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Influence of Nanoparticles and Radiation on Polymer Characteristics for Industrial applications

A graduation project submitted to the Department of Physics in partial fulfillment of the requirements for the degree of Bachelor of Science in Applied Physics

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شكر وتقدير

نتقدّم بخالص الشكر والتقدير إلى سعادة الدكتورة بسمة البدري، مشرفة المشروع، على ما قدّمته من دعم علمي وتوجيهات بنّاءة كان لها الأثر الكبير في إنجاز هذا العمل. إن إشرافها الدقيق وملاحظاتها القيّمة شكّلت أساسًا مهمًا في تطوير المشروع وتحقيق أهدافه.

كما نعبّر عن شكرنا وامتناننا لجامعة الامام محمد بن سعود الإسلامية على ما وفّرته لنا من بيئة تعليمية مميزة ولجميع أعضاء الهيئة التدريسية في قسم الفيزياء، لما بذلوه من جهود في تقديم المعرفة والدعم الأكاديمي خلال فترة دراستنا.

ولا يفوتنا أن نخص بالشكر عائلاتنا الكريمة، التي كانت السند الحقيقي والداعم الأول طوال مسيرتنا التعليمية، فجزاهم الله عنا خير الجزاء.

كما نتقدّم بجزيل الشكر لكلٍ من ساهم معنا في هذا المشروع، على روح التعاون والالتزام المشترك، وما بُذل من جهد ومشاركة فعّالة أسهمت في إتمام هذا العمل على الوجه الأكمل.

ونسأل الله التوفيق والسداد فيما هو آت، وأن يبارك لنا في علمنا وعملنا، ويجعل ما قدمناه خالصًا لوجهه الكريم

Abbreviation&Acronym

PMMA	**Poly(methyl methacrylate)**
TiO_2	**Titanium Dioxide**
UV	**Ultraviolet**
LED	**Light Emitting Diode**
GPS	**Global Positioning System**
LCR	**Inductance, Capacitance, Resistance meter**
Ra	**Roughness Average**
Rq	**Root Mean Square Roughness**
Rz	**Average Maximum Height of the Profile**
Eg	**Energy Gap**
kGy	**Kilo gray (unit of absorbed radiation dose)**
AC	**Alternating Current**
DC	**Direct Current**
MMA	**Methyl Methacrylate**
ZnO	**Zinc Oxide**
XRD	**X-ray Diffraction**
NCRRT	**National Center for Radiation Research and Technology**
ALD	**Atomic Layer Deposition**
OLDE	**Organic Light Emitting Diodes**

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Abstract

The growing reliance on advanced materials in high-tech applications, there is an urgent need to develop polymers with enhanced functional properties without compromising their inherent characteristics. PMMA is a promising material due to its transparency and stability, but its limited electrical and optical properties restrict its broader application. In this context, this study explores a scientific approach to enhance the performance of PMMA by preparing it as a composite material by the incorporation of TiO_2 nanoparticles, followed by different doses of gamma radiation to modify its optical properties, electrical conductivity, and surface roughness. The results showed an increase in the absorbance with addition of TiO_2 and an increase in the gamma dose. A decrease in the optical band gap energy was also observed with the addition of TiO_2 and an increase in the gamma dose. Furthermore, a significant improvement in electrical behavior and a considerable increase in surface roughness were observed. These transformations highlight the effectiveness of the nanoparticles and irradiation in improving the polymer properties and demonstrate the potential of modified PMMA to meet the demands of advanced applications that require high performance and precise functional response.

