutta
Dr. Yatender K. Bhardwaj

Secretary

Dr. P. Mathi

Jt. Secretary

Dr. Beena G. Singh

Treasurer

Dr. Sumana Sengupta

Executive Members

Dr. Atanu Barik	Prof. Shamik Chakraborty	Dr. Sharmistha Dutta Choudhury
Dr. Awadhesh Kumar	Dr. Amit Kunwar	Dr. Jyotirmayee Mohanty
Dr. Sukhendu Nath	Dr. Chandra N. Patra	Dr. R. Puspalata
Dr. Madhab C. Rath	Prof. Geeta K. Sharma	Dr. V. Sudarsan
	Dr. Ankur Saha	

Co-opted Members

Dr. Nihrendu Choudhury	Prof. Hirendra N. Ghosh	Dr. Narender K. Goel
Prof. Sriram K. Gundimeda	Dr. Manoj Kumbhakar	Prof. Avinash Kumbhar
Dr. Nandita Maiti	Prof. Jai P. Mittal	Prof. Tulsi Mukherjee
Prof. Prakash D. Naik	Prof. Anil K. Singh	Prof. Avesh K. Tyagi

Web Master

Dr. Abhishek Das and Shri. Subhamoy Saha

Contact details:
C/o Radiation & Photochemistry Division
Bhabha Atomic Research Centre, Mumbai-400085
E-mail: israps.secretary@gmail.com
Telephone:(022)- 25593771/25592668/25590302

Contents

Radiation-Assisted Preparation of Silicon Nanocomposites: Applications in Sensing and Biomedicine

Priyamdeep Kaur[a], Apurav Guleria*[ab] and Madhab C. Rath [ab]
[a]*Radiation & Photochemistry Division, Bhabha Atomic Research Centre, Mumbai, India*
[b]*Homi Bhabha National Institute, Trombay, Mumbai 400094, India*
(email: aguleria@barc.gov.in*)*

Abstract

Silicon—the cornerstone of modern electronics—has long been celebrated for its abundance, biocompatibility, and cost-effectiveness. Yet, when miniaturized into the nanoscale domain, silicon reveals an entirely new spectrum of properties, including quantum confinement-induced photoluminescence, defect-mediated emission, and versatile surface chemistry. These traits render silicon-based nanocomposites exceptionally promising for applications in biomedical imaging, environmental sensing, and photonics. However, for the impending applications of silicon-based nanocomposites, the synthetic approach must inculcate green and sustainable aspects, generally lacking in conventional chemical synthesis routes. In contrast, ionizing radiations offer a rapid, clean, and controllable alternative. This approach harnesses reactive radicals such as solvated electrons and hydroxyl radicals, generated *in situ* in aqueous media, to initiate nucleation and growth of nanostructures without the need for external reducing agents. In our studies, we have successfully developed silicon nanocomposites via radiation-mediated synthesis. The method allows for precise control over defect-originated emission characteristics by adjusting absorbed dose and surface functionalities. Overall, this article will elucidate how radiation chemical approach provides an environmentally benign, mechanistically rich, and industrially scalable platform for designing advanced silicon nanocomposites with multi-modal applications in sensing and biomedical domains.

Keywords: Silicon, Nanomaterials, Photoluminescence, Radiation, Sensing, Biomedicine

1. Introduction

Silicon (Si), with atomic number Z = 14 and atomic weight A = 28.0855, is a semi-metal belonging to the carbon family (Group 14) of the periodic table. Among the plethora of elements in the universe, Si stands out as a cornerstone for diverse applications. It has a rich natural abundance, accounting for about 27.7% by weight of the Earth's crust, making it the second most plentiful element after oxygen [1-3]. Besides its geographical omnipresence, Si exhibits several attractive traits such as low toxicity, cost-effectiveness, biocompatibility, semiconducting properties, and high thermal conductivity. These features have carved its place across multiple sectors, including energy (photovoltaics), electronics and communication, material science (nanomaterials, NMs), and healthcare (drug delivery, cargo loading, etc.) [4,5,6]. Moreover, Si plays an intricate role in both humans and plants. In humans, it is a trace but essential element involved in metabolic processes and is crucial for skin, hair, and bone health. In the botanical realm, Si contributes significantly to preserving the structural integrity of plants. Seafood, cereals, and vegetables are among the primary dietary sources that furnish this trace essential element to humans [1-3,7]. Some of the key properties of Si are summarized in **Table 1**.

Table 1: Some of the important physical, chemical and electronic properties of Si [8-11].

S. No.	Property	Value
1.	Intrinsic resistivity	2.3×10^5 Ω-cm
2.	Thermal resistivity	1.56 W/cm. K (300 °C)
3.	E_{gap} (Band gap energy)	~1.12 eV
4.	$E_{e\text{-}h}$ (electron-hole pair creation energy)	~3.6 eV
5.	Electron mobility	1500 cm^2/Vs
6.	Hole mobility	400 cm^2/Vs
7.	Electron mass	0.98 m_o (longitudinal electron, $m_{e,l}$); 0.19 m_o (transverse electron, $m_{e,t}$); *where* $m_0 = 9.11 \times 10^{-31}$ *kg*
8.	Hole mass	0.16 m_o (light hole, m_{lh}); 0.46 m_o (heavy hole, m_{hh}); *where* $m_0 = 9.11 \times 10^{-31}$ *kg*
9.	Exciton Bohr radius	~4.5 nm
10.	Excitonic binding energy	~15 meV

It is well-known that when materials are transformed to the nanoscale (1–100 nm), their properties often undergo significant changes. For instance, bulk Si possesses an indirect band gap, which renders it ineffective for optical applications due to the less probable second-order recombination process of electron–hole pairs, as illustrated in **Figure 1** [7-9,13]. But porous silicon nanostructures, owing to the quantum confinement effect, were shown to exhibit photoluminescence (PL) by Prof. Canham in the 1990s [14].

This landmark discovery, coupled with Si biocompatible nature, marked a transformative shift in the utility of its nanocomposites (NCs) for photonic technologies spanning both optical and biomedical domains. While a wide array of semiconductor materials (listed in **Table 2**) have been explored for photoluminescent applications, the inherent advantages of Si continue to place it at the forefront for diverse applications. These include light-emitting diodes (LEDs), toxic metal sensing, forensic analysis, anti-counterfeiting,

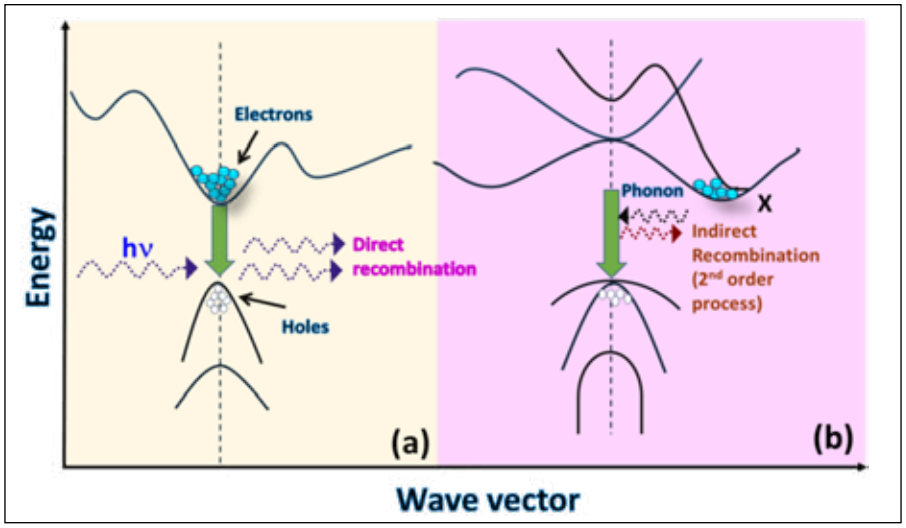

Figure 1. *Energy diagram showing (a) direct and (b) indirect band gap structures.*

Table 2. Some of the common semiconductor NMs employed for PL applications [14,20,21]

S. No.	Semiconductor	Nature of band gap	Bulk Band gap (eV)	Remarks
1.	CdS (II-IV) QDs	Direct	2.42	Tunable PL; toxicity main concern
2.	CdSe (II-IV) QDs	Direct	1.74	
3.	CdTe (II-IV) QDs	Direct	1.5	
4.	PdSe (IV-VI) QDs	Direct	0.27	Near-IR PL; toxicity main concern
5.	PbS (IV-VI) QDs	Direct	0.37	
6.	InP (III-V) QDs	Direct	1.35	Less toxic; alternate for Cd based QDs but cost and scalability issues
7.	GaN (III-V)	Direct	3.36	PL mainly confined to the UV–blue region; cost and scalability issues
8.	ZnSe (n-type)	Direct	~ 2.7 eV	PL mainly confined to blue–green region
9.	Si	Indirect	1.12	*Broad PL tunability from UV-visible to NIR; cost-effective, less toxic, abundance*
10.	Ge	Indirect	0.66	PL generally limited to red–NIR region; cost and scalability issues

bio-analyte sensing, and diagnostics, among others [14-19].

The emission tunability of Si-based NMs is remarkably broad, spanning from the near-infrared (NIR) region (~1.1 eV) to the visible and even the near-ultraviolet (NUV) region (~3.5 eV), surpassing many conventional semiconductors, as shown in **Figure 2**. In general, the quantum confinement effect in Si NMs gives rise to green-to-NIR emission, whereas NUV–blue emission is often attributed to oxide-related defects [2,22,23].

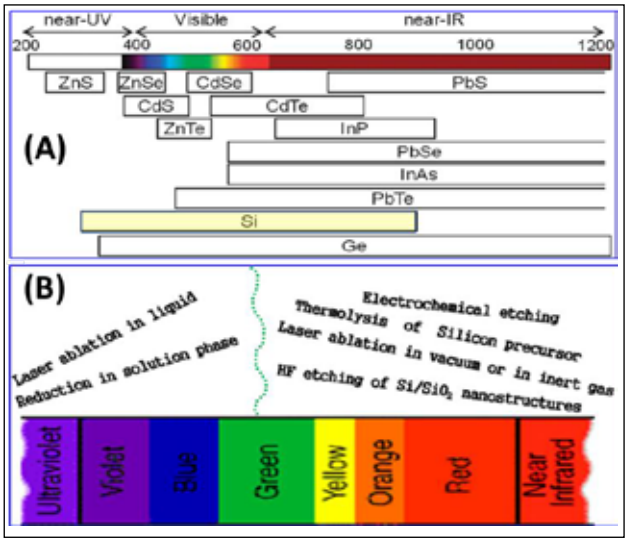

Figure 2. (A) *Tunability of the band gap in various semiconductors [24];* **(B)** *Diversity in emission wavelengths of Si QDs prepared by different methods [2].*

2. Synthetic strategies for Si-based NMs

A wide range of physical, chemical, and biogenic methods have been explored by the scientific community for the synthesis of Si-based NMs [25,26]. These approaches have been extensively employed to tailor the properties of Si NMs for efficient use in a plethora of applications, as summarized in **Figure 3**. Notably, Si NMs fabricated via different strategies display distinct emission characteristics, as highlighted in **Figure 2(B)**. However, the aforementioned methods suffer from certain challenges, including longer reaction times, use of external hazardous reagents, scalability limitations, and requirement for harsh conditions such as high temperature,

pressure, or inert atmosphere [27-29]. These drawbacks pull them away from the paradigm of sustainable and environmentally benign approach [25,26].

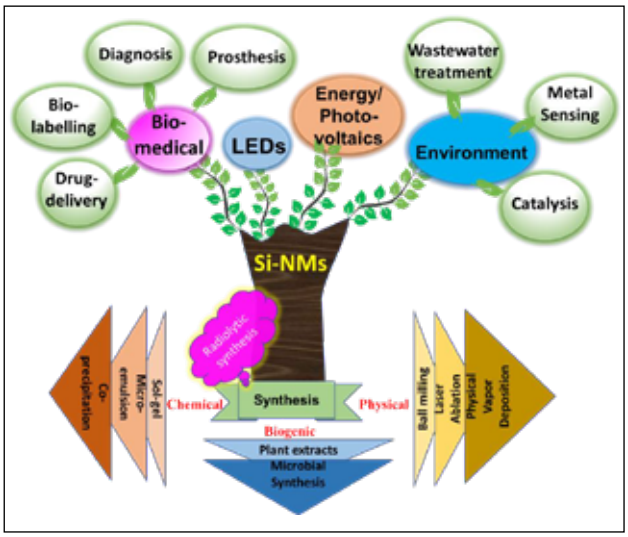

Figure 3. *Schematic representation of major physical, chemical, and biogenic methodologies for synthesizing Si NMs and their applications across diverse fields.*

For the impending applications of nanomaterials, their synthetic methodologies should align with the principles of green chemistry—namely scalability, cost-effectiveness, time efficiency, and environmental compatibility. In this context, ionizing radiations (e.g., electron beam, γ-rays, proton beam, heavy-ion beams) represent a sustainable alternative for fabricating NMs, where *in situ* generation of oxidising and reducing radicals eliminates the need for external toxic reagents [30-33]. To the best of our knowledge, radiolytic route for the synthesis of Si NMs remain relatively underexplored. Our group has successfully demonstrated the fabrication of photoluminescent Si NMs and evaluated their potential in sensing and biomedical applications. Some of the works are discussed in the subsequent sections.

3. Radiation-assisted synthesis of Si NMs

As highlighted above, radiolytic synthesis offers several advantages, including one-pot, single-step, time-efficient, and cost-effective preparation with wide scalability, making it a clean and green synthetic approach. *In situ* generation of oxidising ($^{\bullet}OH$, E_{red} = +2.7 V *vs.* NHE) and reducing (e^-_{solv}, E_{red} = −2.9 V *vs.* NHE and $H^{\bullet}$, E_{red} = −2.3 V *vs.* NHE) species in radiation-chemical synthesis, can be understood by diving into the events that occur after interaction of radiation with aqueous medium [30-31,32,33]. The radiolysis of water is generally represented by the equation shown below [34]:

$$H_2O \rightsquigarrow e^-_{solv}, H^{\bullet}, {}^{\bullet}OH, H_3O^+, H_2O_2, H_2 \quad (1)$$

Depending on the requirements, selective oxidising and reducing conditions can be achieved and maintained by introducing scavengers into the reaction mixture. For instance, oxidising environment can be selectively achieved by saturating the precursor solution with N_2O gas which acts as a scavenger of , as shown in following reaction:

$$e^-_{solv} + N_2O \rightarrow N_2 + O^- \quad (2)$$

$$O^- + H_2O \rightarrow OH^- + {}^{\bullet}OH \quad (3)$$

On the other hand, strong reducing conditions can be obtained by adding t-butanol, which scavenge $H^{\bullet}$ and $^{\bullet}OH$:

$$CH_3(CH_3)_2COH + {}^{\bullet}OH\ (H^{\bullet}) \longrightarrow {}^{\bullet}CH_2(CH_3)_2COH + H_2O\ (H_2) \quad (4)$$

The radical species hence produced, react with the precursors and initiate nucleation followed by growth of NPs. Further, size, shape and other properties of NPs can be tailored and controlled by varying the experimental parameters like absorbed dose, dose rate, precursors, nature of reaction matrix, capping agent, etc. The pictorial representation of the synthesis of NPs via radiation-chemical approach is shown in **Figure 4**.

The radiolytic approach using γ-rays and electron-beam irradiation have been employed by our group for the synthesis of various NMs.

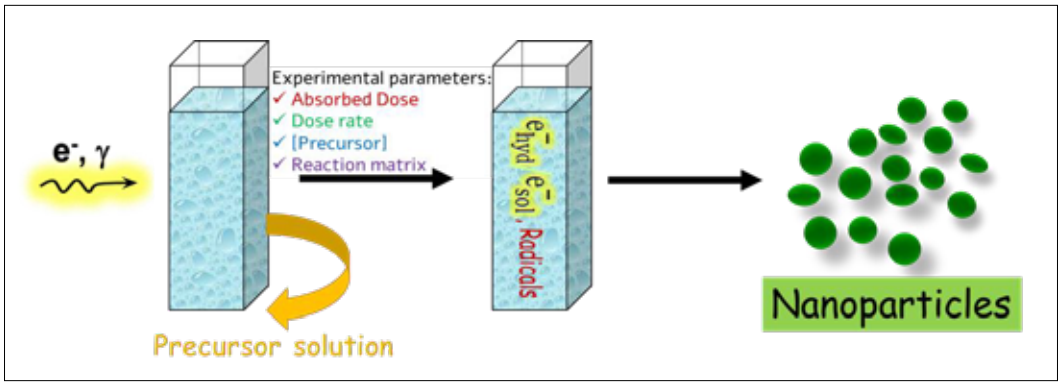

Figure 4. *Pictorial representation of the formation of NPs by radiolytic approach.*

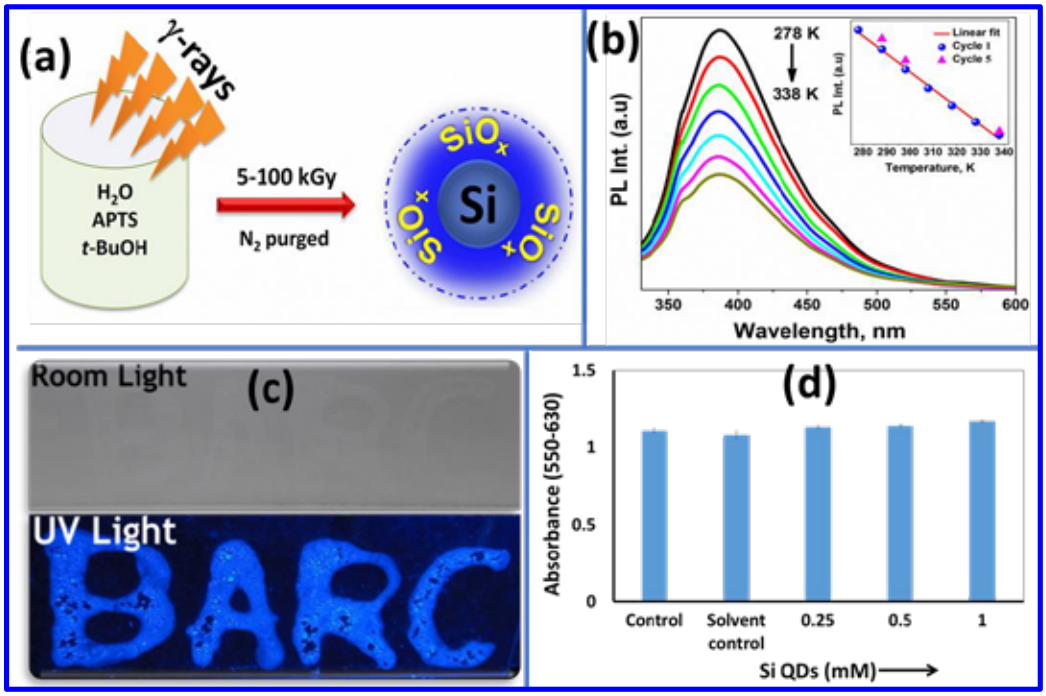

Figure 5. (a) *Schematic illustration of Si QD synthesis;* **(b)** *their thermosensing behaviour;* **(c)** *anticounterfeiting potential, respectively; and* **(d)** *graphical depiction of the MTT assay data [30].*

Among these, Si NMs with unique characteristics such as porosity and amorphous structure were obtained—features that are otherwise difficult to achieve using conventional methods [30-33,35-37]. The potential of radiolytically fabricated Si NMs has been demonstrated across multiple applications, with sensing and biomedicine discussed in the following sections.

In one of our early studies, Si QDs with a shell of silicon oxides (SiOx, $0 < x < 2$) were synthesized via a facile, one-pot radiolytic method using γ-ray irradiation, with 3-aminopropyl trimethoxysilane (APTS) as the precursor (**Figure 5a**) [30]. These QDs exhibited distinct features of porosity and amorphous nature. The average size of QDs was < 2 nm and could be tuned simply by varying the absorbed dose. The QDs displayed blue PL with a quantum efficiency (QE) of ~15%, attributed to defects near the Si/SiO_x interface as well as within the oxide shell. This PL behaviour enabled their application in thermosensing, where the PL intensity showed a linear decrease

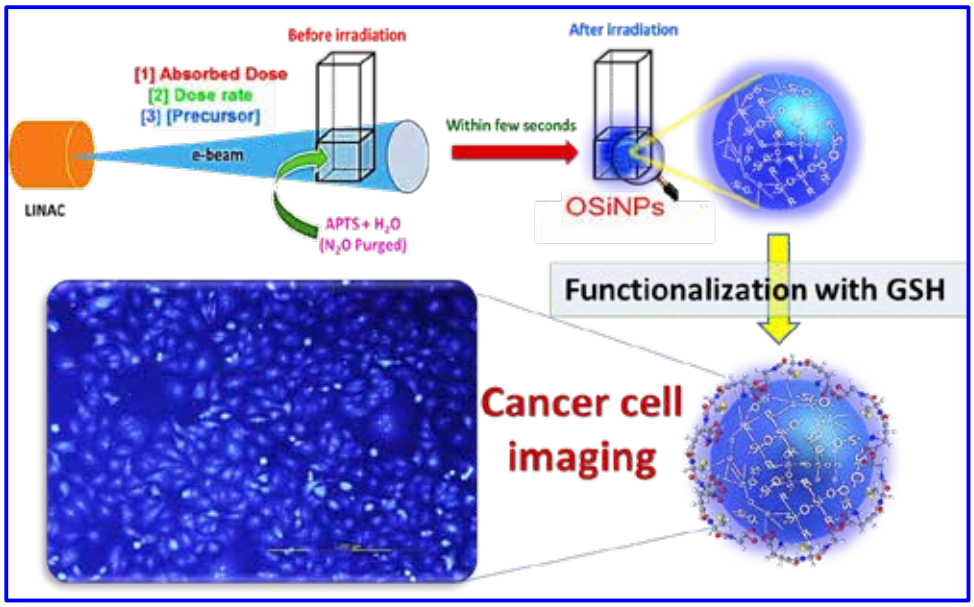

Figure 6. *Schematic illustration of the synthesis of the blue light emitting OSiNPs by electron beam irradiation followed by their functionalization with L-glutathione (GSH), i.e., L-Glu@OSiNPs and demonstration of their application in cancer cell imaging [31].*

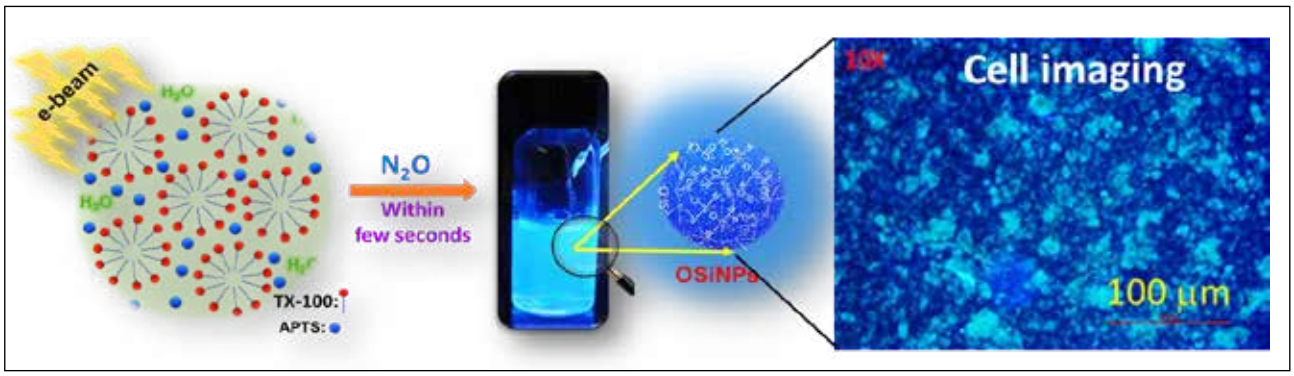

Figure 7. *Electron-assisted synthesis of OSiNPs in TX-100 micellar medium and their application in cell imaging [32].*

in the temperature range of 5–65 °C (robust and reproducible), due to the enhancement of non-radiative relaxation pathways (**Figure 5b**). Additionally, their potential in anticounterfeiting was also demonstrated (**Figure 5c**). Importantly, the fabricated Si QDs were found to be non-cytotoxic up to 1 mM (**Figure 5d**), thereby supporting their safe use in cell imaging applications [30].

In addition to γ-ray irradiation, we have also reported the aqueous-phase synthesis of photoluminescent Si NMs using electron-beam irradiation [31]. For example, blue light-emitting organosilicon oxide nanoparticles (OSiNPs) with an average size of 3–5 nm were synthesized by 7 MeV LINAC electron-beam irradiation, demonstrating a rapid and scalable method suitable for large-scale production with commercial electron accelerators. Mechanistic investigations using pulse radiolysis revealed the crucial role of •OH radicals, which initiated the formation of OSiNPs via silane-radical intermediates. The origin of blue emission was attributed to defects associated with dioxasilirane (=Si(O2)) and a silylene (=Si:) moieties. Further

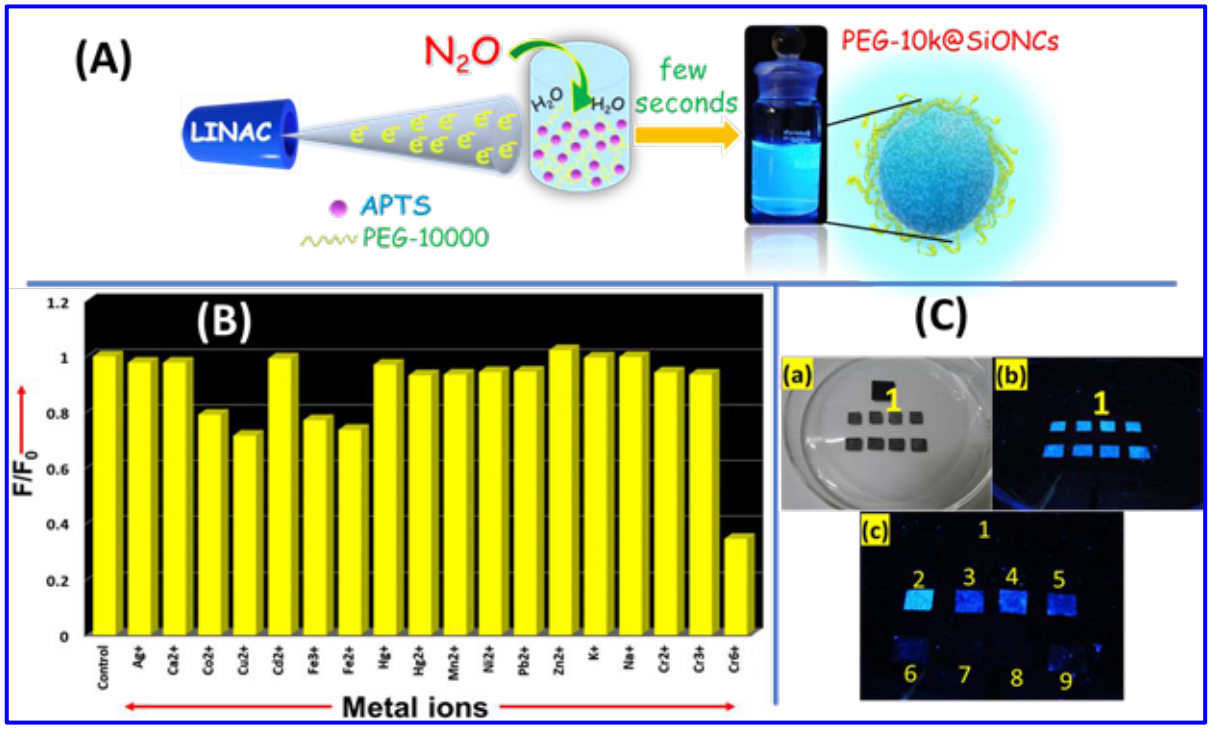

Figure 8. (A) *Preparation of PEG-10K@SiONCs using a 7 MeV electron beam;* **(B)** *Effect of metal ions on PL intensity;* **(C)** *Photographs of NCs-coated paper under room and UV light, demonstrating Cr (VI) sensing. The paper marked with number "***1***" represents the uncoated one. No inherent PL could be seen from the reference under UV light. The number markings are described as follows:* **(1)** *uncoated paper,* **(2)** *NCs-coated paper (as reference). NCs-coated paper drop-casted with following metal ion solutions;* **(3)** *20 µL solution containing various metal ions excluding Cr^{6+}; $[Cr^{6+}]$ = 0.40 µM* **(4)**, *20 µM* **(5)**, *55 µM* **(6)**, *240 µM* **(7)**, *470 µM* **(8)**, *900 µM* **(9)** *[33].*

improvements in colloidal stability and QE (up to ~25%) were achieved by functionalization with L-glutathione (L-Glu). These Glu@OSiNPs exhibited excellent biomedical potential, showing low cytotoxicity (up to ~0.5 mg/mL), tumor selectivity (in A549 human lung cancer cells), and efficient cell imaging with nuclear localization at pH ~6.5 (**Figure 6**). Thus, they represent a non-toxic and cost-effective alternative for bioimaging applications [31]. Beyond biomedical uses, the fabricated OSiNPs were also successfully explored in fingerprinting, anticounterfeiting, and thermosensing [31].

On observing significant changes after functionalizing OSiNPs with L-Glu, our group further explored a variety of other biocompatible capping agents, including α-cyclodextrin (α-CD), Triton X-100 (TX-100), and polyethylene glycol (PEG). Unlike the ex-situ functionalization carried out with L-Glu, these ligands were introduced *in situ* during the radiolytic synthesis itself. For example, in one study, photoluminescent OSiNPs were synthesized in a TX-100 micellar medium using electron-beam irradiation [32]. This led to a remarkable enhancement in both colloidal stability and QE (from 9% to 55%). The as-prepared NPs were readily internalized in the cytoplasmic region of A549 cells (**Figure 7**) [32].