ملخص البحث

مع تزايد الاعتماد على المواد المتقدمة في التطبيقات عالية التقنية، تبرز الحاجة الملحة لتطوير بوليمرات ذات خصائص وظيفية محسنة دون المساس بخصائصها الجوهرية. يُعدّ PMMA مادة واعدة نظرًا لشفافيته واستقراره، إلا أن خصائصه الكهربائية والبصرية المحدودة تُقيد تطبيقه على نطاق أوسع. في هذا السياق، تستكشف هذه الدراسة نهجًا علميًا لتحسين أداء PMMA من خلال تحضيره كمواد مركبة عن طريق دمج جسيمات نانوية من TiO_2، متبوعة بجرعات مختلفة من أشعة جاما لتعديل خصائصه البصرية وموصليته الكهربائية وخشونة سطحه. أظهرت النتائج زيادة في الامتصاصية مع إضافة TiO2 والزيادة في جرعة الجاما. كما لوحظ انخفاض في طاقة فجوة النطاق الضوئية مع إضافة TiO2 والزيادة في جرعة الجاما. علاوة على ذلك، لوحظ تحسن كبير في السلوك الكهربائي وزيادة كبيرة في خشونة السطح. تسلط هذه التحولات الضوء على فعالية الجسيمات النانوية والإشعاع في تحسين خصائص البوليمر وتوضح إمكانات PMMA المعدلة لتلبية متطلبات التطبيقات المتقدمة التي تتطلب أداءً عاليًا واستجابة وظيفية دقيقة.

Introduction

Polymethyl methacrylate (PMMA) is a widely used synthetic polymer known for its excellent transparency, ease of processing, and biocompatibility, making it a material of choice in medical and optical applications. However, despite these advantageous properties, PMMA suffers from limitations in mechanical strength and durability, restricting its use in high-performance environments that demand enhanced stability and toughness. To overcome these challenges, significant research has focused on improving the properties of PMMA by incorporating nanomaterials, particularly titanium dioxide (TiO_2) nanoparticles. TiO_2 is a promising material with unique properties such as high chemical stability, excellent UV-absorption capability, and enhanced mechanical strength. When integrated with PMMA, TiO_2 nanoparticles have shown significant improvements in both the mechanical properties, such as flexural strength, and optical properties, including enhanced UV absorption and better environmental protection, which are critical for applications in medical devices, optical lenses, and protective coatings[1].

Additionally, gamma radiation has been found to have a substantial impact on modifying the physical properties of polymers. Gamma radiation induces structural changes within the polymer, leading to chain scission and cross-linking, which can enhance both the mechanical, optical and thermal properties of the material. It is anticipated that the combination of TiO_2 nanoparticles and gamma radiation will synergistically improve the performance of PMMA, making it more suitable for demanding applications[2], [3]. This study aims to investigate the effects of incorporating TiO_2 into PMMA under varying doses of gamma radiation, analyzing changes in optical absorption, energy band gap, surface roughness, and electrical conductivity. The findings of this research will contribute to advancing the potential of PMMA–TiO_2 nanocomposites in high-performance applications, especially in optoelectronics and radiation-resistant environments[4]

Chapter 1

1.1 Polymers

Polymers play crucial roles in our daily lives and imagine a world without them no plastic, no advanced medical tools, and no modern electronics. Polymers are the unsung heroes of our modern lives, simplifying and enhancing many aspects of our daily experiences. Polymers can be natural, like proteins and DNA, or synthetics, like plastics and nylon. Polymers have diverse applications in industries such as packaging, healthcare, textiles, and electronics due to their lightweight, durability, and flexibility. Their properties can be tailored through different chemical compositions and processing techniques, making them essential materials in modern science and engineering.

The term “polymer” comes from the Greek word’s “poly” (meaning “many”) and “meres” (meaning “parts”), and it perfectly describes what polymers are – long chains of repeating molecular units. These molecular units are called monomers (or monomer in singular), and they are very small molecules that bond with each other to form a polymer. Think of them as molecular LEGO blocks that stack together to form something extraordinary. These blocks, or monomers, connect to form polymers that possess diverse and often remarkable properties [5].

On a molecular level, polymers are large molecules made up of monomers connected by strong covalent bonds, which give them unique properties such as flexibility, strength, and durability. Based on their electrical conductivity, polymers are categorized into two main types: insulating polymers (which do not conduct electricity and are used in products such as electrical insulation) and conductive polymers (which conduct electricity and are used in applications like sensors, batteries, and flexible electronics). Thanks to their incredible versatility and reliability, polymers have become indispensable in various industries, from automotive manufacturing to medical devices. As we continue to explore and experiment with new polymer formulations, the possibilities for innovation are endless [1].

1. 2Polymer classifications

Polymers can be categorized in various ways. The most straightforward classification is by their origin, distinguishing between natural and synthetic polymers. Additional classifications consider factors such as the polymer's structure, the mechanism of polymerization, the methods used in their preparation, or their behavior under thermal conditions.

1.2.1 Natural VS. Synthetic.

Polymers can be classified into two main categories: natural and synthetic. Natural polymers, such as enzymes, nucleic acids, and proteins, are essential for many vital processes in the body, such as converting food into energy, with their deficiency posing a threat to life. These biological polymers are characterized by highly complex structures. On the other hand, plant-based polymers like starch, cellulose, and natural rubber have relatively simpler structures [2].

Humans have harnessed the principles of polymer chemistry to develop synthetic polymers such as polystyrene, polyethylene, and nylon, which have had a significant impact on the development of materials and modern industries. Interestingly, some natural polymers, like natural rubber derived from the Hevea tree, can be reformed in laboratories into synthetic polymers like polyisoprene [6].

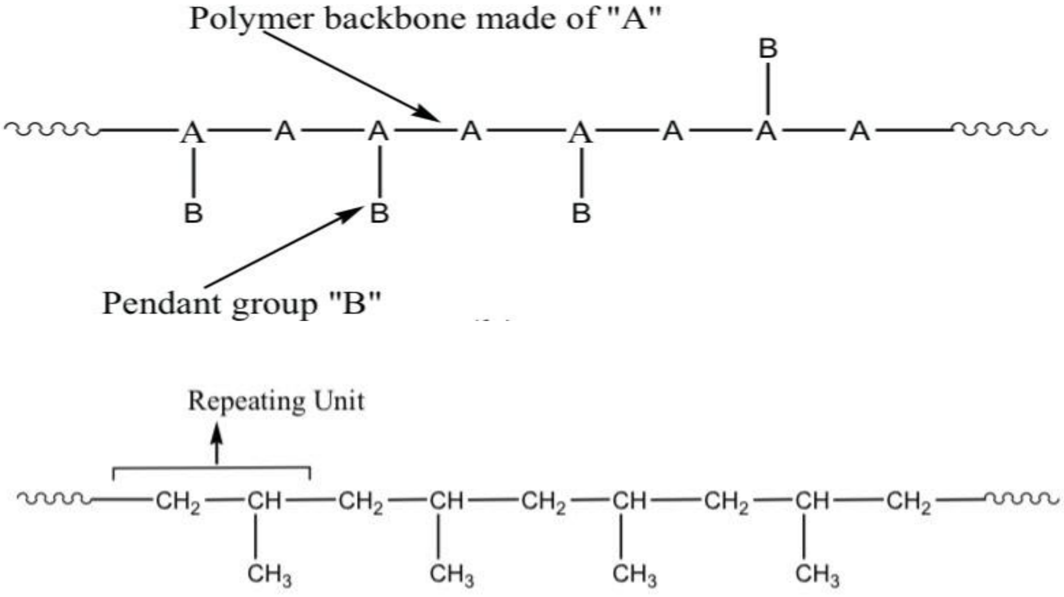
1.2.2 Polymers Structure.

Polymers form when monomers are linked under suitable conditions, although not all small organic molecules are capable of polymerization the functionality of a molecule refers to the number of bonding sites it possesses, and this determines its ability to polymerize molecules are classified as monofunctional, bifunctional, or polyfunctional, based on the available bonding sites. High-quality polymers require pure monomers, as impurities such as oxygen, carbon monoxide, and water can deactivate catalysts, altering the crystallinity and molecular weight of the polymer. Polymerization, the process of linking monomers, involves various methods, each with its own advantages and limitations. Both functionality and monomer purity are crucial for the successful production of polymers [6].