In another study, silicon oxide nanocomposites (SiONCs) functionalised with PEG-1000 exhibited excitation-wavelength-dependant PL (QE ~ 49%) (**Figure 8A**). These PEG@SiONCs were applied in cell imaging as well as in toxic metal ion sensing. Internalisation was again observed in the cytoplasm of tumour cells [33]. Highly selective detection of Cr (VI) ions was achieved via the inner filter effect (IFE) (**Figure 8B**), with an impressively low limit of

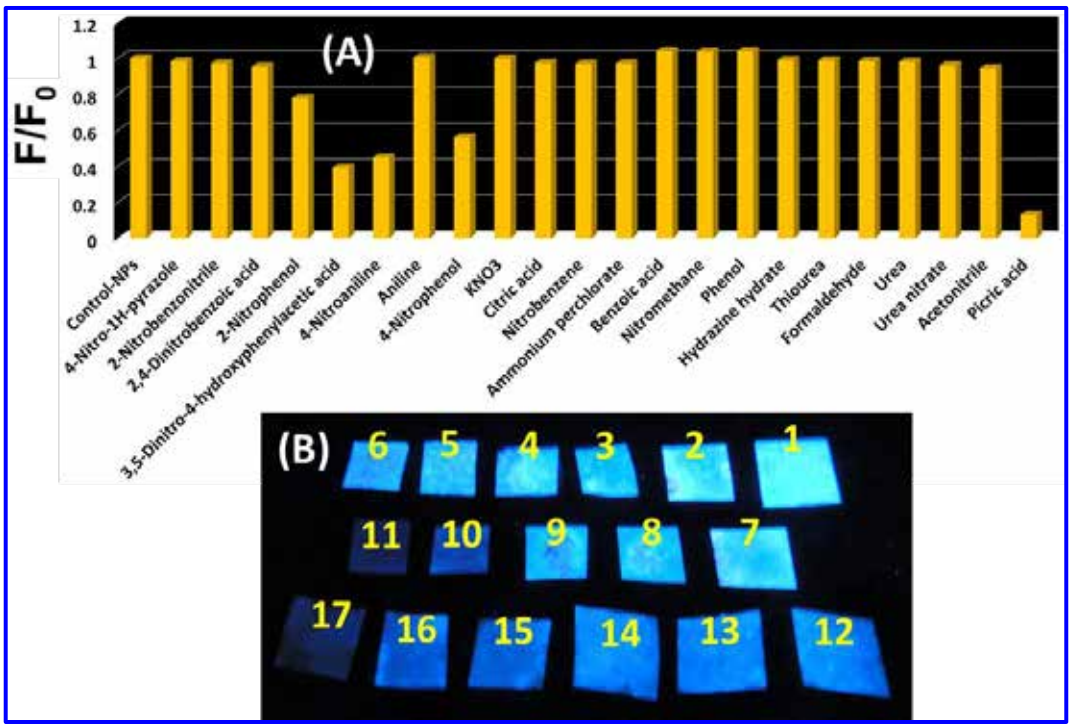

Figure 9. (A) *Effect of various compounds (generally used in explosives) on the PL intensity of PEG@SiONCs;* **(B)** *Digital photographs (under UV light) illustrating the response of PEG@SiONCs coated paper strips to varying PA concentrations, both in the absence and presence of compounds containing various functional groups as interfering entities. The number markings are explained as follows.* **(1)** *PEG@SiONCs coated paper as a reference. NCs- coated papers were drop-cast with solution having following PA concentration:* **(2)** *12.4 µM,* **(3)** *24.9 µM,* **(4)** *49.7 µM,* **(5)** *74.4 µM,* **(6)** *99.0 µM,* **(7)** *123.4 µM,* **(8)** *147.7 µM,* **(9)** *172.0 µM,* **(10)** *240.0 µM,* **(11)** *291.3 µM. NCs-coated papers were drop-cast with a solution of -NO_2 containing compounds (i.e., Sol Y) at effective concentrations of* **(12)** *55 µM,* **(13)** *104.7 µM,* **(14)** *150.0 µM,* **(15)** *191.0 µM,* **(16)** *229.2 µM and* **(17)** *240.0 µM [35].*

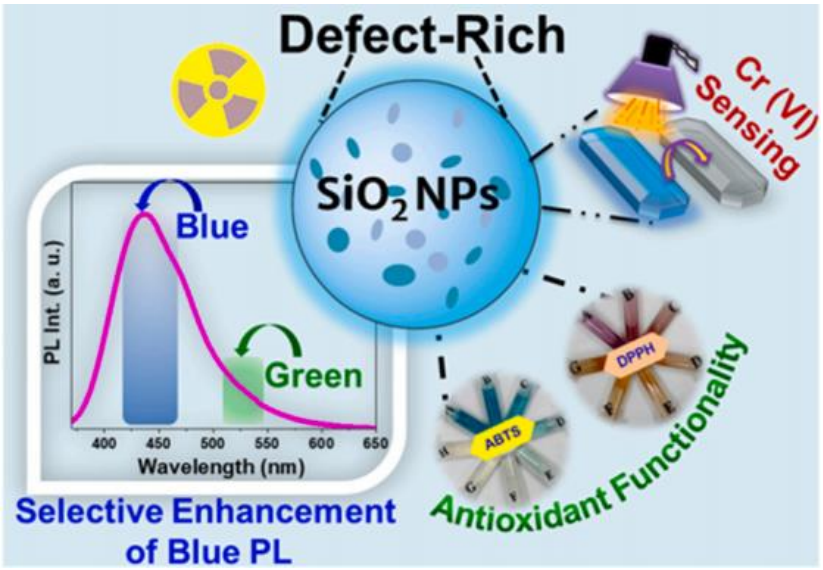

Figure 10. *Depiction of defect rich SiO_2 NPs with selective enhancement of blue emission along with their applications in Cr (VI) sensing and antioxidant activity [37].*

detection (LOD = 0.74 μM). To evaluate the real-time applicability, paper strips coated with PEG@SiONCs were successfully employed for Cr (VI) sensing (**Figure 8C**).

Further, PEG@SiONCs were also applied for picric acid (PA) sensing, achieving an LOD of ~ 0.16 μM in the 2-85 μM range. The sensing mechanism, again based on IFE, showed that PA caused >85% PL quenching, while other nitroaromatics and interfering species displayed only ~60% quenching (**Figure 9A**). The visible detection of PA was further validated using PEG@SiONCs-coated paper strips, which clearly distinguished PA from other -NO_2 containing compounds [35]. **Figure 9B** shows PEG@SiONCs coated paper strips labelled from "12" to "16", which were subjected to drop casting using a solution of -NO_2 containing compounds with each one having an effective concentration of **(12)** 55 μM, **(13)** 104.7 μM, **(14)** 150.0 μM, **(15)** 191.0 μM, **(16)** 229.2 μM, **(17)** 240.0 μM.

In yet another work, α-CD-functionalized SiO_2 NPs (CD@SiO_2) synthesized via electron-beam irradiation exhibited tunable PL (QE ~21%), shifting from blue to green with varying absorbed dose [36]. This tunability was attributed to the formation of different defect-related emission centres at varying doses. Interestingly, these NPs also displayed intrinsic antioxidant activity—a rare observation for silica-based NMs, which are generally considered pro-oxidants. The blue band (~440 nm) increased in intensity within 10 days, whereas the green band (~530 nm) remained nearly constant, suggesting a role of oxygen-related defects such as non-bridging oxygen hole centres (NBOHCs) and silanone (=Si–O) species, though the exact mechanism remains under debate. These CD@SiO_2 NPs were further applied for Cr (VI) sensing via IFE mechanism (LOD = 0.57 μM), with recovery experiments from real water samples. For testing antioxidant activity, ABTS and DPPH assays were carried out, yielding IC50 values of 239.06 mg/mL and 877.0 mg/mL, respectively. Hence, a rare instance of intrinsic antioxidant activity of silica-based NMs have been observed in our report (**Figure 10**) [37].

4. Conclusions and Outlook

Silicon remains a uniquely versatile material—abundant, cost-effective, and inherently biocompatible—positioning it as a frontrunner for applications in energy, healthcare, and environment. This article presents a brief overview of the properties, significance, and synthesis strategies of Si-based NMs, with particular attention to the distinctive advantages of radiation-assisted synthesis approach. Unlike conventional methods, radiation-assisted approach enables clean, one-pot fabrication while simultaneously facilitates defect engineering that impart PL and yield amorphous, porous, and non-cytotoxic Si NCs. These attributes underpin their growing roles, especially in biomedical and sensing applications.

Surface functionalization with biocompatible ligands further extends their biomedical relevance by enhancing colloidal stability and reducing toxicity. Remarkably, radiation-derived silica NPs have even shown antioxidant activity—counter to the usual pro-oxidant nature of silica. Recently, our group have fabricated nearly white-light emitting thiolated organosilicon oxide NCs through radiation-assisted approach, which otherwise involve tedious procedures through traditional conventional methods. Looking ahead, the central challenge is to translate these laboratory advances into scalable and sustainable technologies. This requires greener, reproducible, and safer routes, moving beyond harsh experimental parameters, hazardous reducing agents and aggressive reagents. Radiation-assisted synthesis offers a promising alternative in this pretext, though key challenges remain: gaining deeper mechanistic insights into defect-mediated PL, expanding the library of radiation-compatible precursors, and strategically employing unconventional solvents such as room-temperature ionic liquids (RTILs) and deep eutectic solvents (DESs) for fine control of material properties.

Future breakthroughs will likely arise

from interdisciplinary collaborations spanning radiation chemistry, materials science, and biomedicine. With continued progress, radiation-engineered Si NMs could transition from laboratory curiosities into practical platforms for next-generation sensors, antioxidant therapeutics, and multifunctional nanomedicine.

Acknowledgments

The authors acknowledge the members of the RPCD LINAC facility for their help in irradiation-based experiments. The authors gratefully acknowledge Dr. A. C. Bhasikuttan, Head, RPCD and Associate Director, Chemistry Group, BARC for his support and encouragement.

5. References

1. Croissant, J. G.; Fatieiev, Y.; Khashab, N. M. Degradability and Clearance of Silicon, Organosilica, Silsesquioxane, Silica Mixed Oxide, and Mesoporous Silica Nanoparticles. *Adv. Mater.* **2017**, *29*, 1604634.
2. Ghosh, B.; Shirahata, N. Colloidal Silicon Quantum Dots: Synthesis and Luminescence Tuning from the Near-UV to the Near-IR Range. *Sci. Technol. Adv. Mater.* **2014**, *15*, 014207.
3. Liang, J.; Huang, C.; Gong, X. Silicon Nanocrystals and Their Composites: Syntheses, Fluorescence Mechanisms, and Biological Applications. *ACS Sustainable Chem. Eng.* **2019**, *7*, 18213–18227.
4. Huang, Y.; Li, P.; Zhao, R.; Zhao, L.; Liu, J.; Peng, S.; Fu, X.; Wang, X.; Luo, R.; Wang, R.; Zhang, Z. Silica Nanoparticles: Biomedical Applications and Toxicity. *Biomed. Pharmacother.* **2022**, *151*, 113053.
5. Isa, E. D. M.; Ahmad, H.; Rahman, M. B. A.; Gill, M. R. Progress in Mesoporous Silica Nanoparticles as Drug Delivery Agents for Cancer Treatment. *Pharmaceutics* **2021**, *13*, 1–33.
6. Lee, Y.-T.; Wu, S.-H.; Wu, C.-H.; Lin, Y.-H.; Lin, C.-K.; Chen, Z.-A.; Sun, T.-C.; Chen, Y.-J.; Chen, P.; Mou, C.-Y.; Chen, Y.-P. Drug-Free Mesoporous Silica Nanoparticles Enable Suppression of Cancer Metastasis and Confer Survival Advantages to Mice with Tumor Xenografts. *ACS Appl. Mater. Interfaces* **2024**, *16*, 61787–61804.
7. Morozova, S.; Alikina, M.; Vinogradov, A.; Pagliaro, M. Silicon Quantum Dots: Synthesis, Encapsulation, and Application in Light-Emitting Diodes. *Front. Chem.* **2020**, *8*, 191.
8. Song, B.; He, Y. Fluorescent Silicon Nanomaterials: From Synthesis to Functionalization and Application. *Nano Today* **2019**, *26*, 149–163.
9. Li, Q.; Jin, R. Photoluminescence from Colloidal Silicon Nanoparticles: Significant Effect of Surface. *Nanotechnol. Rev.* **2017**, *6*, 601–612.
10. Bien, D.; Mitchell, N. S. J.; Gamble, H. S. Micro-Machined Passive Valves: Fabrication Techniques, Characterisation and Their Application. In *MEMS/NEMS*; Leondes, C. T., Ed.; Springer: Boston, MA, 2006; pp 741–800.
11. Udisco, S.; La Via, F.; Agodi, C.; Altana, C.; Borghi, G.; Boscardin, M.; Bussolino, G.; Calcagno, L.; Camarda, M.; Cappuzzello, F.; et al. SiCILIA—Silicon Carbide Detectors for Intense Luminosity Investigations and Applications. *Sensors* **2018**, *18*, 2289.
12. Cheng, X.; Lowe, S. B.; Reece, P. J.; Gooding, J. J. Colloidal Silicon Quantum Dots: From Preparation to the Modification of Self-Assembled Monolayers (SAMs) for Bio-Applications. *Chem. Soc. Rev.* **2014**, *43*, 2680–2700.
13. Liang, D.; Bowers, J. E. Recent Progress in Lasers on Silicon. *Nat. Photonics* **2010**, *4*, 511–517.
14. Canham, L. Silicon Quantum Wire Array Fabrication by Electrochemical Dissolution of Wafers. *Appl. Phys. Lett.* **1990**, *57*, 1046–1048.
15. Wang, Y.; Tian, M.; Xie, W.; Li, C. M.; Liu, Y. One-Step Synthesis of Amine-Functionalized Fluorescent Silicon Nanoparticles for Copper(II) Ion Detection. *Anal. Bioanal. Chem.* **2019**, *411*, 6419–6426.
16. Ma, F.; Luo, J.; Li, X.; Liu, S.; Yang, M.; Chen, X. A "Switch-On" Fluorescence Assay Based on Silicon Quantum Dots for Determination of Ascorbic Acid. *Spectrochim. Acta, Part A* **2021**, *249*, 119343.
17. Liu, J.; Zhang, J.; Zhang, Y.; Wang, Y.; Wang, M.; Li, Z.; Wang, G.; Su, X. A pH-Responsive Fluorometric and Colorimetric System Based on Silicon Quantum Dots and 4-Nitrophenol for Urease Activity Detection. *Talanta* **2022**, *237*, 122956.
18. Xu, W.; Yu, L.; Xu, H.; Zhang, S.; Xu, W.; Lin, Y.; Zhu, X. Water-Dispersed Silicon Quantum Dots for On–Off–On Fluorometric Determination of Chromium(VI) and Ascorbic Acid. *Microchim. Acta* **2019**, *186*, 673.
19. D'Amato, R.; et al. Silicon Nanoparticles as Active Materials for LED: Laser Synthesis and Functionalization for Tuning Luminescence. *J. Phys. Conf. Ser.* **2022**, *2315*, 012002.
20. Wang, X.; et al. Toxicity Evaluation of Cadmium-Containing Quantum Dots: A Review of Optimizing Physicochemical Properties to Diminish Toxicity. *Colloids Surf., B* **2021**, *208*, 111609.
21. Chen, W.; et al. Sensitive Immunoassay Based on Biocompatible and Robust Silica-Coated Cd-Free InP-Based Quantum Dots. *Inorg. Chem.* **2021**, *60*, 8709–8716.
22. Dasog, M.; Reyes, G. B. D.; Titova, L. V.; Hegmann, F. A.; Veinot, J. G. C. Size vs Surface: Tuning the Photoluminescence of Freestanding Silicon Nanocrystals across the Visible Spectrum via Surface Chemistry. *ACS Nano* **2014**, *8*, 9636–9648.
23. Dohnalová, K.; Gregorkiewicz, T.; Kůsová, K. Silicon Quantum Dots: Surface Matters. *J. Phys.: Condens. Matter* **2014**, *26*, 173201.
24. Shirahata, N. Colloidal Si Nanocrystals: A Controlled Organic-Inorganic Interface and Its Implications of Silicon Biotechnology. *Phys. Chem. Chem. Phys.* **2011**, *13*, 7284–7294.
25. Vasilyeva, A. A.; Buribaev, R. A.; Gorbunova, M. V.; Apyari, V. V.; Torocheshnikova, I. I.; Dmitrienko, S. G. Silicon-Based Nanoparticles: Synthesis and Recent Applications in Chemical Sensing. *TrAC, Trends Anal. Chem.* **2024**, *171*, 117538.
26. Recent Progress in the Applications of Silica-Based Nanoparticles. *RSC Adv.* **2022**, *12*, 13706–13726. https://doi.org/10.1039/D2RA01587K.

27. Nanomaterials: A Review of Synthesis Methods, Properties, Recent Progress, and Challenges. *Mater. Adv.* **2021**, *2*, 1821–1871.

28. Green Synthesis of Silica and Silicon Nanoparticles and Their Biomedical and Catalytic Applications. *Comments Inorg. Chem.* **2021**, *41*, 317–372.

29. Farjadian, F.; Roointan, A.; Mohammadi-Samani, S.; Hosseini, M. Mesoporous Silica Nanoparticles: Synthesis, Pharmaceutical Applications, Biodistribution, and Biosafety Assessment. *Chem. Eng. J.* **2019**, *359*, 684–705.

30. Guleria, A.; Neogy, S.; Maurya, D. K.; Adhikari, S. Blue Light-Emitting Si Quantum Dots with Mesoporous and Amorphous Features: Origin of Photoluminescence and Potential Applications. *J. Phys. Chem.* C **2017**, *121*, 24302–24316.

31. Guleria, A.; Chavan, A. P.; Neogy, S.; Gandhi, V. V.; Kunwar, A.; Debnath, A. K.; Adhikari, S. Glutathione-Functionalized Organosilicon Oxide Nanoparticles for Bioimaging and Forensics. *ACS Appl. Nano Mater.* **2020**, *3*, 5123–5138.

32. Guleria, A.; Tomy, A.; Baby, C. M.; Gandhi, V. V.; Kunwar, A.; Debnath, A. K.; Adhikari, S. Electron Beam Mediated Synthesis of Photoluminescent Organosilicon Nanoparticles in TX-100 Micellar Medium and Their Prospective Applications. *J. Mol. Liq.* **2021**, *334*, 116072.

33. Guleria, A.; Gandhi, V. V.; Kunwar, A.; Neogy, S.; Debnath, A. K.; Adhikari, S. PEGylated Silicon Oxide Nanocomposites with Blue Photoluminescence Prepared by a Rapid Electron-Beam Irradiation Approach: Applications in IFE-Based Cr(VI) Sensing and Cell-Imaging. *Colloids Surf., A* **2022**, *640*, 128483.

34. Farhataziz; Rodgers, M. A. J. *Radiation Chemistry: Principles and Applications*; VCH Publishers: New York, 1987. Spinks, J. W. T.; Woods, R. J. *An Introduction to Radiation Chemistry*, 3rd ed.; Wiley: New York, 1990.

35. Guleria, A.; Rath, M. C.; Adhikari, S. Radiolytically Prepared Blue Photoluminescent Silicon Oxide Nanocomposites for Highly Selective Sensing of Picric Acid: Mechanism and Development of Paper Strip-Based Detection. *Mater. Chem. Phys.* **2024**, *311*, 128575.

36. Guleria, A.; Chavan, A. P.; Tomy, A.; Baby, C. M.; Neogy, S.; Debnath, A. K.; Adhikari, S. Defect Originated Photoluminescence Tuning of Silica Nanoparticles Prepared by Electron Beam Irradiation and Their Applications. *Ceram. Int.* **2021**, *47*, 2649–2655.

37. Guleria, A.; Chiplunkar, S. S.; Hari, A.; Das, B.; Rath, M. C. Defect-Rich Silica Nanoparticles: Selective Enhancement of Blue Emission, Cr(VI) Sensing, and Inherent Antioxidant Functionality. *Colloids Surf., A* **2025**, *725*, 137599.

	***Ms. Priyamdeep Kaur*** *has obtained her M.Sc. (hons.) Chemistry degree from Panjab University, Chandigarh in 2023. She joined as Scientific Officer/C in Radiation and Photochemistry Division, Chemistry Group of BARC, in August 2024 after graduating from 67th batch of Training school, BARC. Her areas of interest include photochemical and radiation studies, with a particular emphasis on microheterogeneous media such as deep eutectic solvents and room temperature ionic liquids. Her research also focuses on the synthesis of nanomaterials and nanocomposites for biological, optical, and sensing applications employing innovative green techniques and high energy ionizing radiations.*
	***Dr. Apurav Guleria****, Scientific Officer/F in the Radiation and Photochemistry Division, Chemistry Group of BARC, works in the field of Radiation Chemistry and Nanomaterials. His research interests encompass radiation and photochemical investigations, primarily focused on microheterogeneous media like microemulsions, room temperature ionic liquids, and deep eutectic solvents. His research also includes the synthesis of nanomaterials/nanocomposites with novel features through green methodologies and high energy ionizing radiations for biomedical, optical, and sensing applications. He has published more than 60 research articles in peer reviewed national and international journals. Dr. Guleria is a recipient of "Young scientist award-2016" by Department of Atomic Energy and Young Associate, Maharashtra Academy of Sciences-2021.*
	***Dr. M. C. Rath*** *has obtained his M. Sc. degree in Chemistry from Utkal University, Bhubaneswar in 1990, and joined BARC in 1992 as a trainee officer in Chemistry and subsequently joined then Chemistry Division in 1993 after the completion of training. Since then, he has been working in the field of radiation and photochemistry and obtained Ph. D. degree from Mumbai University in 1999. He has worked for two years from 2001 to 2003 at JAIST, Japan in the field of carrier relaxation dynamics in semiconductor quantum well structures. He has been working in the field of radiation induced synthesis of various nanomaterials for more than two decades. His current research interests include free radicals assisted synthesis of chalcogenide, oxide nanomaterials and degradation of toxic chemicals, radiation chemical studies at high temperature high pressure, radiation chemistry of CO2 and exotic solvents like deep eutectic solvents.*

Radiation-Induced Strategies for the Synthesis of Polymer Composites for Biomedical Applications, Precious Metal and Radionuclide Extraction

Amit Kanjilal[1,2], Krishan Kant Singh[1,2], and Juby K. Ajish[1,2]*

[1]*Radiation and Photochemistry Division, Bhabha Atomic Research Centre, Mumbai 400085*

[2]*Homi Bhabha National Institute, Anushaktinagar, Mumbai - 400094*

E-mail: kuttan@barc.gov.in

Abstract

Radiation-induced techniques for developing new materials and modifying existing ones to impart desired properties, have gained significant industrial acceptance in recent years. One of the key advantages of radiation technology is its green, clean, and easily scalable nature. Extensive fundamental studies in radiation chemistry have provided the foundation for numerous radiation-based industrial processes. This article highlights the synthesis of biomaterials using ionizing radiation, with emphasis on glycopolymeric electrospun nanofibers for receptor mediated targeted drug delivery, polyacrylonitrile beads for extraction of radionuclides and polypropylene functionalized sorbent for extraction of Pb(II) and Au(III).

Introduction

Radiation-induced strategies for the synthesis of polymer composites offer several distinct advantages over conventional chemical methods. Unlike traditional approaches, these processes do not require chemical initiators or catalysts, thereby eliminating the risk of contamination and making the resulting composites safer for biomedical and environmental applications. The synthesis can often be carried out under mild conditions such as room temperature and ambient pressure, which is particularly beneficial for preserving sensitive functional groups or biomolecules. Radiation also allows precise control over the structural features of the composites, including crosslinking density, porosity, and surface functionality, simply by adjusting the dose. An additional benefit is that the process ensures simultaneous sterilization of the materials, a feature highly desirable for medical uses. Being a green and eco-friendly technique, it avoids harsh chemicals and solvents, thus reducing unwanted by-products. The method is versatile and applicable to a wide range of natural and synthetic polymers, enabling the development of composites with tailored properties. Moreover, radiation processing enhances the mechanical strength, stability, and durability of the composites, making them suitable for demanding environments. Since radiation technologies like gamma and electron beam are already employed on an industrial scale, the approach is also scalable for large-scale production. Importantly, these composites can be functionalized for dual applications—such as the extraction of metal ions and radionuclides for environmental remediation, as well as in biomedical fields for drug delivery, wound healing, and tissue engineering—demonstrating the broad potential of radiation-induced synthesis.

Radiation induced synthesis of glycopolymers for drug delivery applications

Glycopolymers are synthetic polymers, containing sugar groups on their pendant chains. They have been widely investigated for various biological and biomedical applications due to excellent hydrophilicity, biodegradability, and biocompatibility. Glycopolymers can mimic the biological functions of glycan in recognition processes through multivalent lectin interactions. Stimuli-responsive polymers such as thermo-

responsive, pH-responsive, and light-responsive materials have also attracted much attention in biomedical applications. By incorporation of responsive chains in glycopolymers, they can be responsive to the changes in their surrounding medium. Moreover, this combination provides materials with selective binding to specific cells and the ability to enhance and control the lectin-polymer interactions effectively and selectively with changes in the surrounding environment [1-3].

Radiation-induced synthesis is a clean, efficient, and well-controlled method for creating glycopolymers, which are synthetic polymers with attached carbohydrate units. In drug delivery, these bioconjugates are particularly valuable due to their biocompatibility and ability to mimic biological functions, such as cell recognition. By using ionizing radiation like gamma rays or electron beams, researchers can synthesize and sterilize glycopolymers simultaneously, resulting in highly pure, functional biomaterials. The synthesis of glycopolymers and related biomaterials via radiation involves using high-energy radiation to initiate polymerization and crosslinking without the need for traditional chemical catalysts or initiators. This process can be tuned to control the polymer's properties, making it versatile for drug delivery applications.

Receptor mediated targeted drug delivery to liver cancer cells using stimuli responsive UV-polymerized galactosylated electrospun nanofibers

Selective targeting of overexpressed surface proteins on cancer cells offers a promising strategy for more selective and less toxic cancer treatment[4, 5, 6]. Among the various targeting approaches, the asialoglycoprotein receptor-1 (ASGPR-1) has been widely studied due to its high expression on hepatocytes and HCC cells, while being absent in non-liver tissues[7]. ASGPR-1 specifically recognizes and binds to galactose and its derivatives, making it an ideal target for liver-specific drug delivery[8]. Galactose-functionalized carriers such as nanoparticles, liposomes, and micelles have shown enhanced targeting efficacy[9]. Recent advances in hepatocyte targeting, support the use of galactose-functionalized nanocarriers for liver cancer therapy. Among emerging platforms, nanofiber systems stand out for their high surface area, tunable porosity, and controlled drug release[10]. Electrospinning, a widely used technique for fabrication of nanofibers, allows the development of functionalized surfaces tailored for targeted drug delivery. Innovations in coaxial electrospun nanofibers show promise in cancer therapy by enabling sustained drug release and localized treatment, thus improving outcomes with chemotherapeutic drug loaded fibers.

In addition to targeted delivery, stimuli-responsive drug release enhances the efficacy of nanofiber-based systems by enabling site-specific release in the acidic tumor microenvironment caused by altered metabolism[11]. There is special interest in nanofibers made of naturally occurring materials like chitosan, collagen, gelatin, alginate etc due to their biocompatibility and ease of availability. The combination of ASGPR-1 mediated targeting and pH-responsive drug release offers a synergistic approach for improving drug bioavailability, reducing systemic toxicity, and maximizing therapeutic effects.

In this study, we visualized that, the integration of nanofiber-based delivery systems with ASGPR-1 targeting moiety could enhance targeted drug delivery to liver cancer cells, ensuring efficient uptake and controlled release of therapeutic agents following a pH-sensitive drug release mechanism. The system consists of a coaxial electrospun nanofiber scaffold composed of NSC as the core material, and shell made from a copolymer of polyvinyl alcohol grafted glycidyl methacrylate (PVA-g-GMA) and galactose-based acrylamide (Gal-acryl) (Figure 1). NSC in the core provides pH responsiveness and appropriate functionality for electrostatic loading of DOX while the shell imparts the necessary protection for the drug loaded in the core as well as providing liver specific targeting due to the galactose units.

In electrospinning, in-situ UV polymerization is a powerful strategy that combines fiber formation with simultaneous or subsequent crosslinking/curing of polymers12. This approach brings several advantages. UV curing during/after electrospinning enhances crosslinking within the nanofibers, giving them higher tensile strength, toughness, and resistance to deformation compared to non-crosslinked fibers. Hydrophilic polymers like PVA, PEG, or natural polymers normally dissolve or swell in water. In-situ UV polymerization creates a stable network structure, making the nanofibers insoluble and suitable for drug delivery, tissue scaffolds, or filtration. UV polymerization allows incorporation of functional monomers, photo-crosslinkers, or bioactive molecules, leading to tunable chemical functionality within fibers without post-treatment. UV curing is a fast, energy-efficient, and clean process compared to thermal curing, minimizing the need for additional solvents or high temperatures that might damage sensitive drugs or biomolecules. For drug delivery systems, in-situ UV polymerization prevents premature leakage by locking therapeutic agents in the fiber matrix, allowing for controlled and sustained release.

Preparation of Gal-PVA/NSC and DOX loaded Gal-PVA/NSC (DOX@Gal-PVA/NSC) core-shell nanofibers

Gal-PVA/NSC core-shell nanofibers were synthesized by *in-situ* UV crosslinking in an electrospinning setup. The Gal-PVA solution with UV initiator (the shell solution) and NSC (15 wt%) (the core solution), was taken in different syringes. The core-shell nanofibers were synthesized using coaxial spinneret with two concentrically arranged capillaries. The inner capillary and outer capillary had diameters 0.8 mm and 1.6 mm, respectively and were connected to a high voltage power supply. The flow rates of the two capillaries were controlled by a syringe pump. The fibers were spun on a cylindrical mandrel which was exposed to UV-irradiation leading to crosslinking of the fibers. The applied voltage was 17 KV and distance between the mandrel and coaxial syringe was set at 13 cm. The flow rate of Gal-PVA shell solution was 1 mL/h and that of the NSC shell solution was 0.5 mL/h. The collected nanofibers were purified using a 3.5 KD MWCO dialysis membrane, lyophilized and stored for further studies.

The synthesis of DOX loaded nanofiber (DOX@Gal-PVA/NSC) was carried out by equilibrating the NSC with 0.5 mg/mL DOX solution, which was used as the core solution (DOX@NSC) during co-axial electrospinning. All proportions and parameters were kept as that used for spinning blank fibers.

The DOX loaded nanofibers were assessed for their potential towards selective targeting of liver cancer cells. The pH dependent drug release mechanism ensured that DOX is selectively released in the acidic tumor microenvironment, thereby improving drug bioavailability and minimizing systemic toxicity. To evaluate the efficacy, specificity and safety of the developed system, a series of studies were conducted including haemolysis assays, *in-vitro* cytotoxicity studies, cellular uptake studies, etc. These studies validated the potential of the developed nanofiber-based system for targeted drug delivery to liver cancer cells.

The surface morphology of the synthesized nanofibers was observed by SEM (Figure 1A) and was found to be smooth without any beading. The TEM images distinctly indicates that the diameter of the fibers is uniform and has an average diameter of around 200 nm (Figure 1B). The TEM image clearly shows the core-shell structure of the nanofibers as depicted in figure 1C.

Cellular uptake and internalization time course study of DOX@Gal-PVA/NSC

The intracellular accumulation of DOX and DOX@Gal-PVA/NSC was assessed over time using confocal microscopy. DOX exhibited strong fluorescence intensity from the beginning, indicating rapid passive diffusion into both HepG2 and WRL68 cells. In contrast, the cells treated with DOX@

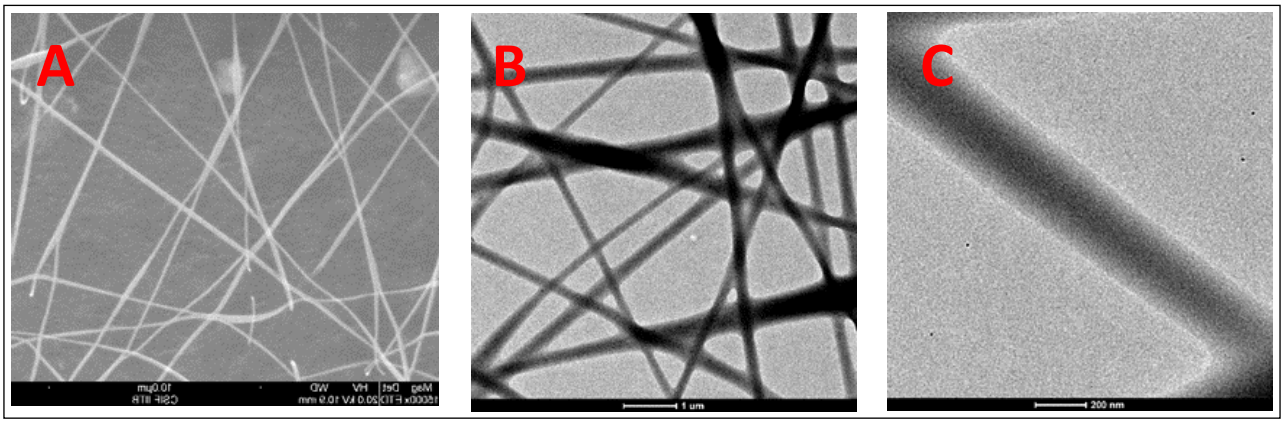

Figure 1: (A) SEM image, (B) & (C) TEM images of Gal-PVA/NSC nanofibers.