A-Liner Polymers

A linear polymer is defined by an extended, chain-like atomic arrangement, known as the backbone. Attached to this backbone are smaller side chains, referred to as pendant groups, which are considerably shorter in length. While pendant groups typically comprise only a few atoms, the backbone can extend to hundreds of thousands of atoms. The backbone itself consists of atoms arranged in a precise, repeating sequence that maintains uniformity throughout the entire polymer chain. For instance, in polypropylene, the backbone is constructed from the repetition of two carbon atoms [8].

a linear polymer made of a "A" molecule



Polypropylene

Figure 1.1: (a) Linear polymer, (b) Polymer with backbone and pendant, (c) Repeating structure [6].

B -Branched and Cross-linked Polymers

polymers can adopt various structures and are not limited to just linear forms. Some polymers contain side chains connected to the main backbone chain, known as branched polymers. For example, polyethylene can be manufactured in both linear and branched forms. Branched chains exhibit unique properties. In some cases, the ends of the branched chains are connected to the backbone chains of different polymer molecules. When many branched chains are connected to the backbone chains in a sample, a giant network is formed. These polymers are known as cross-linked polymers, where the cross-links bind all the polymer molecules together. Cross-linked polymers are typically molded and shaped before the cross-linking process [8].

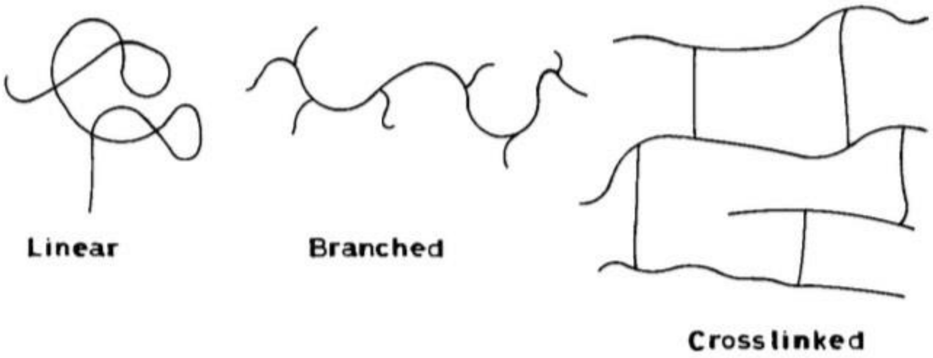


Figure1.2: Linear, branched, and cross-linked polymers [1].

1.2.3 Thermoplastics and Thermosets

Polymers are broadly classified into two primary categories based on their thermal processing behavior: thermoplastics and thermosets. Thermoplastics are polymers that become pliable or moldable when heated, allowing them to be shaped into desired forms. These materials are recyclable, as they can be reprocessed through the application of heat and pressure. Notable examples of thermoplastics include polystyrene, polyolefins (such as polyethylene and polypropylene), and poly (vinyl chloride) [1].

In contrast, thermosets are polymers that undergo irreversible chemical crosslinking during polymerization or subsequent thermal or chemical treatments, forming a rigid, three-dimensional network. Once cured, thermosets exhibit high resistance to heat softening, mechanical deformation, and chemical solvents, making them unsuitable for thermal reprocessing. However, these properties render thermosets highly valuable for applications requiring durability and stability, such as in composites, coatings, and adhesives. Prominent examples of thermosets include epoxy resins, phenol-formaldehyde resins, and unsaturated polyesters, which are widely utilized in the production of glass-reinforced composites like FiberglasClick or tap here to enter text.Click or tap here to enter text.)[7].

1.2.4 Crystalline and Amorphous

Crystalline polymers have a long-range, ordered structure, while amorphous polymers have only short-range order. Melting either type disrupts this order. However, some polymers, called liquid crystalline polymers, partially retain order even when melted. They form fluids that keep some molecular order within a specific temperature range, giving them solid-like properties while still allowing flow. Polybenzamide is an example[6].liquid crystalline polymers are key in making lightweight, strong, and heat-resistant fibers and films[6]. Unlike crystallizable polymers, amorphous polymers have chains that cannot form an ordered structure. In their solid state, they show only short-range order among their repeating units. These polymers become glassy, amorphous solids with randomly arranged and often tangled molecular chains. Examples include poly (methyl methacrylate) and polycarbonate [6].