Gal-PVA/NSC showed a time dependent increase in intracellular fluorescence of DOX, with higher accumulation observed in HepG2 cells compared to WRL68 cells, confirming ASGPR-1 mediated uptake (Figure 2). The sustained increase in fluorescence over 2 to 8 h suggests a controlled release mechanism from DOX@Gal-PVA/NSC, allowing prolonged intracellular retention of DOX

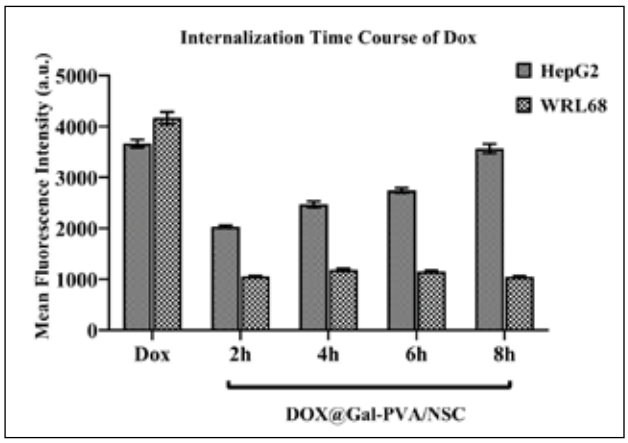

Figure 2: Time dependent intracellular accumulation of DOX in HepG2 and WRL68 cells for 2, 4, 6, and 8 h. Error bars represent mean ± SEM (n=3).

Radiation induced synthesis of polymeric composites for extraction of radionuclides

Polymer-based composites—such as beads, films, membranes, fibres, and nanocomposites—have emerged as highly promising materials for the removal of uranium from aqueous environments[13-16]. Their inherent stability, chemical versatility, and cost-effectiveness make them particularly suitable for solid-phase extraction of radionuclides. Radiation-induced polymerization techniques can be broadly categorized into two main approaches: radiation-induced polymerization and radiation-induced grafting. In radiation-induced polymerization, one or more monomers are directly exposed to ionizing radiation, initiating polymerization uniformly throughout the reaction medium. While this method may lead to the formation of unwanted homopolymers, this issue can be controlled through careful optimization of radiation dose, monomer concentration, and reaction conditions to achieve the desired polymer structure and functionality. On the other hand, radiation-induced grafting involves the covalent attachment of functional monomers onto a pre-existing polymer backbone. This can be achieved through two primary methods: the pre-irradiation method and the simultaneous (mutual) irradiation method. In the pre-irradiation method, the base polymer is first irradiated in the absence of monomers to generate reactive sites (typically free radicals). These sites are then exposed to monomers, leading to grafting. In contrast, the mutual irradiation method involves simultaneous irradiation of both the base polymer and the monomer in the same reaction medium. As radiation generates active species in situ, grafting occurs concurrently, often resulting in a more uniform distribution of grafted chains. Both approaches offer precise

control over the functionalization of polymers, enabling the development of tailored materials with high affinity for uranium and other heavy metals, thereby enhancing their performance in environmental remediation applications[17, 18].

The primary objective of this study was to develop cost-effective polymeric sorbents for the efficient removal of toxic metals and radionuclides from aqueous waste streams. Radiation-induced polymerization was utilized as a green, sustainable, and efficient synthesis method. Polyacrylonitrile (PAN) powder was selected due to its low cost, wide availability, and excellent chemical, mechanical, and radiation stability[19]. Following polymerization, the material was functionalized and converted into a composite form to enhance its practical applicability for metal ion extraction from aqueous environments. The synthesized sorbents were extensively characterized using various analytical techniques to determine their physical and chemical properties. Their sorption performance was evaluated through batch adsorption experiments conducted under different conditions, with emphasis on extraction efficiency, selectivity, and overall practical applicability.

Synthesis of polymeric composite beads

The composite beads were synthesized by integrating the base polymer, polyethersulfone (PES) and sodium alginate, with the polymeric extractant, amidoxime-functionalized polyacrylonitrile (APAN), using the phase inversion technique. This method ensured the homogeneous incorporation of APAN within the PES matrix, enhancing the composite's adsorption properties. The detailed synthesis procedure is as follows:

Synthesis of PAN powder

Polyacrylonitrile (PAN) was synthesized via solution polymerization initiated by gamma irradiation. An aqueous solution saturated with acrylonitrile was exposed to a total gamma radiation dose of 1 M Rad, as illustrated in Figure 3. The high-energy radiation triggered the polymerization of acrylonitrile, resulting in the formation of PAN chains. After irradiation, the reaction mixture was thoroughly washed with water to eliminate unreacted monomers and residual impurities. The resulting polymer was then dried at room temperature to yield a fine, off-white powder. This approach enabled efficient polymerization while preserving the structural integrity and purity of the synthesized PAN [19].

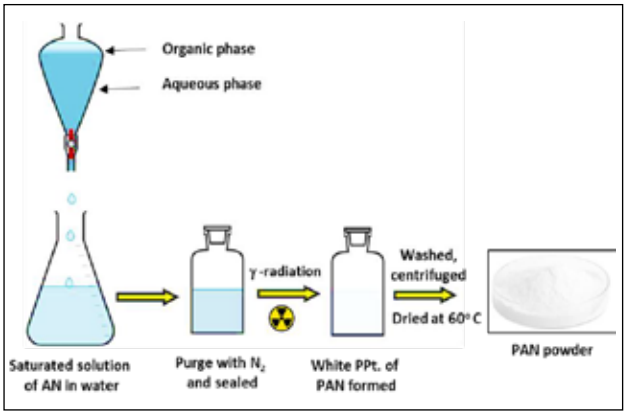

Figure 3. Schematic of synthesis process of PAN powder by Gamma irradiation

Amidoximation of PAN powder

Amidoxime-functionalized polyacrylonitrile (APAN) was synthesized by reacting the previously prepared PAN powder with an amidoximation reagent[20]. Hydroxylamine hydrochloride (1 g) was dissolved in a 50% methanol-water (v/v) mixture, and the pH was adjusted to 7 using KOH before making up the volume to 50 mL. PAN powder (1 g) was added to this solution and heated at 70 °C under constant stirring for 4 hours, using a water-cooled condenser to minimize solvent loss. During the reaction, the PAN color gradually changed from white to light yellow, indicating successful amidoximation. Care was taken to avoid excessive heating or prolonged reaction time, which could cause thermal degradation and result in a brittle, deep yellow product. After completion, the APAN was separated by centrifugation, thoroughly washed with water and acetone to remove residual reagents, and dried to obtain the final product.

Synthesis of APAN-PES bead

APAN-loaded PES beads were synthesized using the phase inversion technique (as shown in Figure 4)[17]. Polyether sulphone (PES) powder was dissolved in 1-methyl-2-pyrrolidone (NMP) to form a solution of suitable viscosity. A measured amount of APAN powder was then dispersed into the PES solution, and the mixture was added dropwise into an aqueous bath using a syringe with a suitable needle. Upon contact with water, soft beads formed within minutes. These beads were cured by incubating in water for 24 hours to ensure complete solidification. The resulting beads were utilized for batch uranium extraction studies. PES was selected due to its excellent thermal, oxidative, radiolytic, and hydrolytic stability, along with its superior mechanical strength. The phase inversion process effectively encapsulated APAN within porous, spherical beads. The porosity and hydrophilicity of the resulting polymer matrix play a critical role in facilitating efficient metal ion exchange.

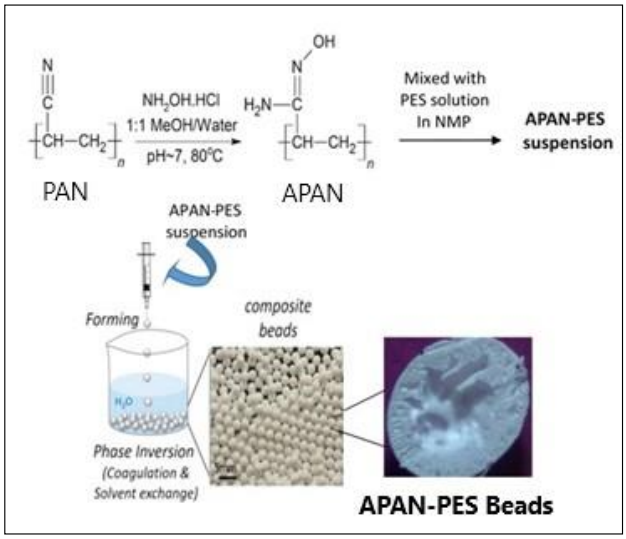

Figure 4: Phase inversion method for Beads formation

Synthesis of APAN-Alginate beads

The formation of APAN-alginate beads involves the ionic crosslinking of sodium alginate with calcium ions (Ca^{2+}) to produce stable, porous hydrogel structures suitable for uranium extraction[18]. Initially, sodium alginate (2–4% w/v) is dissolved in deionized water under continuous stirring to obtain a clear, homogeneous solution. Amidoxime-functionalized polyacrylonitrile (APAN) powder is then gradually incorporated into the alginate solution with stirring, followed by sonication for 1–2 hours to ensure uniform dispersion and prevent agglomeration. The resulting APAN-alginate suspension is introduced dropwise into a calcium chloride (1–5 M) crosslinking bath using a syringe or pipette. Upon contact, calcium ions replace sodium ions in the alginate, instantly forming spherical, gel-like calcium alginate beads [as shown in figure 4(A)]. These beads are left in the $CaCl_2$ bath for 24 hours to ensure complete crosslinking and improved structural integrity. Finally, the beads are washed thoroughly with deionized water to remove residual calcium ions and unreacted materials. The beads can be utilized directly in their hydrogel form for adsorption applications.

A batch sorption study was conducted to evaluate the impact of various physical parameters on UO_2^{2+} ion removal using synthesized beads. Key factors such as equilibration time, pH, initial metal concentration, temperature, and reusability were systematically analysed. This work highlights the key findings from the batch sorption experiments.

The synthesized beads are spherical in shape, with a diameter of approximately 1–2 mm, as shown in Figure 5(A). The SEM micrograph of the cross-section of the beads reveals a highly porous structure, as shown in Figure 5(B), which enhances their surface area and hydrophilicity—key factors for efficient sorption.

These beads were employed for uranium sorption in a batch sorption mode, and the influence of various physical parameters on the sorption process was investigated. As shown in Figure 5(C), an increase in the initial metal ion concentration led to a gradual increase in sorption capacity, reaching a maximum of 30 mg g^{-1} at an initial concentration of 500 ppm. Similarly, sorption was found to vary with the pH of the

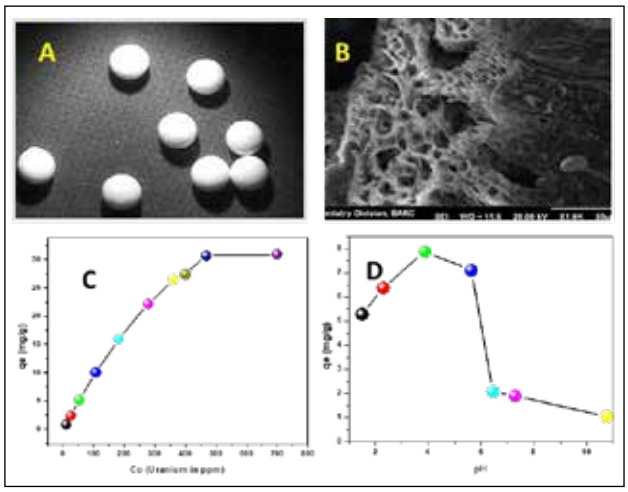

Figure 5: (A) APAN PES beads, (B) SEM micrograph of Cross section of bead, (C) Sorption study, and (D) Effect of pH on uranium sorption by the beads

solution as shown in Figure 5(D). It increased steadily up to pH 4–5, after which it declined sharply. The decrease in sorption at pH values below 5 can be attributed to competition between hydronium ions and uranyl ions for the binding sites, which hinders complex formation. At pH values above 5, the formation of uranyl hydroxide complexes likely reduces the availability of free uranyl ions for sorption[21].

The crosslinked APAN-alginate beads synthesized for this study were found to be oval in shape, as depicted in Figure 6(A). Upon adsorption of uranium, the beads exhibited a visible color change, turning slightly yellowish, which is indicative of successful uranium uptake (Figure 6(B)). The adsorption performance of these APAN-alginate beads was systematically evaluated under various experimental conditions, including different initial uranium concentrations, temperatures, and pH values, to assess their effectiveness in removing uranium from aqueous solutions.

Kinetic studies revealed that an equilibration time of approximately 180 minutes was sufficient to reach sorption saturation, suggesting that the adsorption process proceeds at a relatively moderate rate and achieves steady-state within a practical time frame (Figure 6(D)). The sorption capacity of the crosslinked polymeric beads was notably high, with a maximum uranium uptake of approximately 200 mg g^{-1} of dry beads, as presented in Figure 6(C). This high capacity demonstrates the strong affinity of the APAN-alginate matrix for uranyl ions and highlights its potential as an efficient material for uranium removal from contaminated water sources.

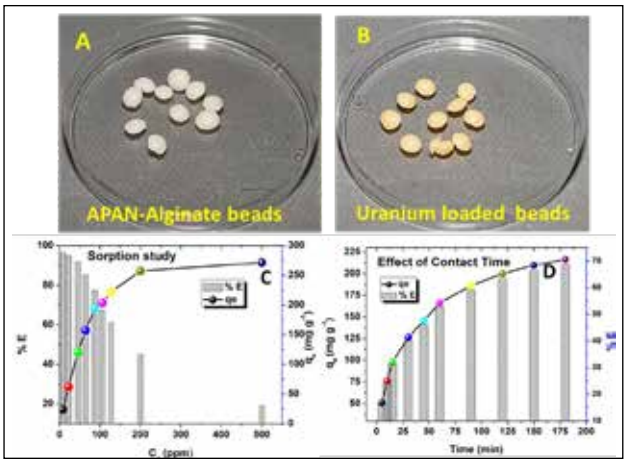

Figure 6: (A) APAN alginate beads, (B)Uranium loaded APAN alginate beads, (C) Sorption study, and (D) Effect of contact time on uranium sorption by the beads

Converting poly-propylene waste into cost efficient adsorbent using radiation technology

Industrialization and urbanization have led to the accumulation of large volumes of municipal solid waste (MSW), with non-biodegradable plastics such as polypropylene (PP) constituting a significant fraction. Improper disposal of these plastics not only exacerbates environmental pollution but also poses serious challenges to sustainable waste management[22]. At the same time, industrial effluents from mining, metallurgy, and electronics frequently release heavy metals such as Pb(II) and precious metals like Au(III) into aquatic environments. Lead is a toxic contaminant with severe ecological and health impacts[23], while gold, though non-toxic, is of considerable economic value. Efficient recovery of these metals from wastewater is therefore critical, serving both environmental protection and resource recovery goals[24]. Radiation-

induced graft polymerization has emerged as an effective method for imparting functional groups onto otherwise inert polymer backbones without the need for chemical initiators[25]. This approach enables uniform modification, enhances physicochemical stability, and offers a versatile route to prepare tailored adsorbents. Transforming waste PP into functionalized sorbents through radiation-induced grafting thus provides a sustainable solution to plastic waste utilization while enabling selective metal ion capture.

In the present study, PP waste from municipal sources was grafted with glycidyl methacrylate (GMA) and further functionalized with diethylene triamine (DETA) and 2-aminomethyl pyridine (AMP) to prepare adsorbents for Pb(II) and Au(III), respectively. The materials were thoroughly characterized, and their adsorption behaviour was evaluated under different conditions with emphasis on capacity, selectivity, and reusability. The findings highlight the potential of radiation-functionalized PP waste as a low-cost, efficient, and sustainable adsorbent for metal recovery.

Radiation induced grafting and subsequent amination

Amine-functionalized PGMA-g-PP fabrics have been developed as efficient and reusable adsorbents through a two-step process: radiation-induced grafting of glycidyl methacrylate (GMA) onto PP, followed by amination with DETA and AMP (Figure 7). PP sections (W_i) were immersed in a GMA solution (1:1 acetone-water), purged with N_2 for 15 min, and irradiated with γ-rays from a ^{60}Co source at 5.5 kGy h^{-1} to a total dose of 25 kGy. The PGMA grafted -PP was washed with DMF and deionized water, then dried at 40°C to constant weight (W_f). Percentage grafting ($\%G$) was calculated as,

$$\%G = \frac{W_f - W_f}{W_i} \times 100 \quad (1)$$

In the second step, PGMA-grafted PP (PGMA-g-PP) were refluxed with DETA or AMP (1:1 amine-solvent (acetonitrile/dioxane/DMF) mixture, 80 °C, 5 h), rinsed, dried, and weighed to calculate epoxide-to-amine conversion using standard equation as follows.

$$\%\ Amination = \frac{(W_a - W_g)/_{molecular\ weight\ of\ amine}}{(W_g - W_o)/_{molecular\ weight\ of\ GMA}} \quad (2)$$

W_a, W_o, W_g denote weights of amine-functionalized, blank, and PGMA-grafted PP fabrics, used for Pb(II) & Au(III) adsorption studies.

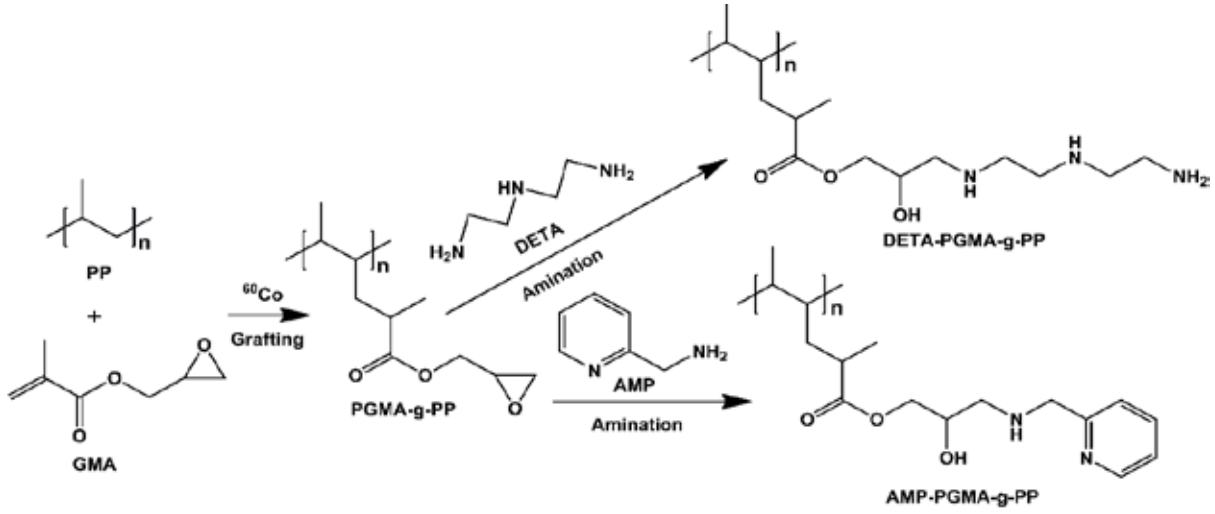

Figure 7: Synthesis scheme- Radiation induced grafting followed by amination with DETA and AMP

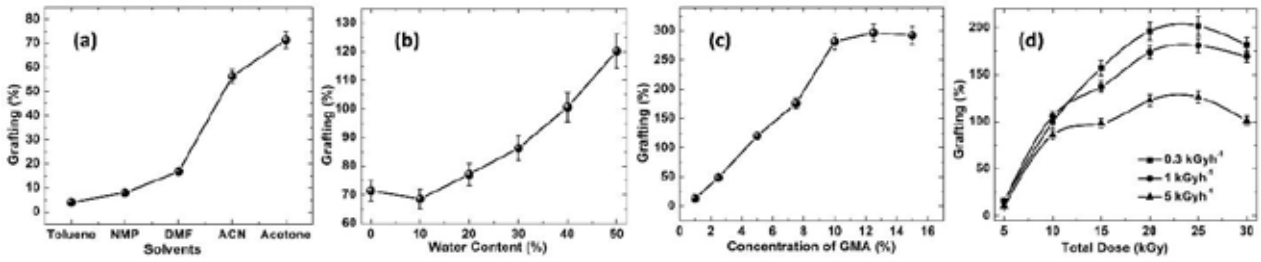

Figure 8: Effect of different experimental parameters on grafting %: (a) Solvent, (b) Water content in the solvent, (c) Concentration of GMA and (d) Total dose given at various dose rates

Radiation grafting offers high grafting yields (%G) with minimal homo-polymer formation, ensuring structural stability. The grafting efficiency is strongly influenced by solvent type, water content, monomer concentration, and radiation dose (Figure 8). Solvents with low chain transfer constants, such as acetonitrile and acetone, extend radical lifetimes and significantly enhance %G[26]. A mixed acetone-water system (1:1) achieves grafting yields up to 120%, although water content above 50% is limited by GMA solubility. Increasing GMA concentration to 10% further enhances %G until diffusion limitations and homo-polymerization induce saturation. Radiation dose also plays a key role: doses up to 10 kGy show little effect, while higher doses promote homo-polymerization, radical mobility reduction, and even PP degradation at very high exposures.

Subsequent amination of PGMA-g-PP using diethylene triamine (DETA) and 2-aminomethyl pyridine (AMP) proceeds via S_N1 or S_N2 pathways, depending on solvent polarity. Polar aprotic solvents (e.g., acetonitrile, DMF) favor S_N2 reactions, enhancing substitution efficiency and metal-binding performance. Acetonitrile proved most effective, achieving 99% amination with DETA and 68% with AMP, yielding sorbents with high Pb(II) and Au(III) adsorption capacity.

Characterization of synthesized adsorbent

SEM images [Figure 9 (a), (b)] revealed increased surface roughness of PGMA-grafted PP after DETA and AMP functionalization, facilitating improved Pb(II) and Au(III) sorption–desorption compared to pristine PP. FTIR spectra [Figure 9(c)] confirmed structural

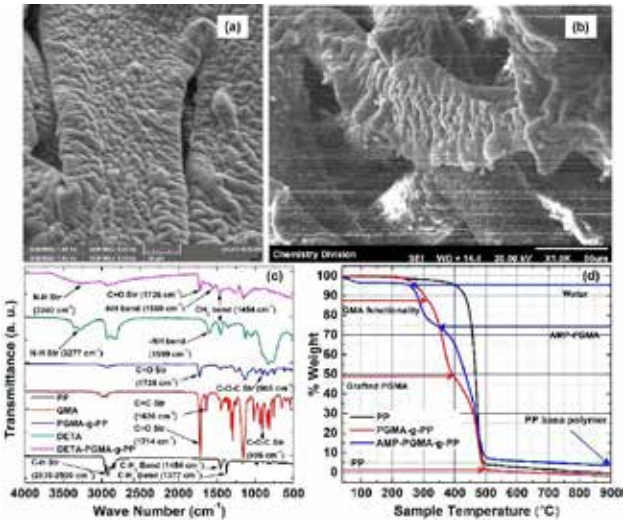

Figure 9: Characterisation of the synthesised adsorbent: SEM [(a) DETA-PGMA-g-PP, (b) AMP-PGMA-g-PP]; (c)FTIR of DETA-PGMA-g-PP and (d) TGA of AMP-PGMA-g-PP

modifications: PP exhibited characteristic $-CH_3/-CH_2$ stretching (2800–3000 cm^{-1}) and C-H bending (1454, 1377 cm^{-1}); PGMA grafting introduced C=O (1726 cm^{-1}) and epoxide (905 cm^{-1}) peaks; while DETA functionalization was evidenced by N-H stretching (3240 cm^{-1}), $-NH_2$ bending (1560 cm^{-1}), and disappearance of the epoxide signal. TGA (Figure 9(d)) showed distinct thermal behaviour: pristine PP degraded in a single step (~400°C), PGMA-g-PP in two stages (~50% each), and AMP-PGMA-g-PP in overlapping stages with ~5% residue at 900°C. Nitrogen adsorption-desorption

isotherms (not shown in figure) indicated a Type IV mesoporous structure for both amine-functionalized materials[27]. BET surface areas were 60.6 $m^2 g^{-1}$ for DETA-PGMA-g-PP and 100.9 m^2g^{-1} for AMP-PGMA-g-PP, with uniform pore diameters of 3-5 nm, supporting efficient metal adsorption.

Kinetics and adsorption of Pb(II) & Au(III) by the adsorbents

Batch adsorption experiments were conducted to evaluate the Pb(II) and Au(III) removal efficiency. The adsorption capacity (q_e, mgg^{-1}) was calculated using the equation:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (3)$$

where C_0 and C_e are the initial and equilibrium concentrations (mgL^{-1}), V is the solution volume (L), and m is the adsorbent mass (g). Kinetics studies were also conducted to understand the rate of the adsorption of Pb(II) & Au(III) and associated mechanism.

Kinetics of adsorption of Pb(II) on DETA-PGMA-g-PP showed the sorption capacity initially increased rapidly, achieving 90% of its saturation capacity within 15 minutes[28]. In case of adsorption of Au(III) on to AMP-PGMA-g-PP, the kinetics was even faster, reaching 96% of saturation capacity within just 5 minutes. The maximum sorption capacities for the two adsorbents for respective metal ions were found to be 230 mgg^{-1} for Pb(II) and 580 mgg^{-1} for Au(III). Recyclability study showed (Figure 10 (a)) that DETA-PGMA-g-PP adsorbent could be successfully used for at least 10 cycles without much loss of its initial adsorption capacity. On the other hand, the AMP-PGMA-g-PP adsorbent was found to be very much selective[29] (Figure 10 (b)) towards separation of Au(III) from a solution having equimolar mixture of various other metal ions commonly present in the electronic waste solutions.

Thus, gamma radiation-induced graft polymerization has been effectively employed to transform polypropylene (PP) into valuable adsorbents like DETA-PGMA-g-PP and AMP-PGMA-g-PP. The DETA-functionalized adsorbent demonstrated efficient removal of aqueous Pb(II) with rapid kinetics and substantial adsorption capacity. Meanwhile, the AMP-PGMA-g-PP adsorbent exhibited extremely rapid kinetics for the selective separation of Au(III) with a high capacity. Both adsorbents were found to be recyclable for at least 10 adsorption-desorption cycles, highlighting the potential of these radiation-processed polymeric materials in real-world applications aimed at implementing a waste-to-wealth strategy.

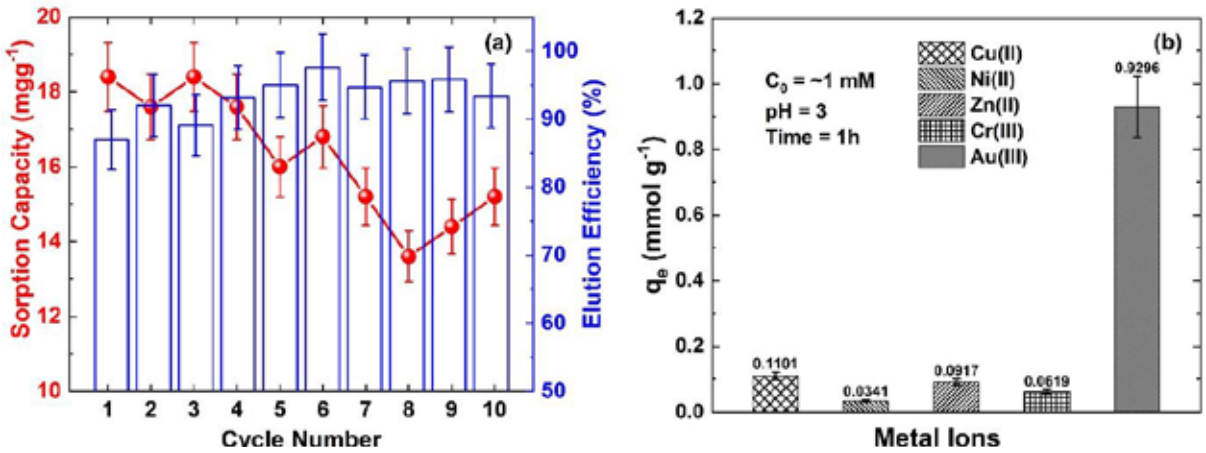

Figure 10: (a) Recyclability of DETA-PGMA-g-PP adsorbent towards Pb(II) adsorption; (b) Selectivity of Au(III) over other metal ions for AMP-PGMA-g-PP adsorbent

Conclusions

In this article, we have tried to bring together various applications of radiation induced techniques for targeted drug delivery and extraction of radionuclides as well as precious metals. Here we have explored the usage of *in-situ* UV polymerization as well as gamma ray induced polymerization for functionalization of polymeric systems. Glycopolymer decorated electrospun nanofibers synthesized by *in-situ* UV polymerization shows promising results for liver cancer targeted drug delivery. The APAN-alginate polymeric beads have shown its potential as an efficient material for uranium removal from contaminated water sources. In addition, the polypropylene functionalized adsorbent for extraction of precious metals, synthesized by gamma irradiation proves to be an ideal example of wealth from waste concept.

Acknowledgement

The authors are thankful to Dr. A. C. Bhasikuttan, Head, RPCD and Associate Director, chemistry group for the constant support and encouragement.