1.3 Importance of Polymers in modern science

Polymers are remarkable materials that have become an integral part of human progress, touching nearly every aspect of our lives. From the clothes we wear to the food we eat, from the vehicles we use to the medical tools that save lives, polymers play a vital role in making our lives more comfortable and efficient. Whether natural or synthetic, these versatile materials demonstrate how science can transform the world around us. In this text, we will explore how polymers contribute to various fields such as clothing, food, transportation, and medicine, and how they have become an indispensable part of our daily lives.

Polymers are characterized by unique properties such as high strength, light weight, flexibility, thermal stability, chemical resistance, and the ability to be rapidly mass-produced and molded into complex shapes. They can be transformed into strong solid materials, flexible rubber-like sheets, or even gel-like substances, making them suitable for a wide range of applications, from clothing and packaging to space vehicles and artificial organs. Polymers are also used in adhesives, coatings, textiles, industrial fibers, and structural plastics, as well as in electronics, biomedical devices, and high-tech composites [8].

In the field of electronics, polymers are used in ion batteries, capacitors, LEDs, and sensors. They are also used in the production of flexible smart cards equipped with piezoelectric sensors. Due to their ability to withstand high temperatures and reactive environments, polymers are ideal for manufacturing gas sensors and filtration membranes. Additionally, polymers are widely used in lightweight and cost-effective plastic containers, as well as in clothing, flooring, garbage bags, and packaging materials, highlighting their essential role in modern life[8].

1.4 Nanocomposites

Nanocomposites are sophisticated materials designed to improve the properties of their base components. These materials are generally categorized into two main types: polymer-based nanocomposites and non-polymer-based nanocomposites[9].

Polymer-based Nanocomposites: Nanocomposites are widely employed across various industries, including automotive, electronics, and healthcare. They are especially valued for their ability to improve the barrier properties of packaging materials. These consist of polymers that incorporate nanoparticles or nanofillers dispersed within the polymer matrix. Their versatile properties enable their use in various applications, including packaging and the manufacturing of medical containers.

Non-polymer-based nanocomposites: This category includes inorganic materials such as metals and ceramics, and is further divided into metal-based, ceramic-based, and ceramic-ceramic nanocomposites. These materials are known for their advanced characteristics, such as high strength and durability, making them ideal for medical applications, particularly in bone implants.

The use of nanocomposites is expanding into new fields like medicine, electronics, and environmental protection, where they offer enhanced performance and advanced capabilities[9].

1.5 Nanoparticles

Nanoparticles, defined as particles with sizes between 1 and 100 nanometers, exhibit distinct properties at the atomic scale, attributed to their small size. These altered properties make nanoparticles highly advantageous in a variety of applications. Nanotechnology has been a focal point of research for over a century, witnessing significant advancements during this time. Nanoparticles are categorized into several types, including metal nanoparticles, non-metal ceramic nanoparticles, semiconductor nanoparticles, and carbon nanoparticles. Due to their small dimensions and large surface-to-volume ratio, nanoparticles demonstrate unique chemical and physical characteristics that set them apart from bulk materials. These properties have garnered considerable attention for their potential uses in fields such as optics, electronics, magnetism, ceramics, and catalysis [7].

Inorganic metal oxide nanoparticles, particularly titanium dioxide (TiO_2), have gained significant attention for their versatile applications across several fields, including microelectronics, sensors, piezoelectric devices, fuel cells, anti-corrosion coatings, and catalysis. Structurally, TiO_2 features a lattice with titanium atoms each coordinated by six oxygen atoms in an octahedral geometry. Conversely, each oxygen atom is bonded to three titanium atoms arranged trigonal-planarly. TiO_2 exhibits a wide bandgap, with energy values of approximately 3.05 eV (415 nm). This wide bandgap enables TiO_2 to predominantly absorb light in the near-ultraviolet (UV) spectrum. Its strong absorption properties in both UV-A (320–400 nm) and UV-B (280–320 nm) wavelengths make it a common component in sunscreens within the cosmetics industry. Additionally, it functions as a pigment, whitening agent, and shimmer enhancer due to its ability to reflect visible light while exhibiting a low extinction coefficient in that range [10].