References

1. Ajish, J. K.; Ajish Kumar, K. S., Synthesis of galactoacrylamide and study of stimuli-responsive fluorescent hierarchical self-assembly-promoted specific interactions with proteins, *Chemistry Select*, 8(37), (2023).
2. Ajish, J. K.; Ajish Kumar, K. S.; Chattopadhyay, S.; Kumar, M., Glycopolymeric gel stabilized *N* -succinyl chitosan beads for controlled doxorubicin delivery. *Carbohydrate Polymers*, 144, 98–105, (2016).
3. Ajish, J. K.; Ajish Kumar, K. S.; Ruhela, A.; Subramanian, M.; Ballal, A. D.; Kumar, M., AIE based fluorescent self-assembled glycoacrylamides for *E.coli* detection and cell imaging, *Sensors and Actuators B: Chemical*, 255, 1726–1734, (2018).
4. Das, S.; Dey, M. K.; Devireddy, R.; Gartia, M. R., Biomarkers in Cancer Detection, Diagnosis, and Prognosis, *Sensors*, 24(1), 37, (2023).
5. Kędzierska, M.; Bańkosz, M., Role of Proteins in Oncology: Advances in Cancer Diagnosis, Prognosis, and Targeted Therapy—A Narrative Review, *Journal of Clinical Medicine*, *13*(23), 7131, (2024).
6. Liyanage, P. Y.; Hettiarachchi, S. D.; Zhou, Y.; Ouhtit, A.; Seven, E. S.; Oztan, C. Y.; Celik, E.; Leblanc, R. M., Nanoparticle-mediated targeted drug delivery for breast cancer treatment. *Biochimica et Biophysica Acta (BBA) - Reviews on Cancer*, 1871(2), 419–433. (2019).
7. Li, Y.-L.; Zhu, X.-M.; Liang, H.; Orvig, C.; Chen, Z.-F., Recent Advances in Asialoglycoprotein Receptor and Glycyrrhetinic Acid Receptor-Mediated and/or pH-Responsive Hepatocellular Carcinoma- Targeted Drug Delivery. *Current Medicinal Chemistry*, *28*(8), 1508–1534, (2021).
8. Battisegola, C.; Billi, C.; Molaro, M. C.; Schiano, M. E.; Nieddu, M.; Failla, M.; Marini, E.; Albrizio, S.; Sodano, F.; Rimoli, M. G., Galactose: A Versatile Vector Unveiling the Potentials in Drug Delivery, Diagnostics, and Theranostics, *Pharmaceuticals*, 17(3), 308. (2024).
9. Kumar, V.; Rahman, M.; Gahtori, P.; Al-Abbasi, F.; Anwar, F.; Kim, H. S., Current status and future directions of hepatocellular carcinoma-targeted nanoparticles and nanomedicine, *Expert Opinion on Drug Delivery*, 18(6), 673–694, (2021).
10. Alfadhel, M., Nanofiber-Based Drug Delivery Systems: A Review on Its Applications, Challenges, and Envisioning Future Perspectives, *Current Drug Delivery*, 22, (2024).
11. Dong, Y.; Yang, J.; Liu, H.; Wang, T.; Tang, S.; Zhang, J.; Zhang, X., Site-Specific Drug-Releasing Polypeptide Nanocarriers Based on Dual-pH Response for Enhanced Therapeutic Efficacy against Drug-Resistant Tumors, *Theranostics*, *5*(8), 890–904, (2015).
12. Lin, W. H.; Tsai, W. B., In situ UV-crosslinking gelatin electrospun fibers for tissue engineering applications, *Biofabrication*, 5(3), 035008 (2013).
13. Hegazy, E.-S. A.; Kamal, H.; Khalifa, N. A.; Mahmoud, G. A., Separation and Extraction of Some Heavy and Toxic Metal Ions from Their Wastes by Grafted Membranes, *Journal of Applied Polymer Science,* 81, 849 – 860 (2001).
14. Shull, K. R.; Kellock, A. J., Metal Particle Adsorption and Diffusion in a Model Polymer/Metal Composite System, Journal of Polymer Science: Part B: Polymer Physics, 33,1417-1422 (1995).
15. Kanjilal, A.; Singh, K. K.; Bairwa, K. K.; Kumar, M., Synthesis and Study of Optimization of Amidoximated PAN-DVB-EGDMA Beads for the Sorption of Uranium from Aqueous Media, *Polymer Engineering & Science*, 59 (4), 863–872 (2019).
16. Radoor, S.; Karayil, J.; Jayakumar, A.; Siengchin, S., Efficient Removal of Dyes, Heavy Metals and Oil-Water from Wastewater Using Electrospun Nanofiber Membranes: A Review, *Journal of Water Process Engineering*, 59, 104983 (2024).
17. Goel, N. K.; Kumar, V.; Dubey, K. A.; Bhardwaj, Y. K.; Varshney, L., Development of Functional Adsorbent from PU Foam Waste via Radiation Induced Grafting I: Process Parameter Standardization, *Radiation Physics and Chemistry*, 82, 85–91 (2013).
18. Singh, K. K.; Goel, N. K.; Kanjilal, A.; Ruhela, R.; Kumar, V.; Bhattacharyya, K.; Tyagi, A. K., Radiation Grafted Polyacrylic Acid–Polyurethane Foam Copolymer for Efficient Toxic Metal Removal from Aqueous Waste: A Sustainable Approach to Waste Management, *Polymer Bulletin*, 81, 13435–13460 (2024).
19. Singh, K.K.; Shah, C.; Dwivedi, C.; Kumar, M.; Bajaj, P. N., Study of Uranium Adsorption Using Amidoximated Polyacrylonitrile-Encapsulated Macroporous Beads, *Journal of Applied Polymer Science*, 127 (1), 410–419 (2013**)**.
20. Singh, K. K.; Kanjilal, A.; Dey, G.R.; Tyagi, A. K., Synthesis

of Amidoximated PAN and their Composites with PES for Extraction of Uranium from Aqueous Waste, *14th National Symposium on Radiation and Photochemistry* (NSRP- 2021)

21. Singh, K. K.; Kanjilal, A.; Tyagi, A. K., Development of Amidoxime-modified Biopolymer Composites from Radiation-Synthesized PAN for Uranium Extraction, *16th National Symposium on Radiation and Photochemistry* (NSRP-2025)
22. Bora, R. R.; Wang, R.; You, F., Waste Polypropylene Plastic Recycling toward Climate Change Mitigation and Circular Economy: Energy, Environmental, and Technoeconomic Perspectives, *ACS Sustainable Chemistry & Engineering*, 8, 16350-16363(2020).
23. Wijayawardena, M. A. A.; Megharaj, M.; Naidu, R., Bioaccumulation and toxicity of lead, influenced by edaphic factors: using earthworms to study the effect of Pb on ecological health, *Journal of Soils and Sediments*, 17, 1064-1072(2017).
24. Syed, S., Recovery of gold from secondary sources—A review, *Hydrometallurgy*,115-116, 30-51(2012).
25. Thinkohkaew, K.; Piroonpan, T.; Jiraborvornpongsa, N.; Potiyaraj, P., Radiation induced graft polymerization of fluorinated methacrylate onto polypropylene spun bond nonwoven fabric, *Surfaces and Interfaces*, 24, 101125(2021).
26. Mori, K.; Koshiishi, K.; Masuhara, K-i., Effect of solubility parameter of monomers on electron beam induced graft-polymerization onto polyethylene films, *Kobunshi Ronbunshu*, 48, 547-554(1991).
27. Demiral, H.; Demiral, İ.; Tümsek, F.; Karabacakoğlu, B., Adsorption of chromium(VI) from aqueous solution by activated carbon derived from olive bagasse and applicability of different adsorption models, *Chemical Engineering Journal*, 144, 188-196 (2008).
28. Kanjilal, A.; Singh, K. K.; Kumar, A., Gamma radiation induced optimized synthesis of amine functionalised poly-glycidyl methacrylate grafted poly-propylene non-woven fabric and its adsorption behaviour towards aqueous Pb(II), *Chemical Engineering Science*, 302, 120886 (2025) .
29. Dong, Z.; Liu, J.; Yuan, W.; Yi, Y.; Zhao, L., Recovery of Au(III) by radiation synthesized aminomethyl pyridine functionalized adsorbents based on cellulose, *Chemical Engineering Journal*, 283, 504-513 (2016).

	***Dr. Juby K. Ajish*** *joined Bhabha Atomic Research Centre in 2010 after graduating from 53rd batch of BARC training school. She obtained her MSc from Calicut University in 2008. She obtained her Ph.D. from Homi Bhabha National Institute, Mumbai, India in 2016, for her work on "Synthesis and study of carbohydrate-based hydrogels for biomedical applications". She is currently working on many important DAE relevant projects apart from directed research in the field of polymer chemistry. Her research interest includes fabrication of plastic scintillators and thin films for radiation detection, synthesis of polymeric hydrogels for various biomedical applications, utilization of synthetic polymers and functionalization of natural polymers for targeted drug delivery applications, synthesis and applications of glycopolymers in lectin recognition and bacterial detection. She has 25 publications in reputed journals with 507 citations and 3 technical reports to her credit.*
	***Dr. Krishan Kant Singh*** *has been associated with the Radiation & Photochemistry Division since 2008. He completed his M.Sc. in Chemistry from the University of Mumbai in 2015, with a focus on the development of polymeric composites for toxic metal extraction. He earned his Ph.D. in Chemical Sciences from the Homi Bhabha National Institute, Mumbai, in 2024. His doctoral research was titled "Development of Polymeric Composites for the Extraction of Radionuclides." His research interests include radiation-induced grafting, polymer modification, development of composite sorbents for the extraction of metals and radionuclides, plastic scintillator development, and the synthesis of novel ligands for selective metal separation. He is also actively involved in the synthesis of MOF–polymer composites for carbon capture and the removal of toxic metals*
	***Shri Amit Kanjilal*** *earned his M.Sc. in Chemistry from the Indian Institute of Technology Madras in 2015. He then joined the Bhabha Atomic Research Centre (BARC) in Mumbai, India, as a Scientific Officer in 2016, following a one-year advanced orientation course (OCES) offered by BARC. Currently, he serves as a Scientific Officer (E) in the Radiation & Photochemistry Division at BARC while pursuing his Ph.D. at HBNI, focusing on polymer chemistry and its applications for the adsorption and separation of critical metals from various industrial sources. His research interests include the synthesis of functionalized polymeric adsorbents through radiation-induced polymerization and traditional thermal polymerization methods. Furthermore, he is investigating the selectivity of these synthesized adsorbents for specific critical metal ions in the presence of various interfering ions found in industrial effluents.*

Radiation Processed Polymeric Composites for Advanced Applications

R. K. Mondal[1,2], K. A. Dubey[1,2], Y. K. Bhardwaj[1,2]
[1]*Radiation Technology Development Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400085*
[2]*Homi Bhabha National Institute, Mumbai 400094*
E-mail: rkmondal@barc.gov.in

Abstract

High energy radiation serves as an additive-free tool for the modification of polymeric materials. Upon irradiation, polymers and polymer composites can undergo intermolecular crosslinking or polymer-filler grafting, leading to structural stabilization and enhanced interfacial properties. In the case of conducting polymer composites (CPCs), such radiation-induced modifications enable their application as chemiresistive sensors for the detection and quantification of volatile organic compounds (VOCs). When exposed to VOCs, the polymeric phase primarily interacts with the analyte, inducing a chemiresistive stress that perturbs the conductive network within the CPC. This disruption manifests as a measurable change in electrical resistance, which can be correlated with the analyte concentration. Thus, the sensing response is largely governed by the polymer-analyte interaction parameter. High energy radiation can modulate this parameter either by introducing an additional barrier through crosslinking or by modifying the polymer-filler interface, thereby altering charge transport pathways and analyte diffusion characteristics. In addition to being low-cost and highly sensitive, radiation processed CPC based chemiresistive sensors offer distinct advantages like simple and scalable fabrication, ability to function as standalone devices and compatibility for integration into sensor arrays enabling analyte identification via pattern recognition. The aim of this report is to summarize recent advancements in the development of radiation-processed CPC-based chemiresistive sensors, with particular emphasis on the role of interfacial modification in governing their sensing characteristics.

Introduction:

Since the discovery of X-rays by Wilhelm Roentgen, radiation technology has become an integral part of human life, with applications spanning diverse fields such as material development, industry, healthcare, environmental monitoring and protection, and agriculture. In the industrial sector, one of the most prominent uses of radiation technology is in the modification of polymers to create advanced materials with tailored properties. When polymers are exposed to high-energy radiation such as gamma rays or electron beams, several fundamental processes can occur like crosslinking, chain scission (degradation), or grafting of functional groups onto polymer chains. The outcome depends strongly on the polymer's chemical structure, physical state, molecular conformation, and degree of crystallinity. These radiation-induced modifications enable the development of polymeric materials with enhanced mechanical, thermal, chemical, and functional properties, thereby expanding their applications in cutting-edge technologies[1]. High-energy radiation can be effectively employed for the modification of polymer composites (PCs), which are typically formed by combining chemically and physically distinct materials but often suffer from poor interfacial interactions[2-5]. Upon irradiation, either the filler surface or the polymer matrix undergoes structural modification, improving compatibility between the two phases. Furthermore, radiation-

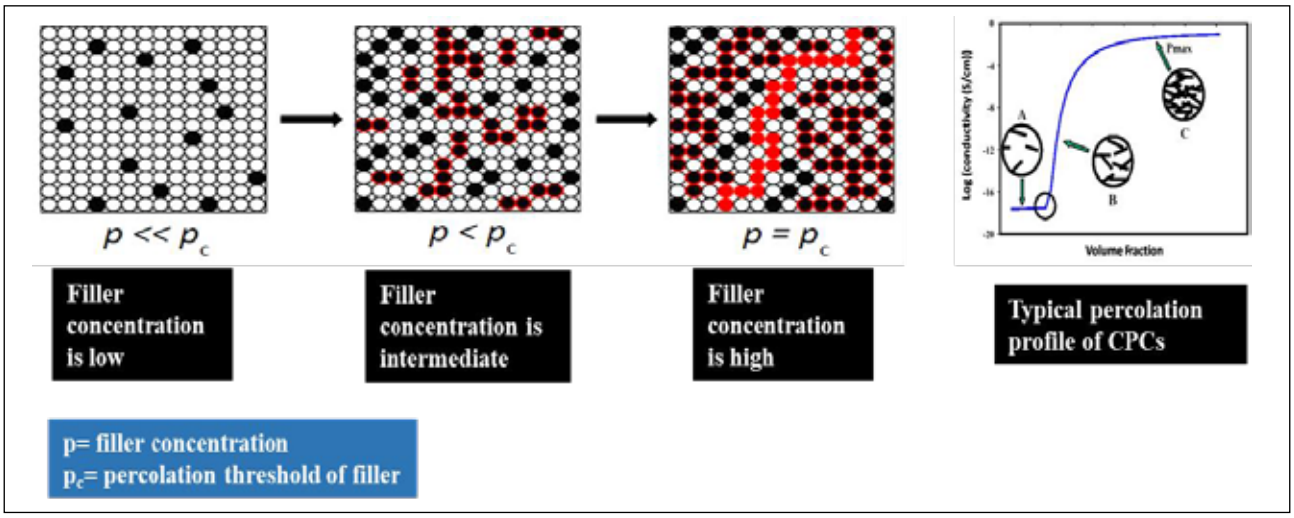

Fig 1: *Evolution of percolation networks of filler in a typical CPC.*

induced uniform crosslinking ensures that well-dispersed fillers remain permanently embedded within the composite, leading to enhanced stability and performance[6]. In particular, the incorporation of conducting fillers such as metal particles, graphene, single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), or nano-conducting carbon (NCB) into an insulating polymer matrix can yield composites with both high mechanical strength and electrical conductivity. These systems, referred to as conducting polymeric nanocomposites (CPCs), exhibit tunable conductivity that strongly depends on the filler loading and distribution (as illustrated in Figure 1). This behavior contrasts with that of intrinsically conducting polymers (ICPs), where conductivity arises from a π-conjugated backbone and cannot be easily tuned by composition. As can be seen from the figure, three distinct regions exist in CPCs in terms of conductivity. Region A, low conductivity region, where the conductivity of CPC is determined by the conductivity of polymer as no practical contact exists between conductive filler. Region B, the percolation region, is the critical concentration of conducting filler from which an appreciable change in conductivity is observed; it is known as the percolation threshold of the particular filler in that polymer matrix[7,8]. Region C, above percolation where already a conducting network formed, and conductivity increases linearly with further addition of filler. The percolation threshold of a filler depends upon several factors, such as the aspect ratio of filler, the functionality of filler[9], polymer's structure, crystallinity of polymers interaction between polymer and filler etc. In the case of carbon nanomaterials, due to strong van der Waals interactions, they form agglomerates, making them difficult to disperse on a highly viscous polymer matrix, resulting high percolation threshold[10,11]. Surface functionalization of carbon materials improves the interfacial characteristics, resulting good dispersion in the polymer matrix and decreasing the percolation threshold value. Radiation further assisted these interfacial morphologies by forming covalent linkages between polymers and the filler surface.

Since CPCs consist of a responsive polymeric matrix, they can function as chemiresistors when exposed to suitable vapor-phase analytes. In particular, when volatile organic compounds (VOCs) with strong thermodynamic affinity toward the polymer matrix interact with CPC-based sensors, the polymer chains undergo relaxation and swelling. This structural change perturbs the percolated conducting network by increasing the spacing between conducting

aggregates or agglomerates, thereby reducing the overall density of the conductive pathways. Such disruptions, or chemically induced internal strains within the matrix, manifest as a measurable change in the electrical resistivity of the composite [12]. These CPC-based sensors have specific advantages likes cost effectiveness, response time, ease of production, real-time monitoring, easy integration into a chemiresistive array, and the ability to create a low-power hand-held device. Additionally, CPC-based chemiresistors offer the advantage of operation at ambient temperatures and exhibit minimal cross-sensitivity to humidity. Unlike conventional metal oxide-based sensors, which rely on surface redox reactions, CPC-based sensors function through physical interactions between analytes and the polymer matrix, making their response more selective and energy-efficient. Notably, detector arrays composed of polymers with different chemical compositions have been shown to discriminate among various vapors by producing distinct response patterns. Polymer-based CPCs are therefore considered promising materials for chemical vapor detection. They can be fabricated into ultrathin films and used as standalone sensing layers without the need for additional functional coatings. Moreover, the molecular structure of the polymer matrix can be tailored to optimize interactions with specific analytes, thereby enabling tunable sensitivity and selectivity.[13] As an example, a methanol vapour sensor has been developed by Han et al. by using PMMA/SWNT electrospun composite nanofibers in combination with inter-digitated electrodes printed on the surface[14]. Taher et al. have described a formaldehyde field detector using a similar PMMA/graphene composites based chemiresistive sensor[15]. An array based chemiresistive sensor has been reported by Kessick et al. by using polymer carbon black based electrospun microsensor for detection of methanol, toluene, 1,5-dichloropentane, and trichloroethylene[16]. PVA/PMMA based polymer blend system is also used for such a chemiresistive sensor[17].

Toxicity counter and non-invasive detection of disease by monitoring VOCs:

Volatile organic compounds (VOCs) are ubiquitous and encompass a wide variety of chemical species. Many VOCs are harmful to human health. Evidence suggests that exposure to VOCs can adversely affect the liver, kidneys, and

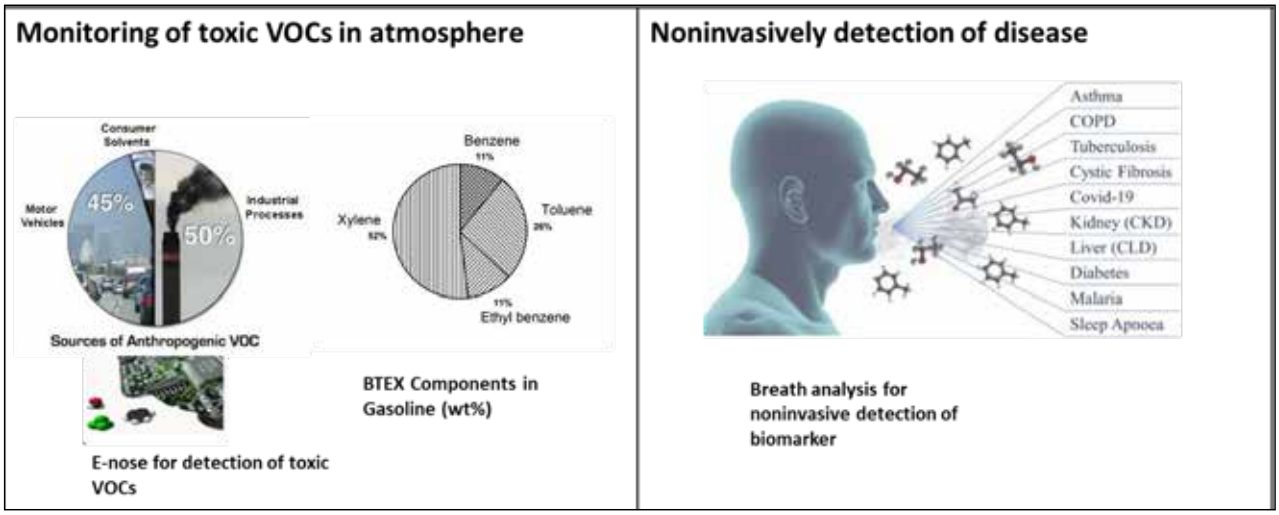

Fig 2: *Potential application range of crosslinked chemiresistive CPC based sensor for monitoring toxic VOCs in atmosphere and non-invasive detection of disease by monitoring exhale human breath. Reproduced with permission from ref. 21. Copyright (2024) Elsevier*

central nervous system (CNS), while also causing eye, nose, and throat irritation, headaches, nausea, and impaired coordination[18]. Some VOCs are recognized carcinogens in humans and animals. For example, benzene is classified as a known human carcinogen by regulatory agencies worldwide. Its most severe effect is hematopoietic toxicity, which can lead to leukemia[18]. Toluene and other alkylbenzenes primarily target the CNS, and instances of renal, cardiac, and hepatic toxicity, along with fatal alcohol-like symptoms, have also been reported [19].

Human exhaled breath contains more than 200 different types of VOCs, along with CO_2, N_2, O_2, and water vapor. These VOCs are generated through various biological processes in the body, many of which are associated with cytochrome P450 activity, oxidative stress, lipid metabolism, and liver enzymes[20]. Monitoring changes in the concentration of VOCs in exhaled breath can provide insights into underlying metabolic and physiological conditions [21]. The detection, identification, and characterization of these VOCs offer great potential for developing novel, noninvasive screening approaches for a wide range of disorders, including cancers malignancies[22-24], liver failure[25], kidney failure[26], diabetic[27] Perkinson's disease[28], etc. This type of breath analysis is now regarded as a cutting-edge, affordable, and sensitive method for the early diagnosis of disease. A disease can be identified by the distinctive pattern of VOCs present. 20 to 30 VOCs are crucial among several substances in exhaled breath in case of disease diagnosis. For instance, gastrointestinal disease and kidney malfunction can be detected by monitoring the ammonia concentration in breath [29,30]. In case of lipid peroxidation the concentration of n-pentane altered in breath which related to pathological disorder [25]. Similarly, breast and lungs cancer be detected by tracking acetone, n-propanol concentration in breath[31]. Typically, immobile methods like GC-MS, HPLC, FTIR are used to detecte VOCs but due to their inherent complication, methods like chemiresistive sensors, surface plasmon resonance, SAW have evolved. In terms of cost, response time, ease of manufacture, real-time monitoring, and the potential for a simple integration into an array, chemiresistive sensors have several benefits over other types of sensors [32,33]. Figure 2 summarises the potential application range of crosslinked CPC based sensors for environmental monitoring as well as for non-invasive detection of disease.

High energy radiation assisted crosslinked CPCs for chemiresistive sensors:

Polymer composites consist of a continuous polymer phase and an embedded, dispersed filler phase. Polymers are usually soft and ductile, while the dispersed phase is typically stronger and therefore often referred to as the reinforcing phase. The polymer matrix acts as a binder for the filler and shares the applied load under stress. Consequently, the distribution and dispersion of fillers play a crucial role in determining the final

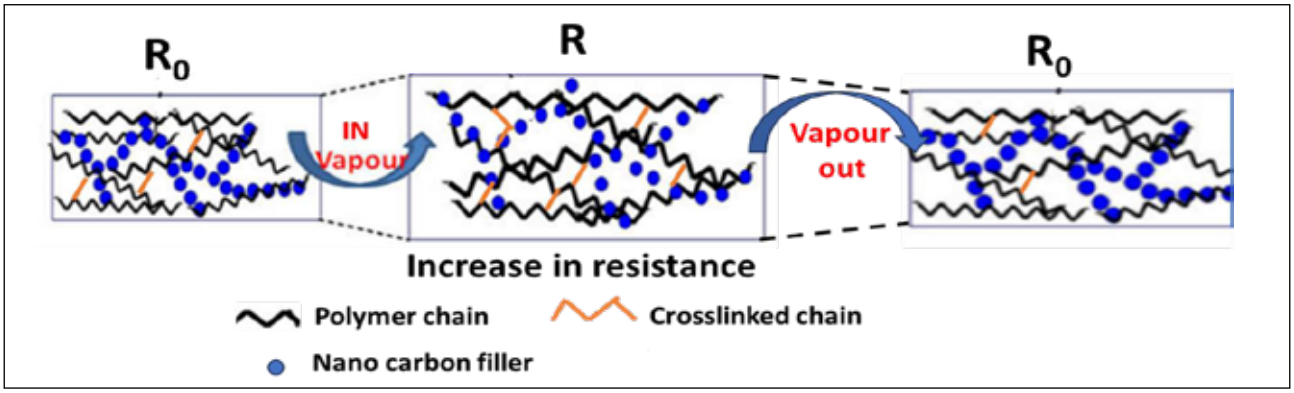

Fig 3: *Schematic diagram of chemiresistive behaviour of radiation crosslinked CPCs.*

properties of composites. All mixing techniques, therefore, aim to achieve a well-distributed and finely dispersed filler morphology. Radiation has been widely utilized not only for uniformly crosslinking finished composites-ensuring that the filler remains permanently embedded-but also for modifying the polymer-filler interface, thereby enhancing compatibility between the two phases[2,34,35]. Crosslinking introduces interlinks at the interface, strengthening the interaction between polymer and filler. A critical parameter influencing the physicomechanical performance of polymers is the crosslinking density (CD). Typically, higher CD reduces elongation at break but improves tensile strength and modulus. High-energy radiation initiates free radical formation on the filler surface, at the polymer–filler interface, and within the bulk matrix, thereby driving a series of reactions that alter the composite structure. The resulting cross-linked networks enhance dimensional stability under chemiresistive stress, significantly improving cyclic behaviour and enabling the development of stand-alone chemiresistors[2] (figure 3). Unlike many conventional methods, high-energy radiation can crosslink polymers without requiring external additives. Owing to the deep penetration of gamma radiation, uniform crosslinking throughout the polymer matrix is achievable, allowing chemiresistors to function independently as sensors. By contrast, conventional metal oxide–based sensors often require a supporting matrix, which complicates device miniaturization and integration into sensor arrays. Radiation-induced crosslinking also modifies analyte diffusion through the polymer matrix by introducing a mesh-like structure, thereby altering sensing characteristics such as response and recovery times. Importantly, unlike chemical crosslinking where external moieties attach to the polymer backbone and may compromise targeted properties radiation crosslinking can be applied at the final stage of processing. This provides better control over the structural design and functional performance of polymer composites.

Detection of VOCs can be broadly categorized based on the underlying operating principles into: (a) Based on spectroscopy and

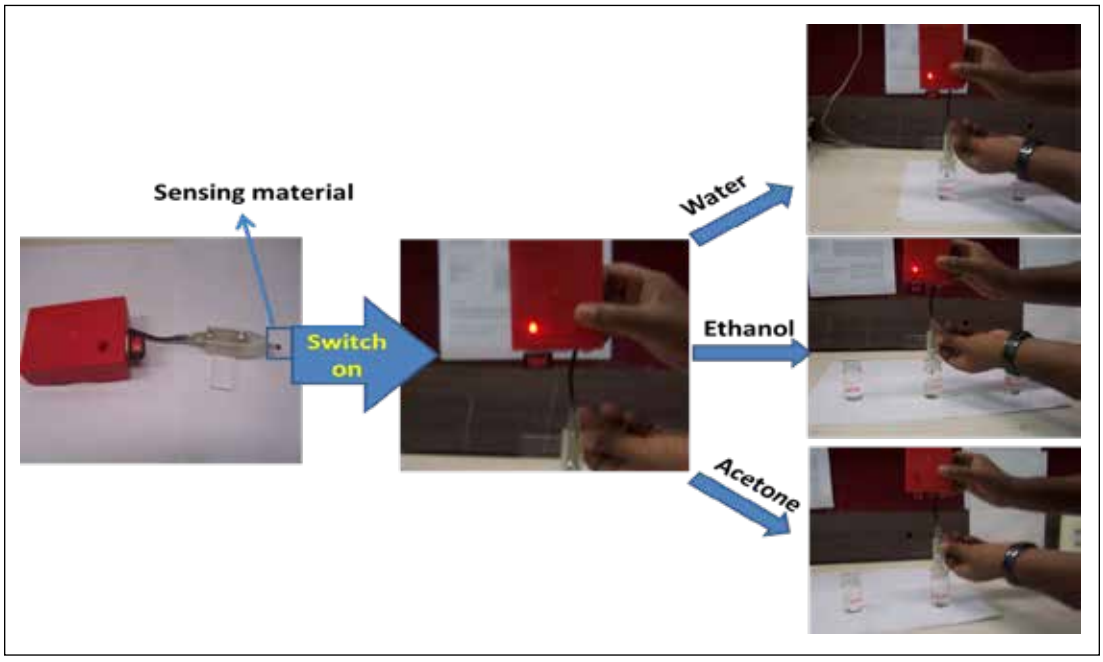

Fig 4: *Miniaturize device can be able to sense different analytes demonstrate easy integration of CPC based chemiresistor into low power electronic device.*

chromatography; (b) SAW based method; (c) Electrochemical detection methods; (d) Optical detection method; and (e) Chemiresistor sensors. Among these, radiation-crosslinked conducting polymer composite (CPC)-based chemiresistors offer distinct advantages over conventional VOC sensors. In a chemiresistor, exposure to an analyte induces a change in electrical resistance, which can be directly correlated to analyte concentration[36,37]. This simple yet effective mechanism makes it possible to fabricate a wide range of VOC sensors. Numerous chemiresistive sensors have been reported for the detection not only of VOCs but also of gases such as ammonia, nitrogen dioxide, carbon monoxide, hydrogen, and methane[38,39]. Traditionally, semiconducting metal oxide sensors have dominated this field. Their sensing mechanism relies on redox reactions between analytes and the oxide surface, leading to electron transfer and resistance changes[40,41]. However, these sensors suffer from several drawbacks, like high power consumption as they operate at high temperatures, the effect of humidity because of the high cross sensitivity for water, poor selectivity making it difficult to distinguish between analytes, etc. In contrast, radiation-crosslinked CPC-based chemiresistive sensors function effectively at ambient temperature, addressing many of the limitations of metal oxide-based systems. Their low power consumption makes them ideal for miniaturized, portable devices (Figure 4). Furthermore, the versatility of CPCs allows the selection of different polymers tailored to specific analytes, enabling the fabrication of application-specific sensors. Another significant advantage is that radiation crosslinking stabilizes the composite structure, allowing CPCs to function as standalone sensors without the need for an external supporting matrix. This feature greatly simplifies integration into sensor arrays for simultaneous detection of multiple analytes[13]. Their inherent mechanical flexibility further enhances their applicability in environments subjected to mechanical stress, expanding their potential use in wearable and flexible electronics.

Radiation induced modification of polymeric phase in CPC and enhanced chemiresistivity

By carefully selecting polymers and tuning the network density via radiation crosslinking, CPC-based chemiresistive sensors can be tailored for selective detection. The principal sensitivity of such sensors arises from the interaction parameter between the polymer chain and the analyte. For example, since the solubility parameter of acetone closely matches that of fluorocarbon elastomers (FCEs), these polymers are an excellent choice for acetone-selective chemiresistors. Acetone is of particular importance because it serves as a biomarker for non-invasive detection of diabetes and ketoacidosis and, at the same time, its acute inhalation poses serious health risks[42,43,44]. FCEs, which are inherently resistant to harsh chemical and thermal environments, thus offer an attractive platform for the development of robust chemiresistive sensors[45]. Radiation-induced crosslinking of the polymer matrix is essential to achieve desirable sensing performance in CPC-based chemiresistors. Crosslinked networks not only improve dimensional stability under chemiresistive stress but also regulate the permeability of analytes without significantly altering polymer–filler interactions. These properties make crosslinked nanocomposites highly suitable for VOC sensing. As a result, radiation-crosslinked CPC-based freestanding chemiresistive sensors offer unique advantages such as: independence from substrate–sensor interfaces, greater effective surface area, and simplified fabrication routes.

Figure 5A illustrates the schematic preparation of an FCE-based chemiresistor via shear compounding, followed by gamma-radiation crosslinking. In contrast, un-irradiated sensors lack inter-macromolecular connections; thus, when subjected to stress, their resistance changes irreversibly because the polymer chains cannot return to their original positions. During chemiresistive stress, FCE chains relax, leading to an increase in bulk resistivity. Without

covalent crosslinks, the un-irradiated matrix lacks the elasticity needed to re-establish its original conductive network once the stress is removed. However, excessive crosslinking is also detrimental. While moderate crosslinking provides dimensional stability and allows recovery of the conducting pathways, too high a crosslink density suppresses analyte diffusion, thereby reducing sensor response. Hence, there exists a critical balance sufficient crosslinking to maintain elasticity and recoverability yet not so much that analyte penetration and polymer-analyte interactions are hindered. Experimental observations confirm that un-irradiated FCE/NCB nanocomposites are unsuitable for sensing applications, while optimally radiation-crosslinked counterparts demonstrate promising chemiresistive performance.

Figure 5B demonstrated reversible and reproducible response for acetone vapour for crosslinked chemiresistors. While the sensing response for the unirradiated one was very low compared to the irradiated chemiresistor and also didn't show a reversible response (figure 5C). After the removal of acetone vapour, the resistance value did not show a significant decrease, which underscores that the unirradiated chemiresistor is unsuitable for use in vapour sensing applications. Un-irradiated sensors, once distorted, do not return to their previous position due to the lack of an intermolecular crosslinked network, resulting in an irreversible change in resistance. Indeed, when immersed in acetone, an unirradiated sensor completely disintegrates within half an hour, whereas a 100 kGy irradiated sample maintains its physical dimensionality. Changes in the behaviour of acetone diffusion in the chemiresistor and changes in the dynamics of NCB aggregation-disaggregation under chemiresistive stress may be the main reasons of the radiation dose-dependent variations in the sensing response. These components have an impact on the contact resistance between NCB aggregates as well as the relaxation of FCE chains under chemiresistive stress.

Enhanced chemiresistivity by high energy radiation assisted modification of polymer filler interface in CPC

The fabrication of CNT-based conducting polymer composites (CPCs) with superior mechanical, electrical, and multifunctional properties has attracted significant research interest [46, 47,48]. To achieve these target properties, two key requirements must be met: (i) efficient dispersion of CNTs and (ii) strong polymer-CNT interfacial interactions. However, the realization of these properties has been hindered by several challenges, including the strong van der Waals interactions between CNTs, variations in chirality, and the presence of impurities or residual catalysts[49]. A further limitation arises from the necessity of achieving a percolation network of CNTs within the polymer matrix to impart conductivity. This often demands a relatively high filler loading[50], which can lead to processing challenges such as increased viscosity, agglomeration, and morphological instability. To mitigate these drawbacks, several strategies have been proposed, including: using hybrid or mixed fillers to assist network formation, employing functionalized CNTs to improve compatibility with the matrix, and localizing CNTs at the interface in multiphase polymer composites to achieve percolation at lower filler concentrations. Among these, covalent functionalization of CNTs has proven particularly effective[51,52]. It not only enhances nanotube dispersion but also promotes favorable thermodynamic wetting with polymer matrices, enabling conductive composites at comparatively lower filler concentrations[53]. It is also important to highlight that CPC systems may undergo both physical and chemical crosslinking. In this regard, high-energy radiation offers unique advantages: it can induce the formation of chemical linkages between CNTs and polymer chains, particularly at the interface[54]. Due to its high penetration power, radiation generates free radicals not only within the bulk matrix but also on filler surfaces and at polymer-filler interfaces. Thus, the combined application of optimal radiation dosage and CNT functionalization

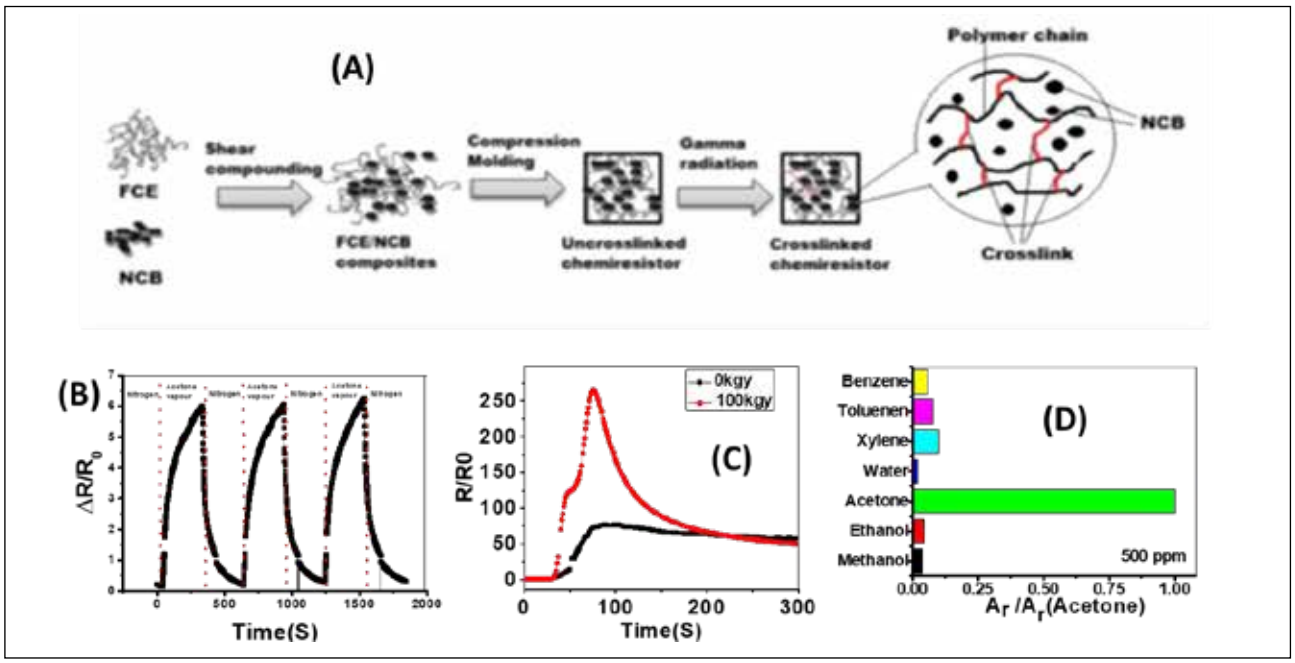

Fig 5: *(A) Schematic representation of preparation and crosslinking by radiation of FCE/NCB based CPC. (B) Cyclic response for Acetone vapour (C) Effect of radiation crosslinking on sensing response (D) Selectivity of chemiresistor towards acetone vapour. Reproduced with permission from ref. 33. Copyright (2018) Elsevier.*

enables effective interfacial modification. This results in enhanced network formation and improved chemiresistive performance of CNT-based CPCs.

The formation of a percolative CNT network within a polymer matrix can be effectively evaluated through rheological analysis. In general, the storage modulus (G′) of CPCs increases with increasing angular frequency. At higher frequencies, the composites exhibit solid-like behavior, whereas at lower frequencies, they behave more like viscous liquids. As CNT loading increases, this frequency dependence gradually diminishes. This behavior arises from the development of interconnected CNT networks within the matrix, which restricts the mobility of polymer chains and reduces their ability to fully relax. The evolution of shear modulus with increasing CNT volume fraction is shown in Figure 6A for PDMS/hydroxyl-functionalized CNT (CNT-OH) and PDMS/carboxyl-functionalized CNT (CNT-COOH) composites[35]. As shown in Figure 6A, the PDMS/CNT-COOH composites exhibited a significantly higher storage modulus compared to PDMS/CNT-OH composites. This enhancement indicates stronger interfacial interactions between carboxyl-functionalized CNTs and the PDMS matrix. Consequently, the percolated CNT network in PDMS/CNT-COOH nanocomposites forms at a lower filler content than in the case of CNT–OH. This behavior highlights the crucial role of interfacial chemistry in governing the rheological and mechanical properties of CPCs. The entanglement and immobilization of polymer chains at the filler interface are largely dictated by interfacial grafting and the strength of polymer–filler interactions. Stronger interactions, as in the case of CNT–COOH, facilitate earlier network formation, improved load transfer, and enhanced dimensional stability of the composite[55,56].

Moreover, the enhanced chemiresistivity observed in the case of PDMS/CNT-COOH CPC is mainly due to the interfacial modification by high energy radiation. The carboxylic group participates in dipolar interactions with oxygen

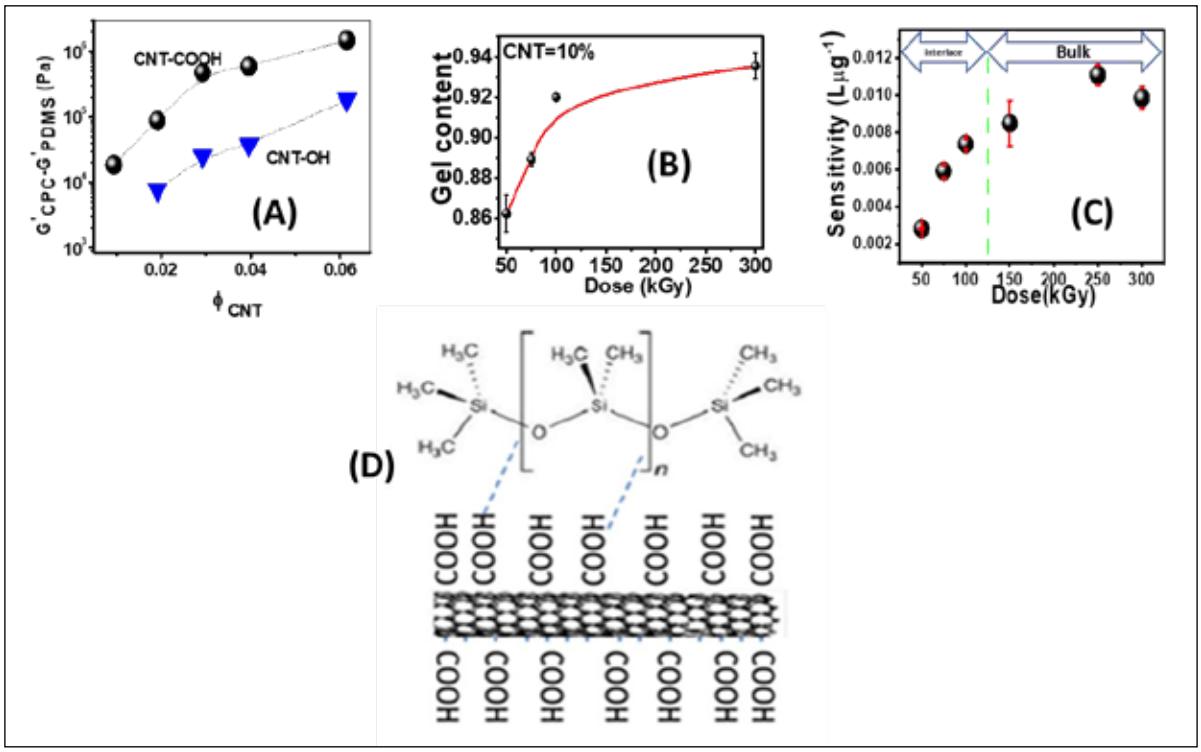

Fig 6: *(A) Change in modulus with vol fraction of CNT for CPC containing two different functionalized CNTs. (B), (C) Effect of radiation dose on gel content and sensitivity, respectively for CPC. (D) Schematic representation of interaction of CNT-COOH with PDMS chain. Reproduced with permission from ref. 34. Copyright (2018) American Chemical Society.)*

atoms in PDMS macromolecules; this allows effective wrapping of CNT-COOH by the PDMS chain. Due to the encapsulation of the polar group by CNT-COOH, the nonpolar methyl group remains on the outer surface, leading to chemiresistive behaviour with nonpolar analytes like benzene, toluene, xylene, etc. The gel fraction which is an indication of creating crosslinked mesh structure, was found to increase upto 100 kGy and saturates thereafter. Similarly, upto 100 kGy, the sensing response increase and saturate afterwards. The corelation between gel fraction and sensing response corroborates that upto 100 kGy dose, the formation of crosslinking and linkage between polymer chain and CNT-COOH synergistically enhanced the sensing response. After that, the diffusion of analyte molecules was hindered due to intermolecular crosslinks between polymer molecules. The hypothesis was further supported by comparing the sensing response between crosslinked PDMS/CNT-COOH and PDMS/unfunctionalized CNT. For unfunctionalized CNT, with radiation dose, the sensing response was found to increase though the magnitude was far less compared to CNT-COOH CPC. It can be suggested that irradiation of CPC generates radicals on PDMS and CNT surfaces, which subsequently recombine to give a crosslinked network in bulk and interface. In the interface, the polymer chain can form a grafting network with CNT, thus forming different characteristics in the interface compared to the bulk of the CPCs. All these studies confirm that the. All these studies confirm that the radiation induced modification of PDMS/functionalized CNT occurs at the interface, thus leading to enhanced chemiresistivity.

Conclusion

High-energy gamma radiation has been demonstrated as an effective tool for producing CPC-based chemiresistive sensors with tunable

crosslinked network densities. Such sensors exhibit promising potential as room-temperature, standalone, sensitive, and selective devices for VOC detection. Radiation not only introduces intermolecular linkages between polymer chains but also modifies the polymer-filler interfacial region, thereby enhancing chemiresistive performance. The diffusion characteristics of VOCs within CPCs are strongly influenced by the radiation-induced crosslinked network. While moderate crosslinking stabilizes the structure and improves sensing response, excessive crosslinking creates additional barriers for vapor adsorption and desorption, leading to longer response and recovery times. Hence, an optimum radiation dose is essential to achieve maximum sensing performance in irradiated chemiresistors. In the case of PDMS/functionalized CNT composites, polar interactions between the PDMS chains and surface functional groups of CNTs promote effective CNT wrapping and dispersion, resulting in enhanced sensing response compared to composites with unfunctionalized CNTs. Experimentally, the sensing response was found to increase with radiation dose up to a threshold level, beyond which it plateaued. This trend suggests that interface modification and crosslinking act synergistically within an optimal dose window; however, excessively high crosslinking density ultimately restricts vapor permeation and reduces sensor efficiency.

Acknowledgement:

We are grateful to our institute, Bhabha Atomic Research Centre (BARC) for providing financial support and facilities.

References:

1. Woods, R. J. & Pikaev, A. K. *Applied radiation chemistry: radiation processing*. (John Wiley & Sons, 1993).
2. Dubey, K. *et al.* Radiation processed ethylene vinyl acetate-multiple walled carbon nanotube nano-composites: effect of MWNT addition on the gel content and crosslinking density. *Lett* **3**, 492-500 (2009).
3. A., D. K. *et al.* Radiation effects on SBR–EPDM blends: A correlation with blend morphology. *Journal of Polymer Science Part B: Polymer Physics* **44**, 1676-1689, doi:doi:10.1002/polb.20822 (2006).
4. Xie, X.-L., Mai, Y.-W. & Zhou, X.-P. Dispersion and alignment of carbon nanotubes in polymer matrix: a review. *Materials science and engineering: R: Reports* **49**, 89-112 (2005).
5. Sahoo, N. G., Rana, S., Cho, J. W., Li, L. & Chan, S. H. Polymer nanocomposites based on functionalized carbon nanotubes. *Progress in polymer science* **35**, 837-867 (2010).
6. Abhinav, D. K., K., B. Y., V., C. C. & Sunil, S. LDPE/EVA/PCR/MWNT nanocomposites: Radiation crosslinking and physicomechanical characteristics. *Polymer Composites* **32**, 737-746, doi:doi:10.1002/pc.21092 (2011).
7. Mittal, V. *Polymer nanotubes nanocomposites: synthesis, properties and applications*. (John Wiley & Sons, 2014).
8. Al-Saleh, M. H. & Sundararaj, U. A review of vapor grown carbon nanofiber/polymer conductive composites. *Carbon* **47**, 2-22 (2009).
9. Tasis, D., Tagmatarchis, N., Bianco, A. & Prato, M. Chemistry of carbon nanotubes. *Chemical reviews* **106**, 1105-1136 (2006).
10. Sung, Y. *et al.* Rheological and electrical properties of polycarbonate/multi-walled carbon nanotube composites. *Polymer* **47**, 4434-4439 (2006).
11. Bauhofer, W. & Kovacs, J. Z. A review and analysis of electrical percolation in carbon nanotube polymer composites. *Composites Science and Technology* **69**, 1486-1498 (2009).
12. Ke, K., Pötschke, P., Wiegand, N., Krause, B. & Voit, B. Tuning the network structure in poly (vinylidene fluoride)/carbon nanotube nanocomposites using carbon black: toward improvements of conductivity and piezoresistive sensitivity. *ACS applied materials & interfaces* **8**, 14190-14199 (2016).
13. Chatterjee, S., Castro, M. & Feller, J.-F. An e-nose made of carbon nanotube based quantum resistive sensors for the detection of eighteen polar/nonpolar VOC biomarkers of lung cancer. *Journal of Materials Chemistry B* **1**, 4563-4575 (2013).
14. Han, L., Andrady, A. L. & Ensor, D. S. Chemical sensing using electrospun polymer/carbon nanotube composite nanofibers with printed-on electrodes. *Sensors and Actuators B: Chemical* **186**, 52-55, doi:https://doi.org/10.1016/j.snb.2013.05.069 (2013).
15. Alizadeh, T. & Soltani, L. H. Graphene/poly(methyl methacrylate) chemiresistor sensor for formaldehyde odor sensing. *Journal of Hazardous Materials* **248-249**, 401-406, doi:https://doi.org/10.1016/j.jhazmat.2012.12.019 (2013).
16. Kessick, R. & Tepper, G. Electrospun polymer composite fiber arrays for the detection and identification of volatile organic compounds. *Sensors and Actuators B: Chemical* **117**, 205-210, doi:https://doi.org/10.1016/j.snb.2005.11.045 (2006).
17. Doleman, B. J., Sanner, R. D., Severin, E. J., Grubbs, R. H. & Lewis, N. S. Use of Compatible Polymer Blends To Fabricate Arrays of Carbon Black−Polymer Composite Vapor Detectors. *Analytical Chemistry* **70**, 2560-2564, doi:10.1021/ac971238h (1998).
18. Bergsagel, D. E. *et al.* Benzene and multiple myeloma: Appraisal of the scientific evidence. *Blood* **94**, 1174-1182 (1999).
19. Mirzaei, A., Leonardi, S. & Neri, G. Detection of hazardous volatile organic compounds (VOCs) by metal oxide nanostructures-based gas sensors: A review. *Ceramics International* **42**, 15119-15141 (2016).

20. Broza, Y. Y., Zuri, L. & Haick, H. Combined volatolomics for monitoring of human body chemistry. *Scientific reports* **4**, 4611 (2014).
21. Moura, P. C., Raposo, M. & Vassilenko, V. Breath biomarkers in Non-Carcinogenic diseases. *Clinica Chimica Acta* **552**, 117692, doi:https://doi.org/10.1016/j.cca.2023.117692 (2024).
22. Peng, G. *et al.* Detection of lung, breast, colorectal, and prostate cancers from exhaled breath using a single array of nanosensors. *British journal of cancer* **103**, 542 (2010).
23. Hakim, M. *et al.* Volatile organic compounds of lung cancer and possible biochemical pathways. *Chemical reviews* **112**, 5949-5966 (2012).
24. Nuciforo, P., Radosevic-Robin, N., Ng, T. & Scaltriti, M. Quantification of HER family receptors in breast cancer. *Breast cancer research* **17**, 53 (2015).
25. Wlodzimirow, K. *et al.* Exhaled breath analysis with electronic nose technology for detection of acute liver failure in rats. *Biosensors and Bioelectronics* **53**, 129-134 (2014).
26. Narasimhan, L., Goodman, W. & Patel, C. K. N. Correlation of breath ammonia with blood urea nitrogen and creatinine during hemodialysis. *Proceedings of the National Academy of Sciences* **98**, 4617-4621 (2001).
27. Choi, S.-J. *et al.* Selective detection of acetone and hydrogen sulfide for the diagnosis of diabetes and halitosis using SnO2 nanofibers functionalized with reduced graphene oxide nanosheets. *ACS applied materials & interfaces* **6**, 2588-2597 (2014).
28 Finberg, J. P. M. *et al.* Sensor Array for Detection of Early Stage Parkinson's Disease before Medication. *ACS Chemical Neuroscience*, doi:10.1021/acschemneuro.8b00245 (2018).
29 Kondratev, V. M. *et al.* Si Nanowire-Based Schottky Sensors for Selective Sensing of NH3 and HCl via Impedance Spectroscopy. *ACS Applied Nano Materials*, doi:10.1021/acsanm.3c01545 (2023).
30 Ricci, P. P. & Gregory, O. J. Sensors for the detection of ammonia as a potential biomarker for health screening. *Scientific Reports* **11**, 7185 (2021).
31 Phillips, M. *et al.* Volatile organic compounds in breath as markers of lung cancer: a cross-sectional study. *The Lancet* **353**, 1930-1933 (1999).
32 Ting, Z., Syed, M., Nosang, V. M. & Marc, A. D. Recent progress in carbon nanotube-based gas sensors. *Nanotechnology* **19**, 332001 (2008).
33 Chiu, S.-W. & Tang, K.-T. Towards a chemiresistive sensor-integrated electronic nose: A review. *Sensors* **13**, 14214-14247 (2013).
34 Mondal, R. *et al.* Network density tailored standalone-flexible fluorocarbon elastomer/nanocarbon black chemiresistors for 2-propanone field detection. *Sensors and Actuators B: Chemical* **265**, 193-203 (2018).
35 Mondal, R. K. *et al.* Carbon Nanotube Functionalization and Radiation Induced Enhancements in the Sensitivity of Standalone Chemiresistors for Sensing Volatile Organic Compounds. *ACS Applied Nano Materials* **1**, 5470-5482, doi:10.1021/acsanm.8b00790 (2018).
36 Feller, J. F. *et al.* Novel architecture of carbon nanotube decorated poly(methyl methacrylate) microbead vapour sensors assembled by spray layer by layer. *Journal of Materials Chemistry* **21**, 4142-4149, doi:10.1039/C0JM03779F (2011).
37 Kennedy, Z. C. *et al.* 3D-printed poly(vinylidene fluoride)/carbon nanotube composites as a tunable, low-cost chemical vapour sensing platform. *Nanoscale* **9**, 5458-5466, doi:10.1039/C7NR00617A (2017).
38 Tanvir, N. B., Laubender, E., Yurchenko, O. & Urban, G. Room Temperature CO Sensing with Metal Oxide Nanoparticles Using work Function Readout. *Procedia Engineering* **168**, 284-288, doi:https://doi.org/10.1016/j.proeng.2016.11.195 (2016).
39 Barsan, N. & Weimar, U. 7.3. 3 Fundamentals of Metal Oxide Gas Sensors. *Proceedings IMCS 2012*, 618-621 (2012).
40 Luo, J. *et al.* The mesoscopic structure of flower-like ZnO nanorods for acetone detection. *Materials Letters* **121**, 137-140 (2014).
41 Berna, A. Metal oxide sensors for electronic noses and their application to food analysis. *Sensors* **10**, 3882-3910 (2010).
42 Fayfman, M., Pasquel, F. J. & Umpierrez, G. E. Management of Hyperglycemic Crises: Diabetic Ketoacidosis and Hyperglycemic Hyperosmolar State. *Medical Clinics of North America* **101**, 587-606, doi:https://doi.org/10.1016/j.mcna.2016.12.011 (2017).
43 Hamed, S. A. Brain injury with diabetes mellitus: evidence, mechanisms and treatment implications. *Expert Review of Clinical Pharmacology* **10**, 409-428, doi:10.1080/17512433.2017.1293521 (2017).
44 Satoh, T. *et al.* Relationship between acetone exposure concentration and health effects in acetate fiber plant workers. *International Archives of Occupational and Environmental Health* **68**, 147-153, doi:10.1007/bf00381623 (1996).
45 Bee, S.-T., Hassan, A., Ratnam, C. T., Tee, T.-T. & Sin, L. T. Investigation of nano-size montmorillonite on electron beam irradiated flame retardant polyethylene and ethylene vinyl acetate blends. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **299**, 42-50, doi:https://doi.org/10.1016/j.nimb.2013.01.040 (2013).
46 Ajayan, P., Stephan, O., Colliex, C. & Trauth, D. Aligned carbon nanotube arrays formed by cutting a polymer resin—nanotube composite. *Science* **265**, 1212-1214 (1994).
47 Chen, R. J., Zhang, Y., Wang, D. & Dai, H. Noncovalent Sidewall Functionalization of Single-Walled Carbon Nanotubes for Protein Immobilization. *Journal of the American Chemical Society* **123**, 3838-3839, doi:10.1021/ja010172b (2001).
48 Collins, P. G., Zettl, A., Bando, H., Thess, A. & Smalley, R. E. Nanotube Nanodevice. *Science* **278**, 100-102, doi:10.1126/science.278.5335.100 (1997).
49 Thomassin, J.-M. *et al.* Multiwalled carbon nanotube/poly (ε-caprolactone) nanocomposites with exceptional electromagnetic interference shielding properties. *The Journal of Physical Chemistry C* **111**, 11186-11192 (2007).
50 Kota, A. K. *et al.* Electrical and Rheological Percolation in Polystyrene/MWCNT Nanocomposites. *Macromolecules* **40**, 7400-7406, doi:10.1021/ma0711792 (2007).
51 Mondal, R. K., Dubey, K. A., Bhardwaj, Y. K. & Varshney, L. Novel hybrid nanocarbons/poly(dimethylsiloxane) composites based chemiresistors for real time detection of hazardous aromatic hydrocarbons. *Carbon* **100**, 42-51, doi:https://doi.org/10.1016/j.carbon.2015.11.055 (2016).

52 Sinha, S. *et al.* Selective interfacial localization in conducting polycaprolactam/ethylene vinyl acetate/carbon black composites. *Polymer Composites* **34**, 912-919 (2013).
53 Liu, P. Modifications of carbon nanotubes with polymers. *European Polymer Journal* **41**, 2693-2703 (2005).
54 Dubey, K. *et al.* Radiation effects on styrene–butadiene–ethylene–propylene diene monomer-multiple walled carbon nanotube nanocomposites: vulcanization and characterization. *Polymers for Advanced Technologies* **22**, 1888-1897 (2011).
55 Whitten, P. G. & Brown, H. R. Polymer entanglement density and its influence on interfacial friction. *Physical Review E* **76**, 026101 (2007).
56 Haugan, I. N. *et al.* Consequences of Grafting Density on the Linear Viscoelastic Behavior of Graft Polymers. *ACS Macro Letters* **7**, 525-530 (2018).

Dr. R. K. Mondal *is presently working as a scientist in Radiation Technology Development Division of Bhabha Atomic Research Centre, Mumbai, India. Dr. Mondal did his MSc from Jadavpur University, Kolkata, India. He has joined BARC in 2012. He has completed his PhD under Homi Bhabha National Institute in the year 2019. His present research interest includes synthesis and characterization of polymer composites and study the effect of high energy gamma and electron beam radiation on these composite materials. He has authored about 25 papers in peer-reviewed international journals and 30 conferences and symposiums.*

Dr. K.A Dubey *is working as a scientist in Radiation Technology Development Division, Bhabha Atomic Research Centre. His research interest includes radiation processing of polymer blends, alloys and nanocomposites for advanced applications. Presently he is engaged in radiation processed conducting polymer composites for various advance applications, biodegradable polymers, over current protection devices, toxic volatile sensors and high modulus composites. He has more than 100 publications in international journals and 70 in conferences and symposiums.*

Dr. Y. K. Bhardwaj *is currently heading the Radiation Technology Development Division, Bhabha Atomic Research Centre. Dr. Bhardwaj did his Ph.D. from University of Mumbai, India in 2001. His present research interest includes utilization of high-energy electron beam and gamma radiation for industrial applications. This includes development of grafted polymer matrices for various applications, elastomer blends and composites for sensing applications and high-performance coatings. He has been actively involved in the studies on radiation polymerization/crosslinking of monomers/polymers, development of radiation processed hydrogels for medical and pharmaceutical applications, synthesis of fast stimuli-responsive hydrogels and radiation crosslinking behaviour of water-soluble polymers. He has more than 220 publications in international journals and conferences.*

Depolymerization of PET Waste by Aminoethylethanolamine and Its Application in Polyesteramide Coatings

Vandana Jamdar[1], Mukesh Kathalewar[1], Devesh Sane[1], Anagha Sabnis*[1]
[1] *Department of Polymer & Surface Engineering, Institute of Chemical Technology*
Nathalal Parekh Marg, Matunga (E), Mumbai-400019
Email: as.sabnis@ictmumbai.edu.in

Abstract

Recycling of poly(ethylene terephthalate) (PET) is of increasing interest due to the large volumes of post-consumer waste generated worldwide. In this study, PET waste was chemically recycled by aminolysis using aminoethylethanolamine (AEEA), a novel aminoglycol containing both amine and hydroxyl functionalities. The depolymerization was carried out under both conventional heating and microwave-assisted conditions. The recycled oligomeric product (OPETAEEA) was characterized by FTIR, ^1H-NMR, and DSC. Polyesteramide (PEA) resins were synthesized by partial replacement of neopentyl glycol with OPETAEEA and subsequently cured with aliphatic and cycloaliphatic polyisocyanates. The coatings obtained were evaluated for mechanical, chemical, thermal, and anticorrosive properties. The results demonstrate that AEEA is an effective depolymerization agent for PET, and the recycled products can be incorporated into high-performance polyesteramide coatings.

Keywords: PET recycling, Aminolysis, Polyesteramide, Coatings, Depolymerization

Introduction

Polyethylene terephthalate (PET) is widely used in packaging, particularly for beverage bottles, owing to its unique balance of properties such as high strength, good clarity, and excellent barrier characteristics against gases and moisture. Its large-scale consumption, however, has led to massive accumulation of waste in the environment, since PET is highly resistant to natural degradation processes and persists for extended periods once discarded. This persistence poses a major environmental challenge, especially considering the ever-increasing demand for PET in packaging and textile applications. Conventional approaches to manage PET waste, such as mechanical recycling, are widely practiced but often lead to deterioration in material quality because of chain scission, reduction in molecular weight, and the presence of contaminants, thereby limiting the end-use of recycled products to low-value applications. In contrast, chemical recycling has received growing attention as it allows the conversion of PET into valuable intermediates or monomers that can be reused for the synthesis of new polymers with properties comparable to virgin materials. Among different chemical methods, aminolysis has been extensively studied, where amine-containing compounds such as ethanolamine or ethylenediamine are used as depolymerizing agents to cleave the ester bonds of PET, producing intermediates like bis(2-hydroxyethyl) terephthalamide (BHETA) or related aminolyzed oligomers. These intermediates are reactive and can serve as useful building blocks for new polymeric materials. The novelty of the present study lies in employing aminoethylethanolamine (AEEA) as the aminolysis reagent, a molecule that is particularly attractive due to the presence of both primary and secondary amine groups along with a hydroxyl group in the same structure, thereby offering multiple reactive sites for PET chain cleavage and enhancing the efficiency and versatility of the depolymerization process. Unlike conventional

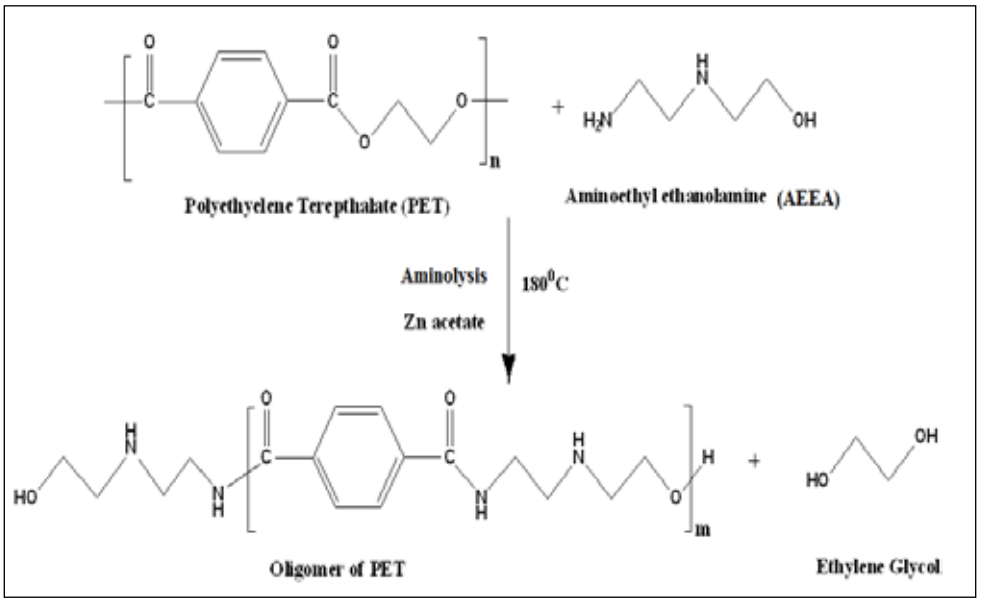

Figure 1. *Reaction scheme of PET depolymerization with AEEA*

Table 1. Effect of depolymerization conditions on OPETAEEA yield

Method	Time (min)	Yield (%)	Amine Value (mg KOH/g)	Hydroxyl Value (mg KOH/g)
Conventional	240	48	318-330	750-800
Microwave	30	52.5	360-380	660-700

amines, AEEA provides multifunctionality that can open new avenues for generating intermediates with enhanced properties and broader applicability. Furthermore, the study integrates microwave-assisted depolymerization, a technique that offers several advantages over conventional heating, including uniform energy distribution, shorter reaction times, and reduced overall energy consumption, making the process more sustainable and industrially relevant. The aminolysis products obtained using AEEA were subsequently utilized in the synthesis of polyesteramide (PEA) resins, which are a class of polymers combining the flexibility, adhesion, and film-forming properties of polyesters with the toughness, abrasion resistance, and chemical resistance of polyamides. Such resins are highly promising for coating applications where durability and performance are critical. The combined approach of using a multifunctional depolymerizing agent and an energy-efficient depolymerization technique, followed by upcycling into high-value polyesteramide resins, highlights the potential of this work to contribute toward sustainable PET recycling strategies that address both environmental concerns and the demand for advanced materials.