1.6 PMMA Polymer

Poly (methyl methacrylate) (PMMA) is a transparent thermoplastic polymer with 92% light transmission and UV resistance. It is synthesized through various polymerization methods, such as bulk, solution, and emulsion polymerization. Due to its high stability and durability, PMMA is widely used as a glass substitute. [11], [12].

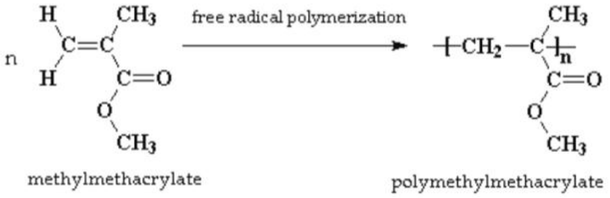


Figure1.3: Linear, branched, and cross-linked polymers [1].

Polymethyl methacrylate has numerous physical and mechanical properties that make it suitable for a wide range of applications. One of its most prominent features is its high transparency, reaching up to 92%, making it an excellent alternative to glass in optical applications. It also has outstanding UV resistance, preserving its optical properties without discoloration or degradation due to weather exposure, making it ideal for outdoor environments. Mechanically, PMMA possesses good rigidity, though it is not as flexible as some other polymers, meaning it can be prone to cracking or breaking under high pressure or sudden loads. To address this issue, PMMA is sometimes blended with other materials to improve its flexibility, optical and strength. The PMMA considered an amorphous material because of the methyl ester pendant groups which block the crystallization by preventing molecules to form crystalline bonds with each other.[11], [12], [13].

PMMA is widely used in medical applications due to its good biocompatibility, such as in prosthetic limbs, eye lenses, and artificial joints. Additionally, it finds use in architecture, automotive, and aerospace industries, where its transparency and high resistance to scratching and environmental factors are highly valued. PMMA is a versatile material combining unique optical and mechanical properties, making it a preferred choice in many industries requiring advanced material characteristics. The molecular structure formula of PMMA is $(C_5H_8O_2)_n$. Poly methyl methacrylate is produced by free radical polymerization of methyl methacrylate in mass or suspension polymerization.

1.7 Radiation

Radiation is the transfer of energy through space in the form of waves or particles. Energy, much like matter, has the ability to move through space from one point to another, either through particles or waves. These energy carriers always originate from a specific source and travel through space until they are absorbed or dissipated by some material. The term “radiation” is used to describe this process of transferring mass and energy through space[14].

Since the recognition of radiation’s potential, it has played a pivotal role in technological advancements across various fields. Radiation exists as energy in the form of waves or streams of particles, manifesting in numerous forms around us. While the term “radiation” is commonly associated with atomic energy, nuclear power, and radioactivity, it also includes other forms such as sound and visible light[15].

1.8 Categories of Radiations

Radiation is considered a fundamental component in many modern applications, ranging from the medical field to communications and industry. Radiation is classified based on its ability to ionize, which contributes to understanding its various uses and effects. This classification facilitates maximizing the benefits of radiation while minimizing potential associated risks.

1.8.1 Ionizing Radiations

Ionizing radiation, also referred to as high-energy radiation, is defined as all forms of radiation that possess sufficient energy to remove electrons from atoms or molecules[15]. This type of radiation includes high energy electromagnetic radiation, such as X-rays and gamma rays (γ), These radiations ionize the medium through which they pass, which is why they are known as ionizing radiation. Ionizing radiation is generated through various sources, including radioactive materials, particle accelerators, and X-ray tubes, and it also occurs naturally in the environment. Different types of ionizing radiation can be classified based on the distance they penetrate through matter[15].