Experimental

Depolymerization of PET Waste

Cleaned and dried PET chips were depolymerized with AEEA at PET:AEEA molar ratios of 1:2–1:4 in the presence of zinc acetate catalyst. Conventional reactions were carried out at 180 °C for 4 h, whereas microwave-assisted reactions were performed at 500 W for 30 min under nitrogen atmosphere. The oligomeric product was isolated by precipitation, washed with acetone, and dried.

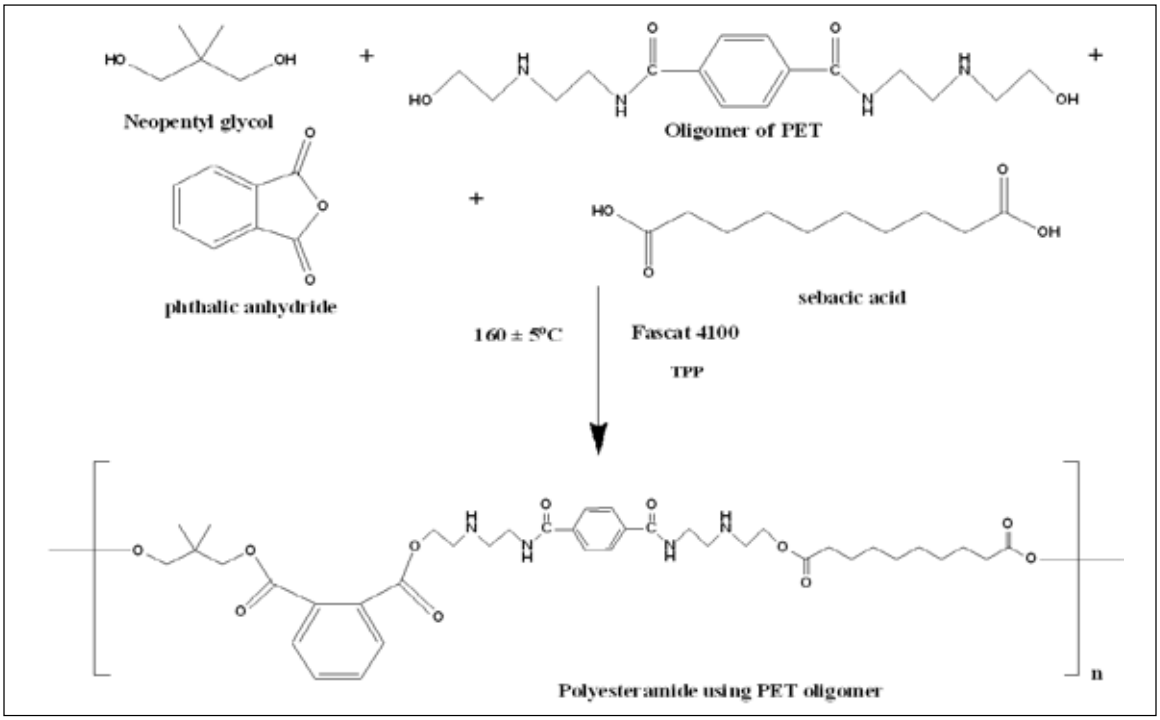

Figure 2. *Reaction scheme of polyesteramide synthesis*

Polyesteramide Synthesis

The oligomeric product obtained from PET aminolysis with AEEA (OPETAEEA) was utilized as a partial substitute for neopentyl glycol in the synthesis of polyesteramide resins. The substitution level of OPETAEEA was systematically varied in the range of 10–40 mol% to study its effect on the polymer structure and properties. Along with this recycled component, sebacic acid and phthalic anhydride were employed as the dicarboxylic acid co-monomers in the formulation. The polycondensation reaction was carried out in the presence of p-toluenesulfonic acid (p-TSA) as a catalyst. The process was continued at 160–180 °C until the acid value of the reaction mixture decreased to below 15 mg KOH/g, indicating completion of the reaction.

Coating Preparation

The synthesized polyesteramide resins were crosslinked using two different polyisocyanates to evaluate their performance in coatings. An aliphatic hexamethylene diisocyanate (HDI) biuret, commercially known as Desmodur N-75, was selected as one of the curing agents. In addition, a cycloaliphatic isophorone diisocyanate (IPDI) trimer, marketed as Desmodur Z-4470, was employed as the second crosslinker. The formulated resin–isocyanate mixtures were applied as coatings onto pretreated mild steel substrates. Finally, the coated panels were subjected to thermal curing at 120 °C to achieve proper film formation and crosslinking.

Results and Discussion

Optimization of Aminolysis

The conventional depolymerization process of PET using AEEA resulted in a yield of approximately 48% after a reaction time of 4 hours. In contrast, when microwave heating was employed, a significantly higher yield in the range of 52–53% was obtained within just 30 minutes of reaction. This clearly demonstrates the efficiency of microwave irradiation in accelerating the depolymerization process. The enhancement can be attributed to the uniform volumetric heating provided by microwaves, which ensures rapid

energy transfer throughout the reaction medium. Additionally, the dipolar interaction of AEEA molecules with microwave radiation promotes faster cleavage of ester bonds, thereby leading to improved yields in shorter times.

Characterization of Oligomeric Product

The FTIR spectra of OPETAEEA showed a broad absorption band at around 3300 cm^{-1}, which confirmed the presence of hydroxyl functional groups in the structure. A sharp and intense band appeared at 1645 cm^{-1}, corresponding to the stretching vibrations of the amide linkages (–CONH–) formed during the reaction. In addition, characteristic peaks were observed in the range of 2914–2996 cm^{-1}, which could be attributed to both aliphatic and aromatic C–H stretching vibrations.

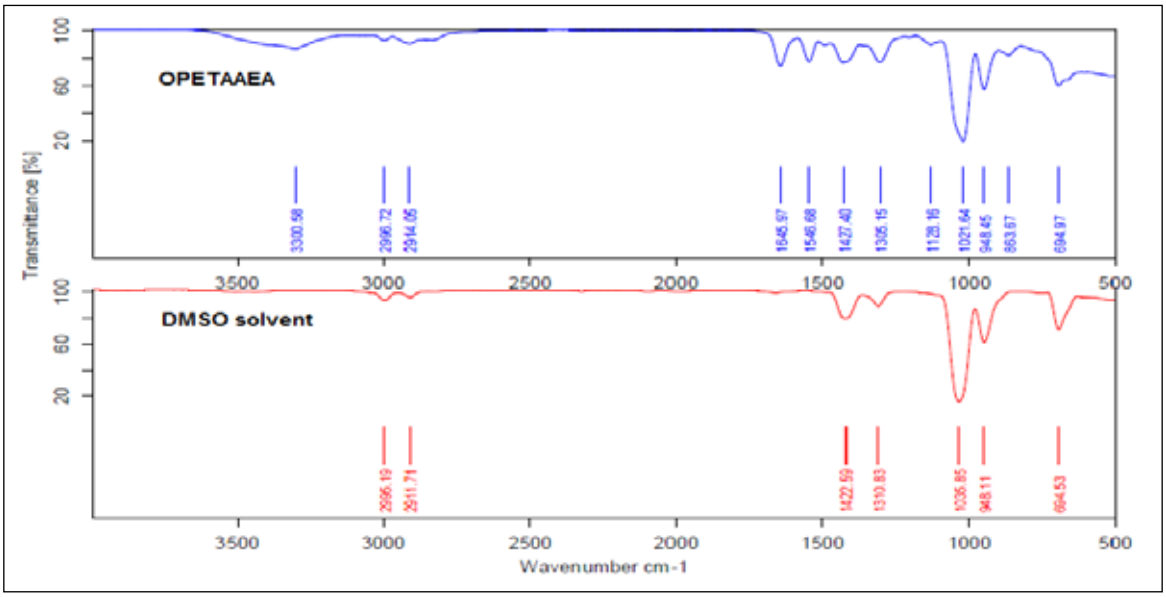

Figure 3. FTIR spectrum of OPETAEEA

Figure 4. ^{1}H-NMR spectrum of OPETAEEA

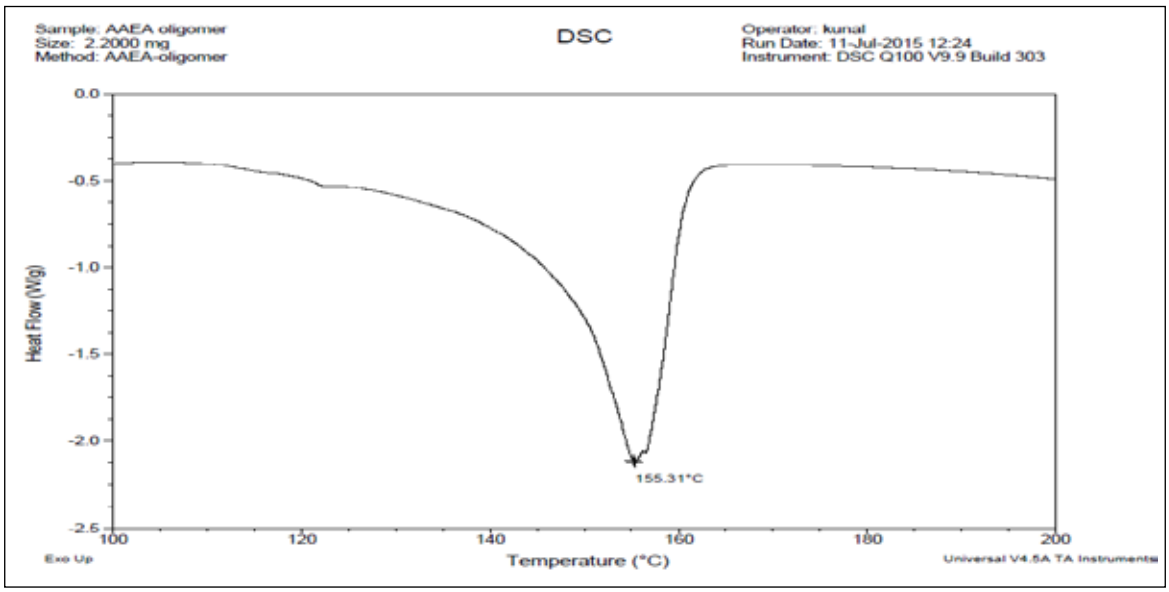

Figure 5. DSC thermogram of OPETAEEA

Table 2. Selected coating performance results

Sample	Gloss (60°)	Pencil Hardness	Scratch Resistance (g)	Salt Spray (500 h)
PE-Conventional	93	4H	1000	Moderate blistering
PEA-20 N75	96	5H	1600	Good
PEA-40 IPDI	102	6H	2900	Excellent

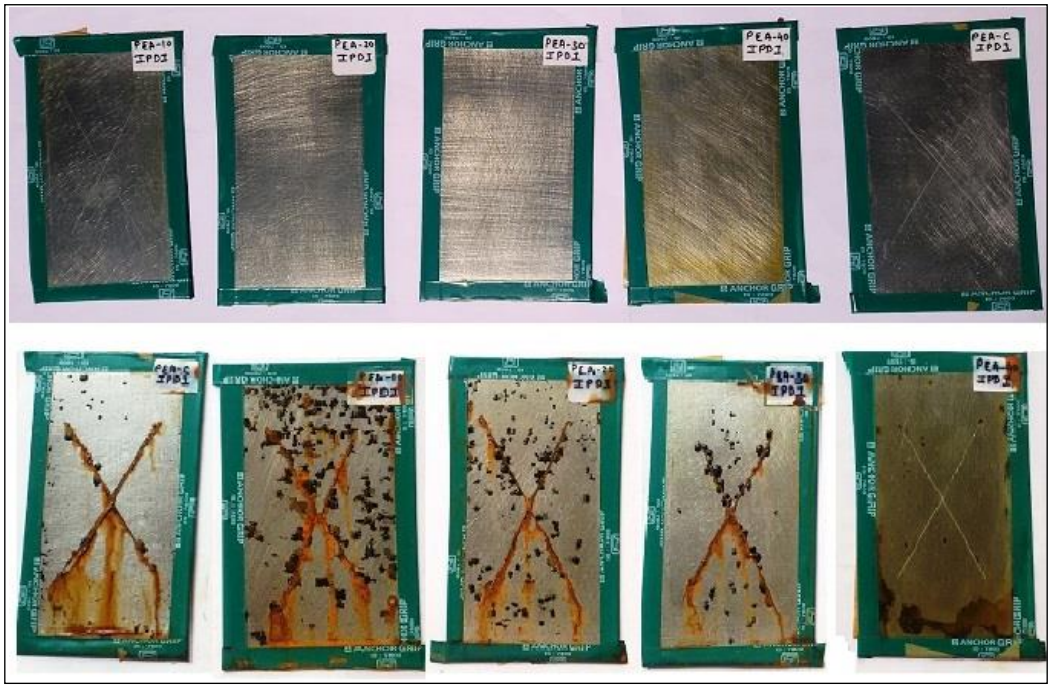

Figure 6. *Salt spray panels of PEA-IPDI coatings after 500 h*

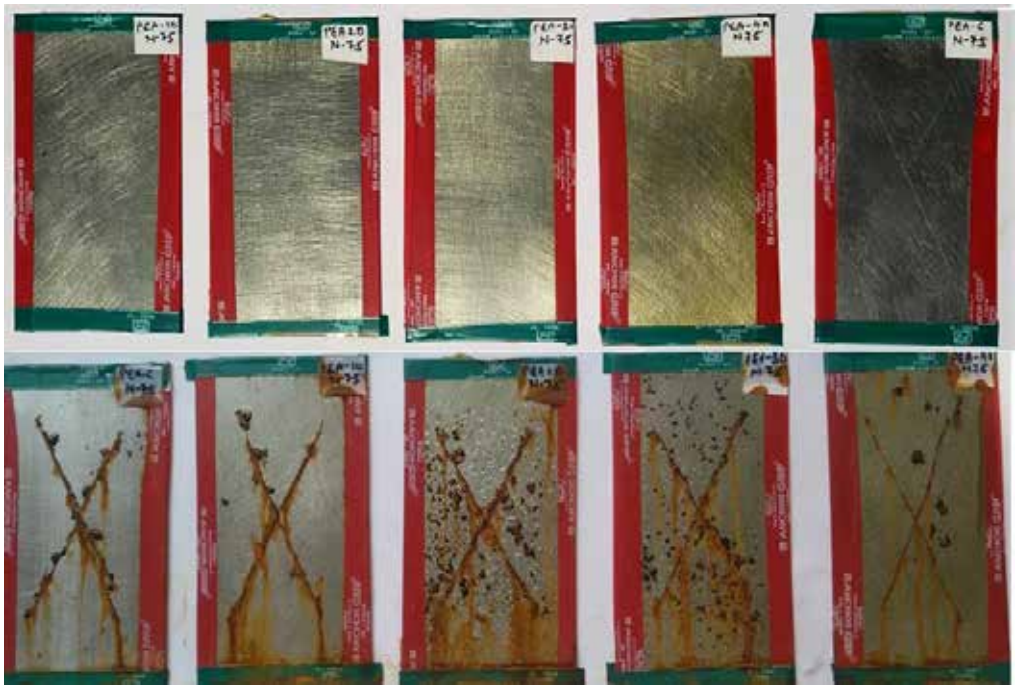

Figure 7. *Salt spray panels of PEA-HDI coatings after 500 h*

^{1}H-NMR confirmed aromatic protons at 7.7 ppm, –OH groups at 3.6 ppm, methylene groups between 2.5–3.5 ppm, and amide NH protons near 7.5 ppm, supporting the proposed structure.

DSC analysis indicated a melting point around 155 °C for the oligomer, suggesting semi-crystalline nature.

Properties of Polyesteramide Coatings

All coatings were clear, defect-free films with thickness of 40–65 µm. Gloss values were above 95 (at 60°), comparable to conventional coatings.

- **Mechanical properties:** The films showed excellent adhesion to mild steel substrates, achieving the highest 5B rating in cross-cut tests. Pencil hardness values reached up to 6H, indicating high surface hardness. Scratch resistance improved progressively with increasing OPETAEEA content due to greater crosslink density. IPDI-cured films exhibited relatively higher hardness compared to HDI biuret systems because of their compact crosslinked structure.
- **Chemical resistance:** Coatings resisted both acid and water immersion for 24 hours without showing any visible damage, such as blistering or delamination. Under alkaline conditions, slight softening was observed, attributed to ester group saponification. Solvent resistance was also strong, with MEK rub tests exceeding 150 double rubs. Resistance against xylene was even higher, exceeding 200 double rubs, highlighting their durability.
- **Thermal properties:** DSC analysis revealed that glass transition temperatures (Tg) increased with higher incorporation of OPETAEEA in the resin formulation. For example, PEA-40 in the N75 system showed a Tg of about 45 °C, while the same composition in the IPDI system reached ~55 °C. This increase is attributed to the presence of aromatic and amide linkages. Such structural features restrict chain mobility, thereby improving rigidity of the coatings.
- **Anticorrosive properties:** Salt spray tests for 500 hours showed that IPDI-based coatings, particularly PEA-40-IPDI, provided superior corrosion resistance. These coatings

maintained surface integrity with minimal rust or blister formation. Electrochemical impedance spectroscopy further confirmed this result, as PEA-40-IPDI showed the highest resistance values. The data suggest that these films act as strong barriers against moisture and corrosive species.

Conclusion

This study clearly demonstrates that aminoethylethanolamine (AEEA) is a highly effective depolymerization agent for polyethylene terephthalate (PET) waste, facilitating rapid and efficient cleavage of ester bonds under microwave irradiation. The process not only significantly reduces reaction time compared to conventional heating but also produces oligomeric products that are rich in hydroxyl and amide functionalities, which are highly reactive and versatile for further polymer synthesis. These depolymerization products can be successfully incorporated into polyesteramide (PEA) resins, serving as partial replacements for conventional glycols such as neopentyl glycol, thereby introducing a sustainable approach to resin formulation. Coatings formulated from these resins exhibit markedly improved performance characteristics, including enhanced surface hardness, excellent chemical resistance against acids, bases, and solvents, increased thermal stability as indicated by higher glass transition temperatures, and superior anticorrosive behavior, particularly when cured with cycloaliphatic polyisocyanates like IPDI trimers. The study demonstrates that such a strategy not only provides an effective route for valorizing PET waste but also produces high-value coating materials with properties comparable to, or even exceeding, those of conventional systems. Overall, this work highlights a practical pathway for transforming post-consumer PET into functional polymeric materials, supporting circular economy principles and advancing sustainable polymer recycling technologies.

References

1. Achilias DS, Redhwi HH, Siddiqui MN, Nikolaidis AK, Bikiaris DN, Karayannidis GP (2010) J Appl Polym Sci 118:3066–3073
2. HH, Siddiqui MN, Nikolaidis AK, Bikiaris DN, Karayannidis GP (2010) *J Appl Polym Sci* 118:3066–3073.
3. Nikles DE, Farahat MS (2005) Macromol Mater Eng 290, 1:13 30. https://doi.org/10.1002/mame.200400186
4. Jamdar V, Kathalewar M, Jagtap RN, Dubey KA, Sabnis A (2015) Polym Eng Sci 55(11):2653–2660,https://doi.org/10.1002/ pen.24158Rashvand M, Ranjbar Z (2013) *Prog Org Coat* 76:1413–1417.
5. Rashvand M, Ranjbar Z (2013) Prog Org Coat 76:1413–1417. https://doi.org/10.1016/j.porgcoat.2013.04.013

***Vandana S. Jamdar**, born in 1976, received her PhD (Tech) from Department of Polymer and Surface Engineering, Institute of Chemical Technology (ICT), Mumbai, in 2018. She is currently serving as Associate professor and head of Polymer Science programme at S K Somaiya college, Somaiya Vidyavihar University, Mumbai. She is also a Research Guide in Polymer Science at Somaiya Vidyavihar University. Her research areas are polymeric waste recycling, synthesis and characterization of various polymers and resins from bioresources, eco-friendly coating, polymeric nanomaterials, sustainable polymers. Her work has garnered over 2800 citations with an h-index of 30 on Google Scholar. Before joining academia, she worked at various senior levels in reputed industries for 12 years*

	***Dr. Mukesh Kathalewar*** *is an accomplished research & development and technical-services professional with deep expertise in polymer science, coatings, and materials chemistry. He is currently affiliated with Pidilite Industries Limited as a lead scientist and maintains connections with the Institute of Chemical Technology, Mumbai. Over his career, Dr. Kathalewar has designed, led, and executed projects spanning polymer synthesis, materials formulation, characterization, and scale-up. His work integrates fundamental chemical science with industrial application in coatings, surface engineering, and polymeric systems. In his roles, he has bridged the gap between laboratory research and technology deployment, managing the challenges of translating novel materials into commercial processes. Dr. Kathalewar's contributions reflect a commitment to innovation in applied polymer and coatings technology. He continues to drive and support research initiatives in materials science, while contributing his technical leadership to industry and academia*
	***Devesh Sane*** *is currently pursuing his Ph.D. in Surface Coating Technology at the Institute of Chemical Technology (ICT), Mumbai. He completed his M.Tech in Surface Coating Technology from ICT, receiving a gold medal for his academic excellence with a CGPA of 9.89. He earned his B.E. in Chemical Engineering from Bharati Vidyapeeth College of Engineering. His research is primarily focused on the chemical recycling of polymer waste such as polyurethane, PET, and polyamide to develop value-added products like coatings, adhesives, and composites. He has hands-on experience in unsaturated polyester, polyurethane, and polyurea chemistries, as well as formulating solvent-borne coatings and hydrogels. Mr. Sane has co-authored four publications with 2 book chapters in peer-reviewed journals and has filed two patents on recycling PET fabric and polyurethane waste, respectively. He is a recipient of the prestigious "INSPIRE FELLOWSHIP" from the Department of Science & Technology (DST), Government of India*
	***Prof. Anagha Sabnis*** *is a Professor and the Head of the Department of Polymer & Surface Engineering at the Institute of Chemical Technology (ICT), Mumbai, India. She earned her Ph.D. in Paint Technology from the same institute in 2006. Dr. Sabnis has extensive experience in both industry and academia, having worked with companies like Pidilite Industries Ltd. before joining ICT. Her primary research focuses on the development of functional materials and coatings, including anticorrosive coatings, bio-based polymers from renewable resources, non-isocyanate polyurethanes, and flame-resistant coatings. She is also actively involved in research on the chemical recycling of polymer waste for value-added applications. Dr. Sabnis has published 82 papers in national and international journals and holds two granted patents, with four more pending. She is a recipient of several awards, including the National Award for Technology Innovation from the Government of India and the Chevening-Rolls Royce Research Science & Innovation Leadership Fellowship (CRISP 2018) from the UK Government. Her work has garnered over 2800 citations with an h-index of 30 on Google Scholar.*

Advancements in the Radiation and Photochemical Sciences for Paints and Coating Industries

Randhirsinh Parmar
Asian Paints R&T Centre, Turbhe, Navi- Mumbai -400703.
Email: randhir.parmar@asianpaints.com

Abstract

The global paint and coating market was at USD 194 billion in 2023, projected to be at USD 263.2 billion in 2029 at CAGR of > 5%. The increased growth is in the area of architectural and industrial automotive coatings where the advanced coating technologies including the radiation cured coatings, photocatalytic coatings, cool roof coatings and anti-radar coatings contributes significantly. The above areas of advancements utilizes the innovative material science and efficient processes for enhancing the functionalities keeping the sustainability as the backdrop. These advancements are utilizing the principles and novel research of radiation science and photochemical sciences as enabling building blocks. The current review paper summarizes the key developments in radiations science and photochemical sciences as enablers for novel functionalities, sustainability and addressing the regulatory and customer specific needs. The research work is also reviewed and traced in light of the UN's SDGs to see how the research work is relevant to address the global sustainability goals at large.

Key Words: Photo-catalytic/self-cleaning coatings, Radiation cured coatings, Radiative cooling, Stealth coatings, Sustainability and UNs SDGs, Advanced paints and coatings.

Introduction:

The market research report from BCC research reported the global paints and coating industries at USD 1.94 Billion in 2023 and expected to reach USD 263.2 Billion by 2029 at a CAGR of 5.2% [1] This shows continuous growth of paints and coating industries globally. The key growth drivers for the technology advancements at paints and coating industry are Sustainability and regulations, smart functionalities and innovations, Urbanisation and infrastructure and AI and digital transformations.

Innovations at Paints and Coating industries:

WIPO published a report [2] on mapping innovations patents and the sustainable development goals of UN. The report demonstrates five sustainable development goals as hot topics for new innovations at paint and coating industries based on the patenting trend and innovation maturity index as depicted in fig.1 below.

These five goals are, SDG 9 (Industry, Innovation and Infrastructure), 2) SDG 11 (Sustainable Cities and Communities), 3) SDG 13 (Climate Action), 4) SDG 3: Good Health and Well-being, 5) SDG 7: Affordable and Clean Energy.

The current paper discusses technology advancements at paints and coating industries in light of the radiation and photochemical sciences to meet the UNs SDGs.

Advancements in Photo-catalytic/ Self Cleaning Coatings:

Paints and coatings are used over any surface for the dual function of protection and the aesthetics. However, due to diverse environmental abuses, they become soiled and

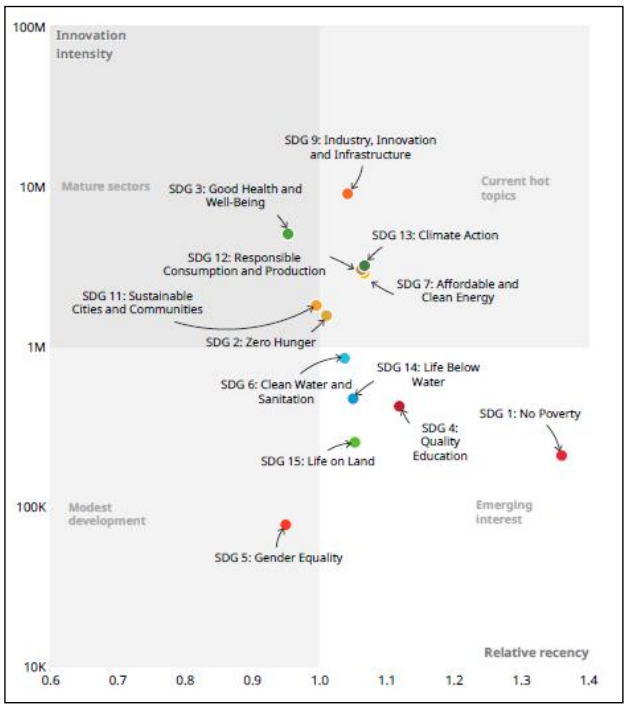

Fig.1 Innovation Maturity Matrix for SDG related patents 2000-2023

declines in performance. Researchers have been making efforts to overcome this shortcoming by developing the technology solutions of self-cleaning coatings by various means of using the photo-catalytic science. Fig. 2 depicts summary of various self-cleaning surfaces for Architectural and industrial applications for sustained clean performance. [3]

Photocatalytic action of the Titanium dioxide is well studied and the research papers describes detailed mechanism of the action of photocatalytic degradation of the pollutants and simultaneously making the surface super hydrophilic which facilitates the water washing of such coatings providing the self-cleanability. Since the mechanism of photocatalytic actions kills any organic molecules in proximity, the films become sustainable source of air-cleaning as well. However, there are challenges of keeping such active TiO2 in film form along with other

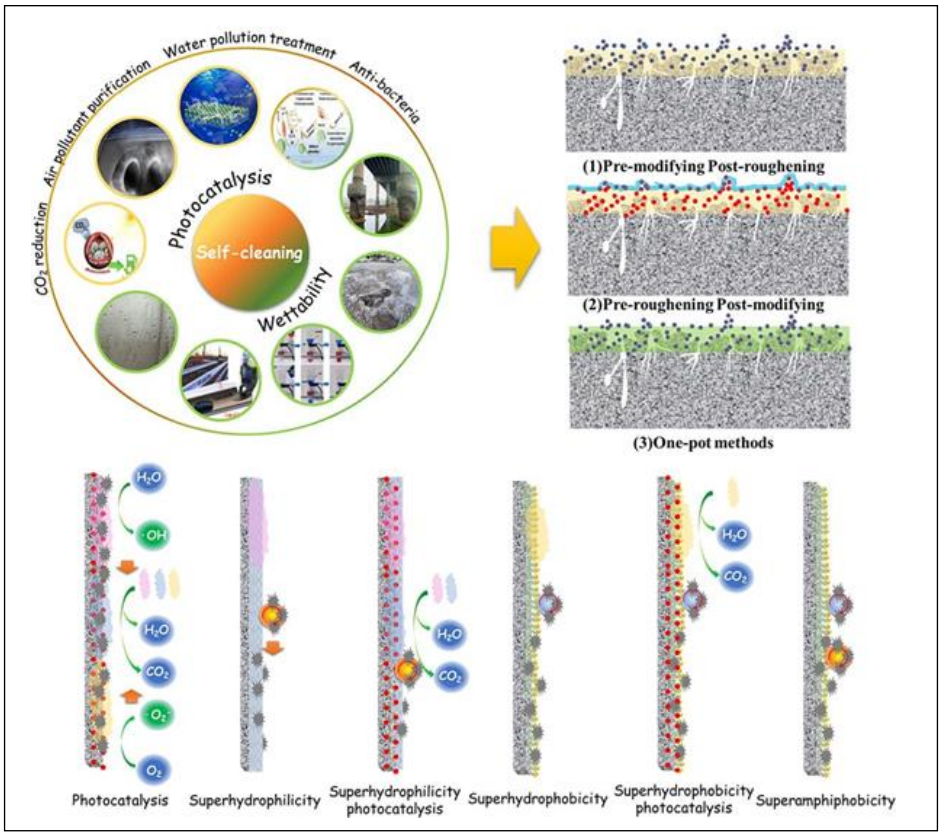

Fig.2 Self Cleaning Coating with varied surface properties
Source: Construction and Building Materials, Volume 409, (December 2023), 134084

organic polymers and additives. Researchers have come out with the inorganic binder and additive approach to ensure such stability in the wet stage (paint preservation) and dry stage (in the cured film). The photocatalytic TiO2 use is extended to multiple applications.

One of the studies synthesized the geopolymer based on ceramic waste and granulated blast furnace slag. The nano SiO2-TiO2 photocatalytic coating was applied over the geopolymer . It was observed that the surface contact angle of 118 ^{0} with superior self cleaning efficiency was established. [4] Arash Fattah-alhosseini et.al. [5] reviewed the approaches to find the alternat solution of the issues like agglomeration etc of photocatalyst powders in decontamination of various pollutants. They described the process of plasma electrolyte oxidation (PEO) over the aluminium surface. The results showed that the PEO coatings display superior photocatalytic properties due to distinctive surface shape and crystalline arrangement.

Self-cleaning coating for solar cells having hydrophobicity and anti-reflective properties are reported by Wenxue Zhang et. al. they created two distinct layers, bottom layer consisting hydrophilic silicone dioxide gel having TiO2 nano particles coupled tungsten nitride nano particles as effective photocatalytic component whereas top layer consisted hydrophobic dimethyl silicone oil (PDMS) modification. The composite film showed superior photocatalytic activity and environmentally sustainability.

Synergistic blend of anti-microbial and photocatalysis was studied by Mankun Li et. al. [6]. An anti-microbial 2D g-C_3N_4/Cu_2O/ Cu coating was synthesized, where 2D g-C_3N_4 Provides ample sites for Cu_2O & Cu deposition enhancing current efficiency and electron transfer capabilities enabling the mitigation of the microbial corrosion prevention and photocatalysis simultaneously.

M.J. Mateos et. al. studied photocatalytic coating based on TiO2 with self cleaning properties for indoor air purification. It was shown that combination of TiO2 nano particles with different crystal structures and sizes improves the photocatalytic performance. [7]

Jéssica D. Bersch et. al. comprehensively reviewed the literature on photocatalytic TiO2 based coatings in light of their efficiency (which is determined by self-cleaning, de-polluting and anti-microbial effect) durability and sustainability. [8]

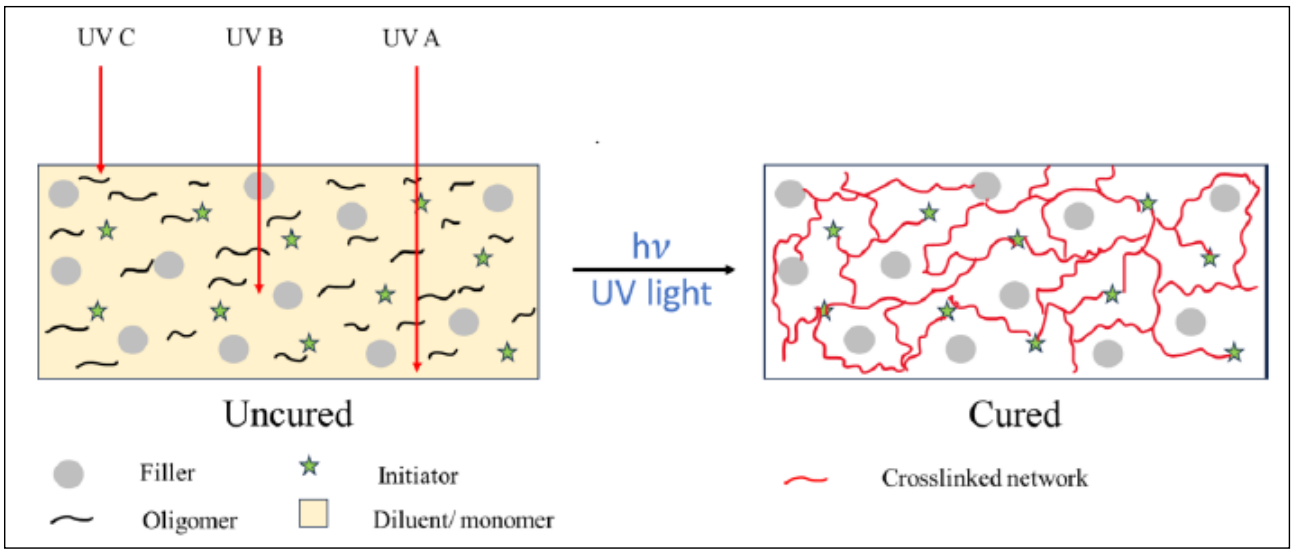

Fig. 3 Radiation cured coating- Curing
Source : J. Compos. Sci. 2023, 7, 513 Mechanism

Researchers have also made efforts to demonstrates the visible light induced self cleaning coatings by various chemistries [9] [10]

Advancements in Radiation Cured Coatings:

Radiation cured coatings are the compositions that hardens by free radical / cationic polymerization when exposed to high intensity ultraviolet or electron beam radiation. These coatings are gaining more popularity due to their very high curing speed, energy efficiency in curing and lower impact on environment. Coatings, adhesives and inks are the key segments and Automotive coatings, wood furniture, packaging, electronics are key areas of applications. The compositions containing oligomers, photo-initiators, monomers/ reactive diluents and additives. Fig 3 illustrates the curing mechanism of UV curable coating system.

Recently LED UV curing has got more acceptance due to longer lamp life, lower heat and energy efficiency. Below is the summary of few of the advancements.

Ashwarya Sheel Wali et. al. reviewed in detail the key advancements in radiation cured coatings. Currently the major developments are happening in the area of photo-initiators, light source/ Equipments and oligomers/resins. [11]. Photo-initiators with good water dispersibility, Reactivity, low migration rates, low odor/ color and ability to facilitate cure with visible/ NIR radiations are the major research activities.

One of the studies identified that the new photo-initiator 1,3- Dioxane methylcoumarin (DOMC) is more effective compared to benzophenone [12]

At the same time for the oligomers, the major developments are happening for improving durability, enhanced optical properties, reduced toxicity, reduced C foot print and increased Bio-based content. Oligomers with lower skin irritations and toxicity as well as improved adhesion on varied surfaces is also one of the major research efforts. On the curing equipment, UV LED with high energy efficiency, longer lifespan, less heat emission and reduced cost are the key thrust areas of research.

More recently the UV curing application has been extended to powder coatings for the applications on plastics and composites as they

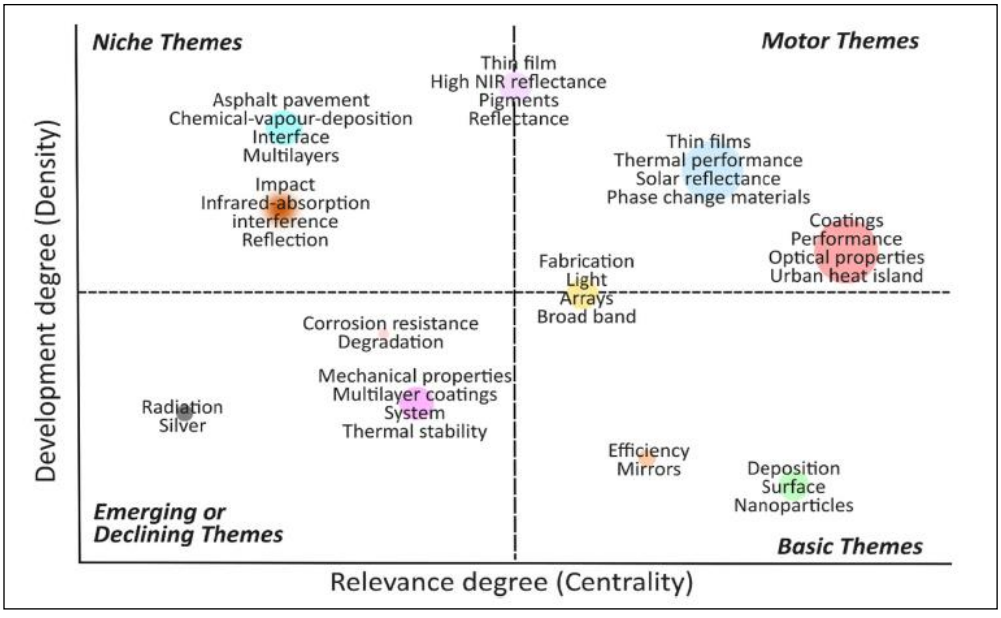

Fig. 4 Thematic evolution of Radiative Cooling technology from 2000 to 2025

Source : Journal of Cleaner Production 511 (2025) 14563 Mechanism

are heat sensitives and finding more applications due to light weight and cost. The UV LED is the preferred way of coating for such heat sensitive substrates, with several environmental benefits over conventional mercury lamp. [13]

Advancements in Radiative Cooling paints and Coatings:

Due to increased urbanization and the resultant growth of the building constructions in high populated cities, releases more anthropogenic heat and a higher blockage effect against urban ventilation, causing absorption of solar radiations and reduced long wave emissions. This causes increased ambient temperature and the related health issues, increased consumption of energy at HVAC system etc.[14]

Paints and coating industries making efforts to address the issue by developing the radiative cooling paints and coatings which can cool the surfaces below the ambient temperature. They possess typically high solar reflectance and high thermal emissivity. The passive day time radiative cooling is an emerging sustainable technique to address the cooling requirements in various sectors majorly in building and industries with best energy saving potential

AC Consumes 10% of the global total electricity hence this can be best sustainable way to address the issue.

Some of the advancements in the area of engineered radiative cooling systems are based on nature inspired designs, use of chromatic materials for surface cooling, meta – structures and multilayered coatings. Due to current challenges of durability and sustainability of such paints and coatings, the research efforts are to mitigate the same.

The comprehensive review [15] by Mohammad A. et. al. summarizes the advancements in the area of nanomaterials for radiative cooling applications. They found that the applications of such nano materials is two fold, to minimize the surface temperature and protecting the surface. Fig.4 below summarizes the thematic evolution of radiative cooling technology.

It was observed that with nano material technologies in radiative cooling the temperature reduction up to 13 degree centigrade compared to ambient temperature was achieved. However there are challenges that need to be addressed.

Green buildings- Roof / glass windows/ cool generation of air cooling, Power generation – solar cell cooling, Thermal power plant cooling, Climate engineering- Urban hear island mitigation, Automobiles and industrial structure – Cooling and power saving are few of the applications where the radiative cooling coatings are in use currently.

Though various specification for radiative cooling paints are available commercially specifying the parameters like Total solar reflectance (TSR), Emissivity and Solar reflective index (SRI), however there is need for standard comprehensive test protocol taking into consideration of the sustenance of such performance and reproducibility and repeatability.

Advancements in Stealth coatings:

Stealth coatings are the materials used over the war equipments for the purpose of absorbing the radar/ heat hence makes it harder to get detected by the enemies. Various war equipments include military aircrafts, submarines, war tanks and trucks, shelter houses and bunkers etc. Primarily the coatings work by absorbing incoming radar waves rather than reflecting back to the source. The coating composition absorbs such energy and convert into heat. Moreover the materials like RAMA (Radar absorption and multispectral adaptive) help absorb and dissipate the heat in a manner for the object to blend with the surrounding environment temperature, to have the camouflage effect. Ground vehicles (Fig 5), commercial vehicles, military aircrafts and submarines use this kind of coatings.

Nidi Shirke et. al. reviewed the recent advances in stealth coatings [16] The materials

Fig. 5: Stealth coating over ground vehicle

used in stealth coating preparations are based on polymer composite from graphene, carbon nano tubes, carbon fibers and other carbonaceous materials and fillers. The binder chemistry used are epoxy, polyurethane, poly carbonates and poly imide. The current advancements are in the areas of developing the coatings with multispectral compatibility – Metamaterials with effective absorption bandwidth gives multispectral compatibility, Photonic crystals with multispectral compatibility are also being researched.

There are MIL specifications specifying the IR reflectance and visible reflectance for effective stealth and camouflage effect for defence applications.

Conclusion:

The below table 1 summarizes various applications of coatings using the electromagnetic radiations of varied wavelengths and serving different applications ranging from architectural to industrial and automotive- marine – aircrafts etc.

The technological advancements are continued in each of the areas of self-cleaning coatings, radiative cooling coatings, radiation cured coatings and stealth coatings. These advancements are addressing the current challenges of respective industries/applications keeping sustainability

Table 1: Summary of Innovations addressing the SDGs for each of the EMRs applications in paint and coating industry.

Role of EMRs in Paints and Coatings SDGs	Anti-Radar/ Stealth Coating	IR Reflective/ Photocatalytic/ Self cleaning	Radiative Cooling/IR reflective	Rad- cured Visible/ LED/ UV
9 : Industry, Innovation and Infrastructure	Anti-Radar with multifunctional properties (self healing / thermal insulation)	Efficient Photocatalysis		
11:Sustainable Cities and Communities		Self cleaning surfaces/ Anti-fouling	Enhanced durability	
13:Climate Action		Bio-inspired self-cleaning coating	Reduced energy consumption Low C footprint	Bio-based renewable materials
3:Good Health and Well-being	Noise reduction, corrosion resistance	Air-purification Waste water treatment	Urban heat island heat reduction	VOCs and Toxic Reduction
7:Affordable and Clean Energy	Energy efficiency	Sustainable energy Efficient photovoltaic Photovoltaic	Energy Efficient cooling solutions	Visible light curing

as backdrop. We can see excellent co-relation of UNs sustainable development goals (SDGs) for each of the above four applications and respective technology advancements. The future scope include the addressing the gaps and making the offering more on sustainability and feasibility for the wider usage.

Acknowledgements :

I would like to acknowledge the support from Asian Paints Management for encouragement and required resources.

References:

1. Global markets and advanced technologies for paints and coatings, market research report CHM049H, BCC Publishing Chemicals, July 2024
2. Mapping innovations patents and the sustainable development goals, WIPO, 2024
3. Guanyu Liu, Tianzheng Zhao, Hailiang Fei, Fen Li, Wenya Guo, Zhaolin Yao, Zhen Feng, A review of various self-cleaning surfaces, durability and functional applications on building exteriors, Construction and Building Materials, Volume 409, (2023), 134084
4. Ying Wang, Na Zhang , Shuai Zhang, Yidi Wang, Ruoyun Xia, Yihe Zhang, A novel self cleaning ceramic waste- slag geopolymer with nano SiO2-TiO2 photocatalytic coating, ceramic international, 50, (2024) , 17135-17144
5. Arash Fattah-alhosseini a, Razieh Chaharmahali a, Sajad Alizad a, Kazem Babaei a, Stevan Stojadinovi´c, A review on the revealed improved photocatalytic activity of PEO coatings applied on Al alloys, Nano-Structures & Nano-Objects 39, (2024), 101233
6. Mankun Li, Zishuai Hu, Dan Liu, Yongmei Liang, Shijia Liu, Bo Wang, Chunmei Niu, Dake Xu, Jianhui Li, Baochen Han, Efficient antibacterial and microbial corrosion resistant photocatalytic coating: Enhancing performance with S-type heterojunction and Cu synergy, Chemical Engineering Journal 495, (2024), 153519
7. M.J. Mateos, A. Lao-Zea, M.P. Alcacera, B. S´anchez, S. Su´arez, Photocatalytic coatings with self-cleaning properties for indoor air treatment, Journal of Photochemistry & Photobiology, A: Chemistry 457, (2024), 115880
8. Jéssica D. Bersch, Inês Flores-Colen, Angela B. Masuero and Denise C. C. Dal Molin, Photocatalytic TiO2-Based Coatings for Mortars on Facades: A Review of Efficiency, Durability, and Sustainability, Buildings 2023, 13, 186
9. Ahmet Yavas, Fethullah Günes, Mustafa Erol, Mücahit Sütçü, Erdem Tevfik ¨Ozdemir, Visible light-induced self-cleaning ZnO coated-clay roofing tiles: The role of coating concentration on structural and photocatalytic properties, Surfaces and Interfaces 46, (2024), 103975.
10. Alireza Saberyoun, Arash Fattah-alhosseini, Minoo Karbasi, Reza Hosseini, Mosab Kaseem, Boosting the visible-light-driven photocatalytic efficiency in porous Cu/TiO2 ceramic coatings, Ceramics International 50, (2024), 31313–31325
11. Ashwarya Sheel Wali, Sandeep Kumar, Debashish Khan, A review on recent development and application of radiation curing, Materials Today: Proceedings 82, (2023), 68–74
12. A. Eibel, D.E. Fast, G. Gescheidt, Choosing the ideal photoinitiator for free radical photopolymerizations: predictions based on simulations using established data, Polym. Chem. 9,(41) (2018), 5107–5115.
13. Ed. Kiyoi, The State of UV-LED Curing: An Investigation of Chemistry and Applications, RADTECH REPORT ISSUE 2 2013, 32-36
14. Parham A. Mirzaei, Recent challenges in modeling of urban heat island, Sustainable Cities and Society,19, (2015) , 200-206
15. Mohammad A. Alim, Zhong Tao, H M Imran, Md Arifur Rahim, Zainab Malik, Ataur Rahman, A scoping review on reflective coatings with nano materials: Progress since 2000 and current challenges, Journal of Cleaner Production 511 (2025) 14563
16. Nidi Shirke, Vaijayanti Ghase & Vandana Jamdar, Recent advances in stealth coating, polymer bulletin, Volume 81, (2024), 9389–9418,

Dr. Randhir Parmar *completed masters (industrial polymer chemistry-1994) and Ph.D.("Water borne epoxies and acrylic dispersions for coatings"-2003) from Sardar Patel University, Vallabh Vidyanagar Gujarat. He served as lecturer at the institute of science and technology for advanced studies and research (ISTAR) teaching the post graduate students of paint technology for 7 years, Also worked with several paint and allied industries for joint research projects and helped several Masters and research students for their thesis work. He has also published and presented number of research papers in peer reviewed national and international journals and various forums and contributed for several patents in the area of paints and coatings. Since April 2005 he is working for Asian Paints limited at Research and Technology Centre and currently responsible for the technology support to industrial paints and coatings business of Asian Paints Limited.*

Valorisation of Polymer Waste via Advanced Chemical Recycling: A Review of Novel Depolymerization Strategies and High-Value Applications

Devesh Sane[1], Anagha Sabnis*[1]

[1] *Department of Polymer & Surface Engineering, Institute of Chemical Technology Nathalal Parekh Marg, Matunga (E), Mumbai-400019*

Email: as.sabnis@ictmumbai.edu.in

Abstract

The escalating environmental burden of post-consumer polymer waste, particularly from poly(ethylene terephthalate) (PET) and polyurethane (PU), necessitates advanced recycling strategies that promote a circular economy. This review provides a comprehensive overview of recent advancements in the chemical upcycling of PET and PU waste, focusing on an application-driven approach that transforms these materials into high-value chemical feedstocks. The review highlights key innovations in depolymerization chemistry, including the use of novel glycol and amine agents (e.g., 2-methyl-1,3-propanediol, aminoethylethanolamine, isophoronediamine) to create functional oligomeric building blocks. Furthermore, it examines the role of process intensification techniques such as microwave irradiation, electron beam, and gamma-ray pre-treatment, alongside statistical optimization methods like the Taguchi design, in enhancing reaction efficiency. The successful valorization of these waste-derived intermediates into a diverse portfolio of high-performance materials is detailed, including UV-curable coatings, bio-hybrid polyurethane systems, hybrid polyester-urethanes, polyesteramides, epoxy hardeners, and new rigid foams. Through a synthesis of these studies, this review demonstrates that comprehensive characterization and performance evaluation of upcycled materials offer a viable and strategic pathway toward sustainable polymer management.

1. Introduction

The rapid expansion of polymer production and consumption has fundamentally reshaped modern society, but it has also precipitated a global environmental crisis related to plastic waste management . Among the most produced polymers, poly(ethylene terephthalate) (PET) and polyurethanes (PU) represent significant contributors to the waste stream. PET consumption is projected to be 42 million tons in 2030, while global sales of PU reached nearly 24.7 million metric tonnes in 2021. The extensive use and inherent durability of these materials, coupled with their resistance to natural degradation, have led to their accumulation in landfills and ecosystems worldwide.

Conventional waste management strategies have proven inadequate. Landfilling is increasingly unsustainable due to land scarcity and the potential for leaching hazardous chemicals into the soil and groundwater. Incineration, while capable of energy recovery, raises concerns about the emission of greenhouse gases and toxic pollutants. In this context, recycling has emerged as the most viable and environmentally responsible solution. Recycling methodologies are broadly categorized as mechanical and chemical. While mechanical recycling is suitable for clean, homogeneous thermoplastic waste, it often results in downcycling the production of lower-quality materials and is largely ineffective for cross-linked thermosets like many PUs or for heavily contaminated post-consumer waste.

Chemical recycling, conversely, offers a pathway to true upcycling. By employing chemical processes to depolymerize waste polymers back into their constituent monomers or functional oligomers, it enables the production of virgin-quality materials and closes the loop on polymer lifecycles, aligning with the principles of a circular economy. The primary chemical recycling routes include glycolysis, aminolysis, hydrolysis, and alcoholysis, each utilizing a different reagent to cleave the polymer's ester, urethane, or amide bonds. This approach is critical for transforming polymer waste from an environmental liability into a valuable secondary feedstock, thereby reducing reliance on virgin, petroleum-derived resources.

This review consolidates a body of work from a single research group that has systematically explored and advanced the field of chemical recycling for PET and PU waste. The research presented herein moves beyond simple depolymerization, adopting a sophisticated "reverse-synthesis" philosophy. This strategy involves the deliberate selection of depolymerization agents and process conditions not merely to break down waste, but to strategically engineer the chemical structure of the resulting intermediates. The functionality of these recycled building blocks whether they possess terminal hydroxyl, amine, or a combination of reactive groups is tailored for specific, high-performance end-use applications. For instance, glycolysis is employed to generate hydroxyl-terminated oligomers ideal for synthesizing polyesters and polyurethanes [2, 6-8], whereas aminolysis is used to create amine-functionalized intermediates perfectly suited for use as epoxy curing agents or for incorporation into polyesteramides. This application-driven approach transforms polymer waste from an environmental burden into a valuable chemical feedstock, demonstrating a clear and versatile pathway toward sustainable polymer valorization.

2. Chemical Upcycling of Polyethylene terephthalate (PET) Waste

The research group has undertaken extensive investigations into the chemical recycling of PET, primarily sourced from post-consumer beverage bottles. These efforts are organized around two principal depolymerization strategies glycolysis and aminolysis each designed to yield distinct functional intermediates for subsequent valorization into high-performance materials.

2.1. Glycolytic Pathways to Functional Monomers and Oligomers

Glycolysis involves the transesterification of PET's ester linkages with a diol, producing hydroxyl-terminated monomers or oligomers. This research explores various facets of this process, from utilizing conventional and novel diols to implementing advanced process intensification techniques to enhance efficiency and yield.

2.1.1. Depolymerization Strategies and Process Intensification

The foundational work in this area involves the glycolysis of PET waste with ethylene glycol (EG) using zinc acetate as a catalyst at approximately 190°C, which yields the monomer bis(2-hydroxyethyl terephthalate) (BHET). This conventional heating method serves as a benchmark for evaluating more advanced techniques.

A significant innovation introduced is the pre-treatment of PET waste with ionizing radiation prior to glycolysis. Both gamma (γ) and Electron Beam (EB) radiation have been investigated to induce chain scission in the polymer, effectively reducing its molecular weight and making it more susceptible to chemical attack. When absorbed by the material, high-energy radiation provides enough energy to excite electrons, leading to the formation of smaller polymeric radicals with lower molecular weights, as depicted in Figure 1.

Table 1. Comparative Analysis of PET Glycolysis Methods and Products.

Depolymerizing Agent	Heating Method	Pre-treatment	Optimized Conditions (Ratio, Temp, Time)	Recycled Product	Product Yield (%)	Product Characteristics (Mn, OH Value)	Final Application	Reference
Ethylene Glycol (EG)	Conventional	γ-Radiation (100 kGy)	1:6, 190°C, 6 h	BHET	62.4	Mn not specified, OH Value: 454 mg KOH/g	Polyurethane Coating	[8]
Ethylene Glycol (EG)	Conventional	EB Radiation (500 kGy)	1:6, 190°C, 6 h	BHET	60.52	Mn not specified, OH Value: 454 mg KOH/g	Polyurethane Coating	[7]
Ethylene Glycol (EG)	Microwave	EB Radiation	1:6, 190°C, 40 min	BHET	74.90	Mn not specified, OH Value: 454 mg KOH/g	Polyurethane Coating	[7]
Ethylene Glycol (EG)	Conventional	None	1:6, 190°C, 6 h	BHET	55.26	Mn not specified, OH Value: 454 mg KOH/g	Hybrid UPE Resin	[2]
2-Methyl-1,3-propanediol (MP-diol)	Microwave	None	1:8, 200°C, 30 min	OPET-MPD	~60	Mn: 327 g/mol, OH Value: 339 mg KOH/g	UV-Curable Wood Coating	[6]

In one study, PET waste was pre-treated with gamma radiation at doses ranging from 30 to 100 kGy, which resulted in a molecular weight reduction of approximately 15% to 40%, respectively. This pre-processing step was found to significantly enhance the subsequent conventional glycolysis reaction. For instance, after 6 hours of reaction, PET irradiated with a 100 kGy dose yielded 62.4% BHET, compared to just 50% for the non-irradiated sample under identical conditions. Similarly, pre-treatment with EB radiation at doses up to 500 kGy caused a ~25% reduction in molecular weight. When this EB-irradiated PET was subjected to conventional glycolysis, the yield of BHET increased notably. After 6 hours, PET irradiated with a 500 kGy dose yielded 60.52% BHET, compared to 55.26% for the non-irradiated sample. This enhancement allows for either a higher yield in the same amount of time or a similar yield in a shorter time, demonstrating an effective strategy to overcome the kinetic hurdles of depolymerizing high-molecular-weight polymers.

To further improve process efficiency, microwave-assisted heating was investigated as an alternative to conventional thermal methods. Microwave energy interacts directly with polar

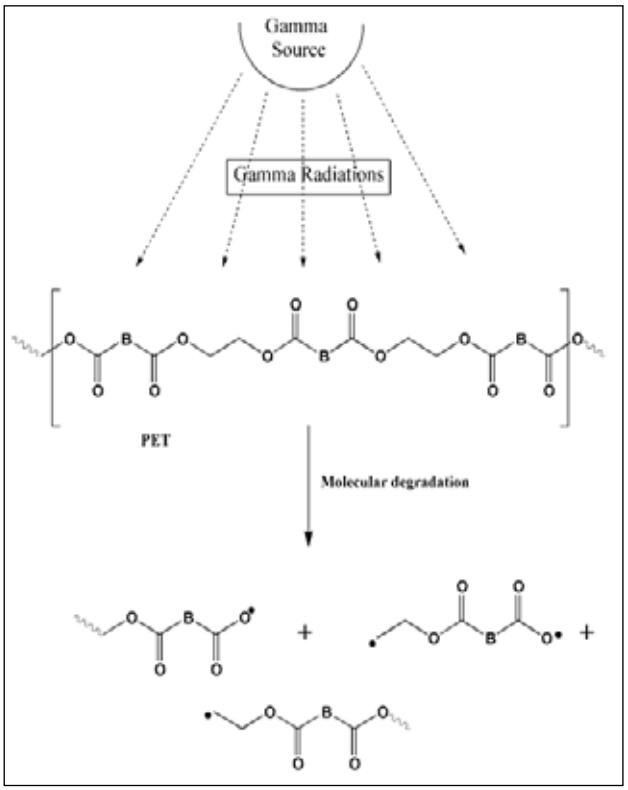

Figure 1. *Schematic representation of PET chain degradation under the effect of gamma irradiation [8] .*

molecules in the reaction mixture, leading to rapid and uniform heating. This technique drastically reduces reaction times from several hours to mere minutes. In the glycolysis of PET with EG, microwave heating achieved BHET yields of over 70% in just 20-40 minutes. Similarly, in another study, the optimal yield of an oligomeric product was achieved in only 30 minutes of microwave irradiation. This represents a substantial improvement in energy efficiency and process throughput.

Beyond process enhancements, the research also explored the use of a novel glycolysis agent: 2-methyl-1,3-propanediol (MP-diol), a branched aliphatic diol not widely reported for PET recycling. Using a microwave-assisted technique, the reaction parameters were systematically optimized. The highest yield (~60%) of the oligomeric product, designated OPETMPD, was obtained with a PET:MPD molar ratio of 1:8, at 200°C for 30 minutes using 500 W of microwave power. The resulting oligomer was characterized by a low number-average molecular weight (Mn) in the range of 327-506 g/mol and a high hydroxyl value of up to 339.07 mg KOH/g, making it a highly functional precursor for further synthesis. This work demonstrates how the choice of depolymerizing agent can be used to tailor the molecular architecture of the recycled product.

2.1.2. Valorization into High-Performance Coatings and Resins

A central tenet of this research is that the recycled intermediates are not end-products but are valuable building blocks for new materials. The hydroxyl-terminated products from glycolysis were successfully valorized in several high-performance applications.

The BHET monomer, produced via both γ-ray and EB-assisted glycolysis, was used as a platform chemical for synthesizing eco-friendly, bio-hybrid polyols . One synthetic route involved an initial esterification of BHET with linseed oil fatty acid, followed by epoxidation of the fatty acid's double bonds and subsequent hydrolytic ring-opening to generate additional hydroxyl groups. The resulting bio-hybrid polyol (HBEFA), combining a recycled aromatic core with a bio-based flexible chain, was then cured with commercial polyisocyanates to produce high-performance polyurethane coatings. Another approach utilized BHET along with other bio-based monomers like dimer fatty acid, glycerol, and sebacic acid to create a polyester polyol, as shown in the reaction scheme in Figure 2.

In a different application, the oligomeric product from MP-diol glycolysis (OPETMPD) was chemically modified to create a novel UV-curable resin. The terminal hydroxyl groups of OPETMPD were reacted with methacrylic acid in an esterification reaction to attach polymerizable methacrylate groups, yielding a dimethacrylated UV oligomer (Figure 3). This waste-derived oligomer was then formulated into UV-curable wood coatings, partially replacing a commercial epoxy acrylate resin. Performance evaluation

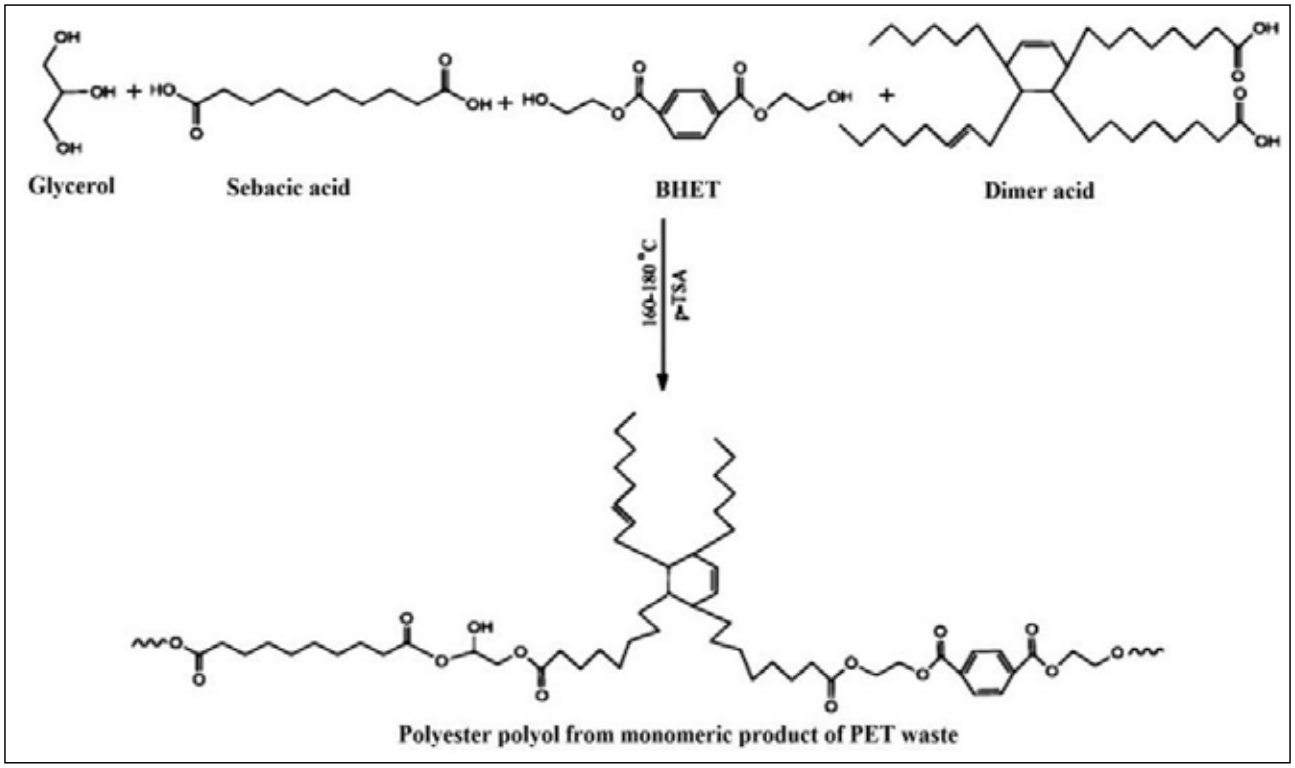

Figure 2. Reaction scheme for the synthesis of a polyester polyol using recycled BHET and bio-based monomers [8].