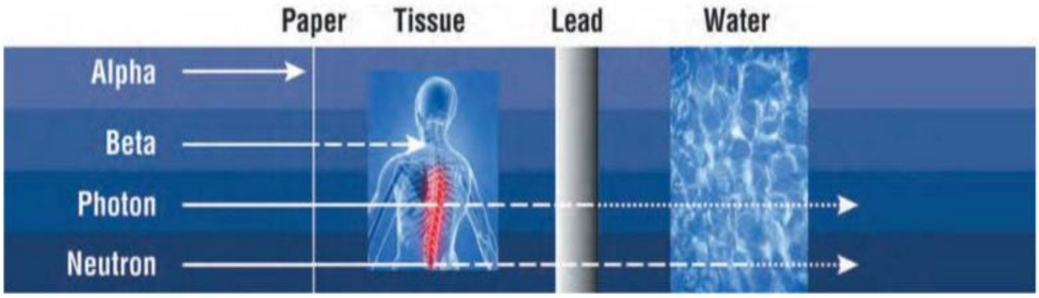


Figure1.4: Penetration of alpha, beta, photon, and neutron radiation through different shielding materials (paper, tissue, lead, and water)[13]

- Alpha Decay **(α)**: is made up of alpha particles, which consist of two protons and two neutrons and carry a double positive charge. Due to their substantial mass and strong charge, these particles have a very limited ability to penetrate materials. Alpha radiation can be stopped by something as simple as a piece of paper or the outer layer of dead skin cells. As a result, alpha radiation from external sources does not present a significant radiation risk. However, if alpha-emitting radioactive materials are ingested or inhaled, the energy from the alpha radiation is entirely absorbed by the body's tissues, making it a serious internal hazard. A notable example of a substance that undergoes alpha decay is radon-222, which transforms into polonium-218[15].

- Beta Decay **(β):** During beta decay, a neutron inside the nucleus changes into a proton, and an electron is released from the nucleus. This process causes the atomic number to increase by one, while the mass number remains almost the same, with only a slight reduction. Examples of isotopes that emit pure beta radiation include Strontium-90, Carbon-14, Tritium, and Sulfur-35[15].

- Gamma ray **(γ)**: Gamma rays are a form of high-energy electromagnetic radiation characterized by their extremely short wavelengths. These rays, emitted by specific radionuclides, can either possess a consistent energy level or a set of discrete energy values unique to each radionuclide. As gamma rays travel through matter, they interact in a particle-like manner, generating high-energy secondary electrons. These electrons are primarily responsible for causing radiation-induced damage. Their movement patterns resemble those created by beta particles, and the resulting chemical changes in the target material are similar to those caused by electron beam irradiation. However, unlike beams that affect specific regions, gamma radiation initiates energy deposition uniformly throughout the exposed material.

- X-ray: X-rays are actually a form of light, or electromagnetic radiation, with very short wavelengths. These rays are generated through electron interactions within the atom. When electrons absorb high amounts of energy, they move to higher-energy orbits. Upon returning to their original orbits or to lower-energy ones, the excess energy is emitted as X-rays. Due to their ability to penetrate materials and reveal fine details, X-rays are widely used in fields such as medicine (for radiography) and materials science (for polymer analysis), where they can reveal the fine structures of materials in ways that other techniques cannot achieve.

- Neutron Radiation (n): Neutrons have the ability to penetrate human tissues and organs when the source of radiation is outside the body. However, they can also pose a risk if neutron-emitting substances are absorbed into the body. The best materials for shielding or absorbing neutron radiation are those containing hydrogen atoms, such as paraffin wax and plastics, as neutrons and hydrogen atoms have similar atomic masses and interact efficiently during collisions[15].

1.8.2 Nonionizing Radiations

Non-ionizing radiation has lower energy than ionizing radiation and is incapable of producing ions. It encompasses a variety of forms, including visible light, infrared radiation, radio waves, microwaves, and sunlight. Several everyday technologies utilize non-ionizing radiation, such as global positioning systems (GPS), mobile phones, television broadcasting, FM and AM radio, baby monitors, cordless phones, garage door openers, and ham radios. Other sources include the Earth's natural magnetic field, and the electromagnetic fields emitted from nearby transmission lines, household electrical wiring, and appliances. These are categorized as extremely low-frequency (ELF) waves, which are generally not considered harmful to health[15].