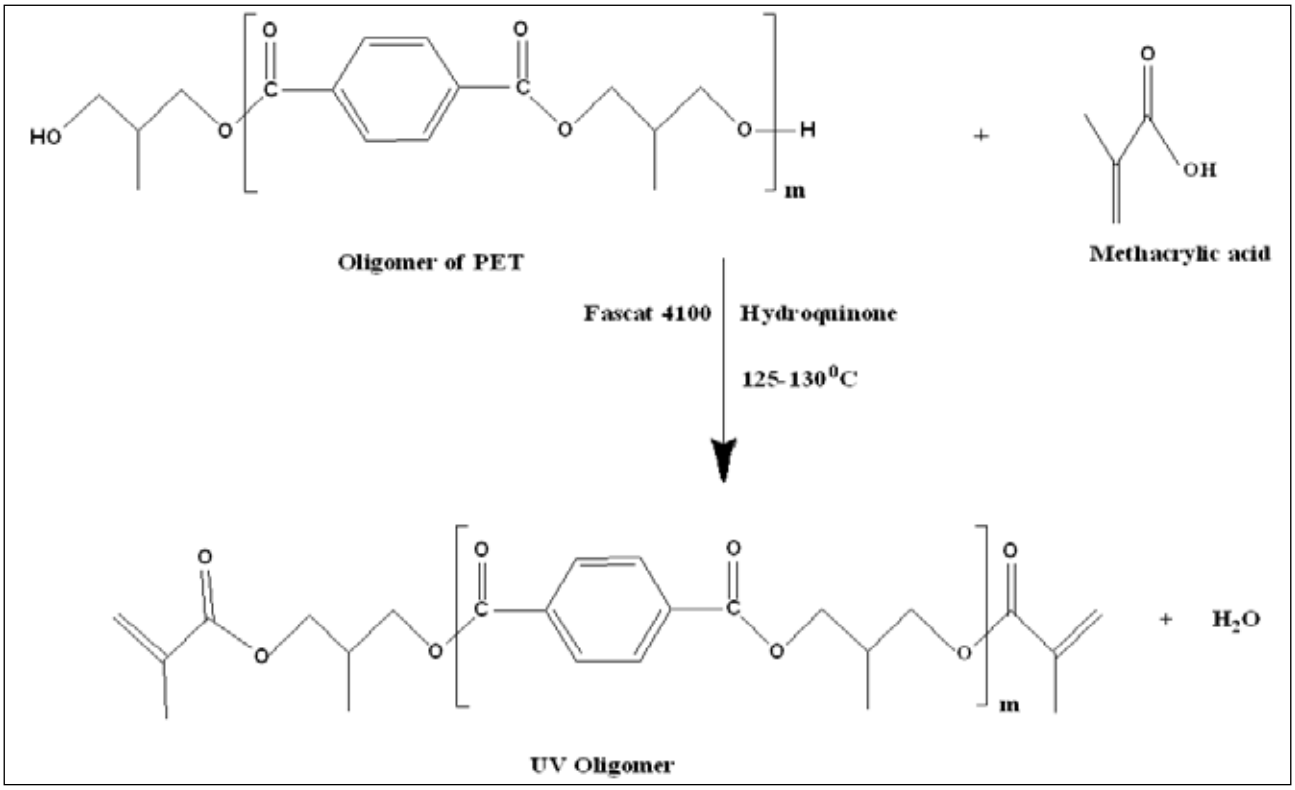

Figure 3. Reaction scheme for the synthesis of a UV-curable oligomer via methacrylation of the recycled PET oligomer (OPETMPD) [6].

showed that formulations containing up to 50% of the recycled UV oligomer exhibited coating properties such as adhesion (5B), pencil hardness (4H), solvent resistance (>200 MEK rubs), and water absorption that were comparable to the control formulation made with 100% commercial resin . This demonstrates the potential of waste-derived materials to serve as effective drop-in replacements in advanced coating systems.

Furthermore, BHET was utilized in the synthesis of hybrid unsaturated polyester-urethane (UPE) resins. These novel resins were synthesized using recycled BHET, a urethane diol (prepared via a non-isocyanate route), maleic anhydride, and other acids like dimer fatty acid or phthalic anhydride to modify properties. The resulting hybrid polymers, containing both ester and urethane linkages, were cured at room temperature to form coatings. The incorporation of the urethane linkages is known to enhance properties like adhesion and hardness, showcasing another pathway to create high-value materials from PET waste.

2.2. Aminolytic Depolymerization for Amide-Functional Building Blocks

Aminolysis, the cleavage of PET's ester bonds using amines, produces intermediates containing robust amide linkages. This functionality can impart enhanced thermal stability, hardness, and chemical resistance to the final products. The research group explored this route using

Table 2. Performance of High-Value Coatings Derived from PET Waste.

Coating System	Recycled Precursor	% Recycled Content in Resin/Formulation	Curing Mechanism	Key Mechanical Properties (Pencil Hardness, Adhesion)	Solvent Resistance (MEK rubs)	Thermal Stability (Tg °C)	Corrosion Resistance	Reference
UV-Curable	OPETMPD (from MP-diol glycolysis)	Up to 50% oligomer replacement	UV Free Radical	4H, 5B	>200	Not specified	Not applicable	[6]
Polyurethane	HBEFA (from BHET/ LOFA)	100% of polyol component	Isocyanate (HDI, MDI)	Not specified	Not specified	Not specified	Not specified	[7]
Polyesteramide	OPE-TAEEA (from AEEA aminolysis)	Up to 40% polyol replacement	Isocyanate (IPDI)	6H, 5B	>150	58.6°C	Excellent	[10]
Epoxy (DGEBPA)	OPETIPDA (from IPDA aminolysis)	100% of hardener component	Epoxy-Amine	6H, 5B	>200	62.4°C	Excellent	[9]
Epoxy (Cardanol)	OPETIPDA (from IPDA aminolysis)	100% of hardener component	Epoxy-Amine	6H, 5B	>200	43.2°C	Excellent	[9]

novel, multifunctional amines, demonstrating a sophisticated strategy of functional repurposing.

2.2.1. Depolymerization with Novel Amine Agents

A key study focused on using aminoethylethanolamine (AEEA), a molecule possessing primary amine, secondary amine, and hydroxyl functionalities, which had not been previously explored for PET aminolysis . The depolymerization was optimized using both conventional and microwave-assisted heating. Once again, the microwave technique proved far more efficient, achieving an oligomer yield of 52-58% in just 30 minutes, compared to 4 hours required for a lower yield (~48%) with conventional heating. The resulting oligomeric product, OPETAEEA, was a highly functional material with both amine and hydroxyl reactive sites.

Another novel agent investigated was isophoronediamine (IPDA), a cycloaliphatic diamine containing both a primary and a secondary amine group. The aminolysis reaction using IPDA was optimized via conventional heating. The maximum yield of the oligomeric product, OPETIPDA, approaching 80%, was achieved with a PET:IPDA molar ratio of 1:3 at a reaction temperature of 170°C for 4 hours. Characterization of the product confirmed the formation of an oligomer with terminal primary amine groups and internal amide linkages, with an estimated molecular weight corresponding to approximately three repeating PET-IPDA units.

2.2.2. Functional Repurposing of Aminolyzed Oligomers

The true innovation of the aminolysis work lies in the intelligent valorization of the products, where their unique chemical functionalities are leveraged for specific, high-performance roles. The OPETAEEA oligomer, with its rich amine and hydroxyl functionality, was used as a direct replacement for a portion of neopentyl glycol in the synthesis of polyesteramide (PEA) resins. In this application, the amide linkages from the recycled oligomer are incorporated directly into the main chain of the new polymer. When these PEA resins were cured with polyisocyanates, the resulting coatings showed a clear structure-property relationship: as the percentage of the recycled OPETAEEA was increased (from 10% to 40% replacement), the coatings exhibited progressively greater pencil hardness (from 4H to 6H), improved scratch resistance (from 1500g to 2900g), and enhanced corrosion resistance. The pull-off adhesion for the 40% system reached 2.94 MPa, a significant improvement over the control. This performance enhancement is directly attributable to the incorporation of the rigid aromatic rings and thermally stable amide groups from the recycled PET feedstock.

The OPETIPDA oligomer was repurposed in an even more functional role as a novel curing agent (hardener) for epoxy resins. Here, the terminal primary amine groups of the oligomer are the active sites that react with and cross-link the epoxy groups. The oligomer is not a passive component but the primary agent responsible for building the thermoset network. OPETIPDA was successfully used to cure both a conventional diglycidyl ether of bisphenol-A (DGEBPA) epoxy and a bio-based cardanol epoxy. The resulting coatings displayed exceptional performance, often surpassing that of a commercial polyamide hardener. For example, the DGEBPA system cured with OPETIPDA achieved a pencil hardness of 6H and a pull-off adhesion of 2.14 MPa, compared to 5H and 1.76 MPa for the commercial system. The high glass transition temperatures (Tg) observed (e.g., 62.4°C) are a direct result of the rigid cycloaliphatic and aromatic structures present in the OPETIPDA backbone. This work transforms the recycled product from a simple extender into a performance-enhancing, functional component.

3. Advanced Recycling of Polyurethane (PU) Waste

Recycling polyurethanes presents a greater challenge than PET due to their typically cross-linked, thermoset nature. The research group's work in this area demonstrates highly tailored strategies that are specific to the type of PU

Table 3. Summary of PU Waste Recycling Strategies and Outcomes.

PU Waste Source	Recycling Method	Depolymerizing Agent (s)	Process Control	Recycled Product	Key Product Specs	Final Application	Key Performance Highlight	Reference (s)
PU Shoe Sole (Elastomer)	Aminolysis	4,7,10-trioxatridecan-1,13-diamine & 1,3-propanediamine	Manual Parameter Variation	Amine/ Hydroxyl Functional Hardener	Amine Value: 142 mg KOH/g, Hydroxyl Value: 264 mg KOH/g (for optimal 60:40 ratio)	Epoxy Coating Hardener	Achieved 6H pencil hardness; superior to commercial system when using combined amine-hydroxyl equivalent.	[11]
Rigid PU Foam	Glycolysis	Diethylene Glycol (DEG)	Taguchi L9 Statistical Optimization	Recovered Polyol	Hydroxyl Value: ~500 mg KOH/g, Viscosity: ~850 cP	New Rigid PU Foam	Up to 60% replacement of virgin polyol; resulted in *improved* compressive strength.	[12]

waste and the desired end-product, showcasing a sophisticated understanding of polymer chemistry and process engineering.

3.1. Aminolysis of PU Elastomers for Novel Epoxy Hardeners

A significant portion of PU waste comes from end-of-life consumer goods, such as footwear. This research stream targets the upcycling of elastomeric PU shoe soles, a complex waste stream, into a valuable chemical additive, as illustrated in Figure 4.

The chosen depolymerization strategy was aminolysis, conducted at a relatively mild temperature of 140°C for 3 hours using a NaOH catalyst. The key innovation was the use of a novel binary amine system as the aminolyzing agent, consisting of a long, flexible ether diamine (4,7,10-trioxatridecan-1,13-diamine) and a short, rigid diamine (1,3-propanediamine). By varying the molar ratio of these two amines, it was possible to tune the properties (e.g., amine value, hydroxyl value, viscosity) of the resulting depolymerized liquid product.

This aminolyzed product, a complex mixture containing both amine and hydroxyl functionalities, was valorized directly, without any costly purification steps, as a hardener for commercial epoxy resins. The study critically evaluated the curing process by calculating hardener amounts based on only the amine equivalent weight versus a combined amine and hydroxyl equivalent weight. The results conclusively showed that formulations cured considering both functionalities exhibited far superior properties. This indicates that both

the amine and hydroxyl groups participate in the cross-linking reaction, leading to a denser, more robust network. Coatings prepared with the ASH approach achieved excellent pencil hardness (6H), superior adhesion (5B), and a high degree of cross-linking (gel content >98%), significantly outperforming both the AS systems and a standard commercial epoxy system. The

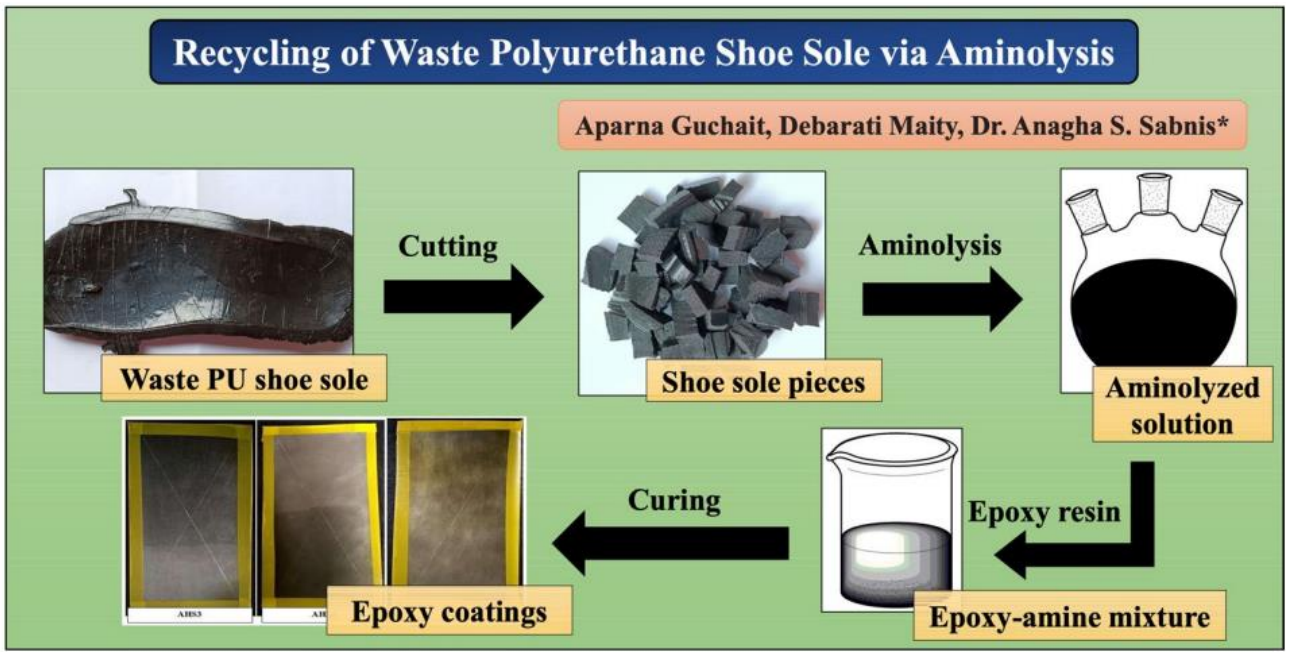

Figure 4. Process overview for the aminolytic recycling of PU shoe soles into epoxy hardeners [11].

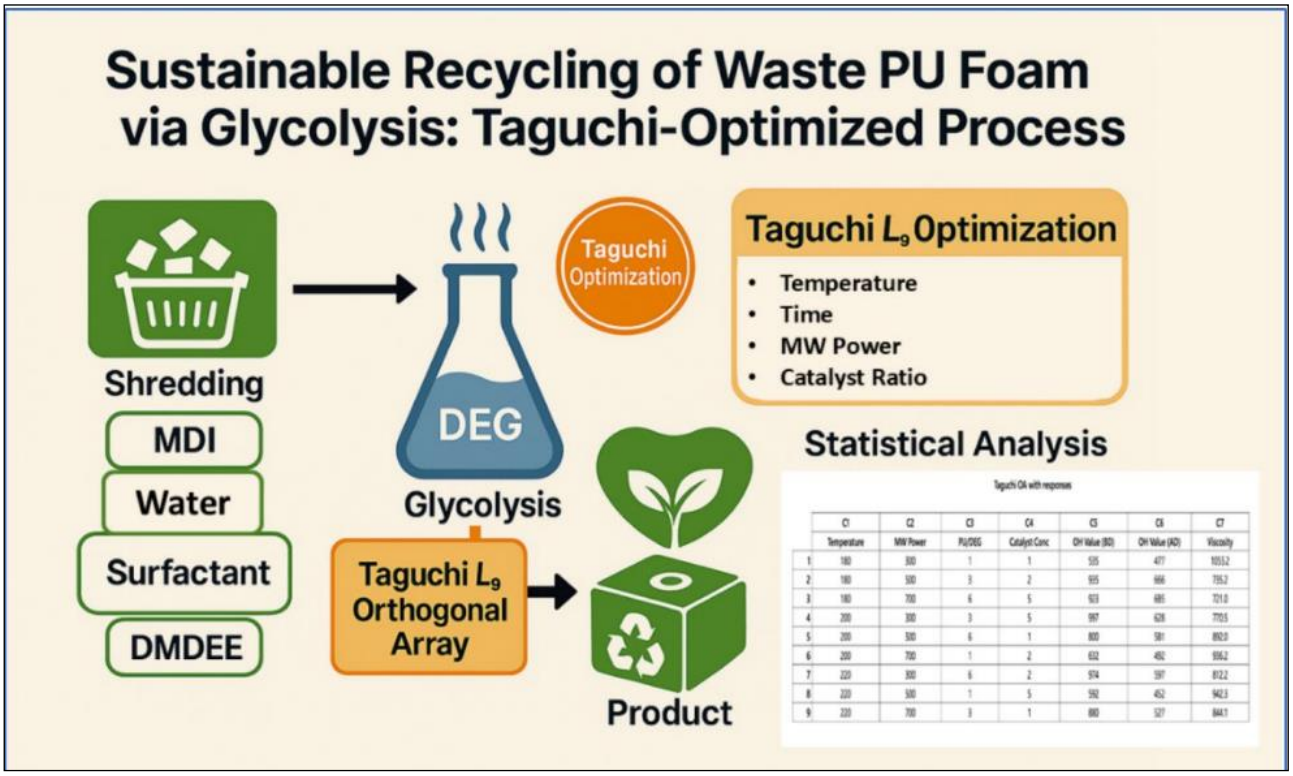

Figure 5. *Workflow for the statistically optimized glycolysis of rigid PU foam and its reuse in new foam formulations [12].*

optimal balance of properties was achieved using a depolymerized product from a 60:40 molar ratio of the long-chain to short-chain amines. This work successfully converts a challenging solid waste into a high-performance liquid chemical, creating value where none existed.

3.2. Statistically Optimized Glycolysis of Rigid PU Foam

Rigid PU foam, widely used for thermal insulation in appliances and construction, is another major contributor to thermoset waste. This research focuses on recovering a high-quality polyol from this waste stream that can serve as a direct, drop-in replacement for virgin material in new foam production, following the workflow in Figure 5.

Depolymerization was carried out via glycolysis using diethylene glycol (DEG) as the solvent and NaOH as the catalyst, with microwave irradiation employed for process intensification. The most significant innovation in this work was the application of a formal statistical design of experiments, the Taguchi L9 orthogonal array, to optimize the process. This powerful methodology allows for the efficient study of multiple process variables simultaneously. Four key parameters—reaction temperature (180-220°C), microwave power (300-700 W), PU:DEG weight ratio (1:1 to 1:6), and catalyst concentration (1-5%)—were systematically varied. The goal was to identify the optimal conditions to produce a recovered polyol with specific target properties essential for foam production: a hydroxyl value in the range of 500-600 mg KOH/g and a viscosity of 800-900 cP . The statistical analysis predicted that optimal results could be achieved at 220°C, 700 W, a PU:DEG ratio of 1:1.43, and 5% catalyst concentration.

The recovered polyol from the optimized process was then used to formulate new rigid PU foams, replacing a substantial portion of the virgin polyol. The study demonstrated that foams could be successfully produced with up to 60% recycled polyol content (PUR 60). Crucially, these foams not only met but, in some cases, exceeded the performance of the 100% virgin foam (PUR 0). The foams containing recycled polyol exhibited faster reaction times (cream time, rise time), and the PUR 60 foam showed a higher core density (69 kg/m^3 vs. 25 kg/m^3 for PUR 0). Most importantly, the compressive strength of the PUR 60 foam was *higher* than the virgin foam (26.0 psi vs. 24.4 psi), while maintaining a comparable thermal conductivity (0.036 W/mK vs. 0.02 W/mK) .

This work exemplifies a highly engineered approach to recycling. The strategy is meticulously tailored to the specific waste form (rigid foam) and the end-use (a direct raw material replacement). The use of the Taguchi method reflects a focus on process control and product consistency, which are paramount for industrial adoption. It demonstrates that recycled feedstocks, when produced under optimized conditions, can be high-quality materials that enhance, rather than diminish, the performance of the final product.

4. Concluding Remarks and Future Perspective

The collective body of work reviewed herein presents a compelling case for the potential of advanced chemical recycling to address the challenge of polymer waste. The research demonstrates a consistent and strategic philosophy: viewing waste not as refuse to be disposed of, but as a valuable resource for the synthesis of new, high-performance materials. This application-driven "reverse-synthesis" approach, which tailors the depolymerization chemistry to create functional intermediates for specific end-uses, represents a significant advancement over simple monomer recovery.

Several key innovations are highlighted throughout these studies. First, the exploration of novel depolymerizing agents such as MP-diol for PET glycolysis and AEEA, IPDA, and mixed diamines for aminolysis has expanded the chemical toolbox for recycling, enabling the creation of recycled oligomers with unique structures and functionalities. Second, the successful implementation of process

intensification techniques, particularly microwave irradiation and radiation pre-treatments (gamma and electron beam), has proven to dramatically improve reaction efficiency, reducing process times from hours to minutes and increasing product yields [6-8, 10]. Third, the application of sophisticated process control, exemplified by the Taguchi statistical optimization of rigid PU foam glycolysis, demonstrates a pathway toward producing recycled feedstocks with the consistency and quality required for industrial applications.

The ultimate success of these strategies is validated by the performance of the final materials. The valorization of PET and PU waste has yielded a diverse portfolio of products, including UV-curable coatings, polyesteramides, and epoxy hardeners that exhibit properties comparable or even superior to their conventional, petroleum-derived counterparts. Furthermore, the demonstration that up to 60% of virgin polyol can be replaced with a recycled equivalent to produce rigid PU foams with enhanced mechanical properties is a powerful testament to the potential of closed-loop recycling.

This research provides a robust and versatile platform for the development of a circular economy for polymers. It moves the conversation beyond waste management to value creation. Looking forward, the logical next steps would involve techno-economic analyses to assess the scalability and commercial viability of these promising lab-scale processes. Further research could also extend these tailored depolymerization strategies to other challenging polymer waste streams, such as composites and multi-layer plastics, continuing the mission to transform today's waste into tomorrow's resources.

5. References

1. Thiounn T, Smith RC. Advances and approaches for chemical recycling of plastic waste. J Polym Sci 2020;58:1347–64.
2. Jamdar, V.; Kathalewar, M.; Sane, D.; Sabnis, A. Chemical recycling of PET waste and utilization of recycled product for synthesis of hybrid unsaturated polyester-urethane coatings. Polym. Bull. 2025, 82, 1625–1642.
3. Sane, D.; Gadekar, A.; Jamdar, V.; Sabnis, A. Recycling of Polyurethanes. ACS Books Symposium Series Chapter. 2023.
4. Zia KM, Bhatti HN, Ahmad Bhatti I. Methods for polyurethane and polyurethane composites, recycling and recovery: A review. React Funct Polym 2007;67:675-92.
5. Shojaei B, Abtahi M, Najafi M. Chemical recycling of PET: A stepping-stone toward sustainability. Polym Adv Technol 2020;31:2912–38.
6. Jamdar, V.; Kathalewar, M.; Sabnis, A. Glycolytic depolymerization of PET waste using MP-diol and utilization of recycled product for UV-curable wood coating. J. Coat. Technol. Res. 2018, 15 (2), 259–270.
7. Jamdar, V.; Kathalewar, M.; Dubey, K. A.; Sabnis, A. Recycling of PET wastes using Electron beam radiations and preparation of polyurethane coatings using recycled material. Prog. Org. Coat. 2017, 107, 54–63.
8. Jamdar, V.; Kathalewar, M.; Jagtap, R. N.; Dubey, K. A.; Sabnis, A. Effect of y-Irradiation on Glycolysis of PET Waste and Preparation of Ecofriendly Coatings Using Bio-Based and Recycled Materials. Polym. Eng. Sci. 2015, 55 (11), 2653–2660.
9. Jamdar, V.; Kathalewar, M.; Wazarkar, K.; Sane D; Sabnis, A. Aminolysis of PET waste and utilization of subsequent amido-amine as a curing agent for epoxy coatings.
10. Jamdar, V.; Kathalewar, M.; Sabnis, A. Depolymerization Study of PET Waste Using Aminoethylethanolamine and Recycled Product Application as Polyesteramide Synthesis. J. Polym. Environ. 2018, 26, 2601–2618.
11. Guchait, A.; Maity, D.; Sabnis, A. S. Recycling of waste polyurethane shoe sole via aminolysis route. J. Mater. Cycles Waste Manag. 2024, 26, 860–871.
12. Pranavabalaji, R.; Sane, D.; Maity, D.; Sabnis, A. Parametric optimization of depolymerization of rigid polyurethane foam using microwave irradiation by L9 Taguchi method. Polym. Bull. 2025.
13. Deng Y, Dewil R, Appels L, Ansart R, Baeyens J, Kang Q. Reviewing the thermo-chemical recycling of waste polyurethane foam. J Environ Manag 2021;278:111527.
14. Siddiqui MN, Redhwi HH, Al-Arfaj AA, Achilias DS. Chemical Recycling of PET in the Presence of the Bio-Based Polymers, PLA, PHB and PEF: A Review. Sustainability 2021;13:10528.
15. Datta J, Włoch M. Recycling of polyurethanes. In: Thomas S. Datta J. Recycling of Polyurethane Foams. Elsevier; 2018. p. 15-55.
16. Bhanderi KK, Joshi JR, Patel J V. Recycling of polyethylene terephthalate (PET Or PETE) plastics – An alternative to obtain value added products: A review. J Indian Chem Soc 2023;100:100843.
17. Liu Y, Fu W, Liu T, Zhang Y, Li B. Microwave pyrolysis of polyethylene terephthalate (PET) plastic bottle sheets for energy recovery. J Anal Appl Pyrolysis 2022;161:105414.
18. Zhang Y, Tian F, Wu Z, Li X, Liu X, He Y. Chemical conversion of waste PET to valued-added bis(2-hydroxyethyl) terephthalamide through aminolysis. Mater Today Commun 2022;32:104045.
19. Simón D, Borreguero AM, de Lucas A, Rodríguez JF. Glycolysis of viscoelastic flexible polyurethane foam wastes. Polym Degrad Stab 2015;116:23-35.

	***Mr. Devesh Sane** is currently pursuing his Ph.D. in Surface Coating Technology at the Institute of Chemical Technology (ICT), Mumbai. He completed his M.Tech in Surface Coating Technology from ICT, receiving a gold medal for his academic excellence with a CGPA of 9.89. He earned his B.E. in Chemical Engineering from Bharati Vidyapeeth College of Engineering. His research is primarily focused on the chemical recycling of polymer waste such as polyurethane, PET, and polyamide to develop value-added products like coatings, adhesives, and composites. He has hands-on experience in unsaturated polyester, polyurethane, and polyurea chemistries, as well as formulating solvent-borne coatings and hydrogels. Mr. Sane has co-authored four publications with 2 book chapters in peer-reviewed journals and has filed two patents on recycling PET fabric and polyurethane waste, respectively. He is a recipient of the prestigious "INSPIRE FELLOWSHIP" from the Department of Science & Technology (DST), Government of India.*
	***Prof. Anagha Sabni**s is a Professor and the Head of the Department of Polymer & Surface Engineering at the Institute of Chemical Technology (ICT), Mumbai, India. She earned her Ph.D. in Paint Technology from the same institute in 2006. Dr. Sabnis has extensive experience in both industry and academia, having worked with companies like Pidilite Industries Ltd. before joining ICT. Her primary research focuses on the development of functional materials and coatings, including anticorrosive coatings, bio-based polymers from renewable resources, non-isocyanate polyurethanes, and flame-resistant coatings. She is also actively involved in research on the chemical recycling of polymer waste for value-added applications. Dr. Sabnis has published 82 papers in national and international journals and holds two granted patents, with four more pending. She is a recipient of several awards, including the National Award for Technology Innovation from the Government of India and the Chevening-Rolls Royce Research Science & Innovation Leadership Fellowship (CRISP 2018) from the UK Government. Her work has garnered over 2800 citations with an h-index of 30 on Google Scholar*

INDIAN SOCIETY FOR RADIATION AND PHOTOCHEMICAL SCIENCES
(Reg. No. 617/1985, GBBSD, Bombay; Trust No. F-10965)
Radiation & Photochemistry Division
Bhabha Atomic Research Centre, Mumbai - 400 085

Member Enrolment Form

1. Name in Block Letters:
2. Date of Birth:
3. Highest Academic Qualification:
4. Present Position:
5. Addresses:

Photograph

Office	Residence
Telephone E-mail	Telephone E-mail

6. Address for Correspondence: Office / Residence
7. Category of Membership Applied for: Annual / Life /Corporate member

Category	Fees	Admission fee	Total Amount
Annual	Rs 200/-	Rs 100/-	Rs 300/-
Life Member	Rs 2000/-	Rs 100/-	Rs 2100/-
Corporate Member	Rs 20000/-	Rs 1000/-	Rs 21000/-

8. *Remittance: DD in favour of 'ISRAPS' payable at MUMBAI
For Bank Transfer:
A/c No.10536133801, SBI, BARC Branch, IFSC SBIN0001268
(e-mail the money transfer details along with the details requested above to: **israps.secretary@gmail.com** and copy to **mathip@barc.gov.in)**
**Payment can be made after the approval of application by Secretary, ISRAPS*

9. Brief Resume of activities and research interests:
(min. 500 words, in a separate attachment)
10. List of memberships of other professional bodies, if any:
11. List of prizes/awards/fellowships received, if any:
12. Number of Publications
(Pl. attach complete list)

I agree to abide by the constitution and bye-laws, and rules and regulations of the SOCIETY.

Place:

Signature

Date:

Contents

Published by ISRAPS, C/o RPCD, BARC, Mumbai 400 085

Designed & Printed by Ebenezer Printing House
Tel.: 2446 2632 / 3872, E-mail: outworkeph@gmail.com