1.9 Impact of Ionizing Radiation on Polymer

Ionizing radiation significantly affects the structure and properties of polymeric materials. The molecular structure of irradiated polymers has been a focus of study since the development of radiation chemistry in the 1950s, leading to guides for predicting property changes. Some polymers exhibit chain scissions, while others become crosslinked under ionizing radiation. These effects are often useful, leading to the development of various radiation processing techniques, such as crosslinking of insulation, curing coatings, vulcanization of rubbers, sterilization of medical devices, controlled degradation of polymers, grafting onto fibers, and the production of hydrogels[16]However, in certain applications, such as space vehicles and nuclear power plants, polymeric materials need to resist ionizing radiation. Thus, radiation-resistant polymers are essential[16].

In general, exposure to ionizing radiation leads to changes in polymer structure and properties. The primary event is the ejection of a high-energy electron, which can cause ionization in other molecules, triggering a localized chain reaction. Some interactions transfer insufficient energy to ionize but result in excited electronic states. These states may decay to the ground state, producing heat or light through fluorescence or phosphorescence. Excited states can also undergo chemical reactions via bond cleavage, forming ions or free radicals[8].

Free radicals are the most effective agents in radiation-induced chemical processes in organic materials. After radical formation, several processes can occur, such as:

A. Chain Scission and Crosslinking: These processes affect the mechanical properties of irradiated polymers. Chain scission breaks bonds, reducing the molecular weight, while crosslinking creates large molecular networks. Polymers like polyisobutylene and poly (methyl methacrylate) primarily undergo scission, while polyethylene and polystyrene mostly undergo crosslinking. Aromatic group-containing polymers are more resistant to these effects[8].

B. Unsaturation and Colour Changes: Irradiation can create double bonds, leading to colour changes in polymers due to the formation of unsaturated chromophores or trapped radicals. For instance, poly (vinyl chloride) darkens at doses between 50-150 kGy, while many polyolefins yellow at around 100 kGy.[8].

C. Gas Evolution: Irradiation can cause gas formation through atom or side-chain abstraction, with the type of gas depending on the polymer's composition. For example, polyethylene leads to H2, poly (vinyl chloride) forms HCl, and fluoropolymers produce HF[8].

1.10 Literature review

A. Yousefi et al. (2023) investigated the UV-shielding efficiency of PMMA thin film coatings integrated with TiO_2 and ZnO nanoparticles. Their findings revealed that TiO_2 significantly improved UV absorption, making the films more suitable for protective coatings in environments exposed to sunlight or UV radiation[17].

B. Zhou et al. (2019) examined the influence of TiO_2 inclusion on the structural and electrical characteristics of polymer-based composites. Their study showed enhancements in dielectric strength and electrical conductivity, suggesting potential applications in electronic devices and insulation technologies[18].

C. Li et al. (2015) explored the improvement of PMMA performance by incorporating TiO_2 nanoparticles for biomedical applications. The results indicated enhancements in surface hardness, smoothness, and biocompatibility, thereby broadening PMMA's applicability in the medical field[19].

D. Alwan (2019) analyzed the effect of gamma irradiation on PAni.MWCNT/PMMA films. The research demonstrated significant alterations in physical and electrical properties post-irradiation, highlighting the material's viability for use in radiation-intensive and electronic environments[20].

E. Mosalman et al. (2017) conducted a mechanical study on PMMA nanocomposites reinforced with TiO_2 nanoparticles at different weight percentages. Their work showed that TiO_2 improved mechanical characteristics such as impact and flexural strength, with optimal enhancement observed at 2 wt%. SEM analysis also confirmed uniform dispersion of the nanoparticles in the matrix[21].

F. Aldaghri et al. (2022) studied how gamma irradiation alters the optical behavior of the conjugated copolymer B-co-MP. Increasing the irradiation dose caused a blue shift in absorption and fluorescence spectra, attributed to chain scission and conformational changes. These results support the use of B-co-MP in photonic and laser-based applications[22].

Chapter2

2. Experimental Details

2.1 Materials

Polymethyl methacrylate (PMMA) and titanium dioxide (TiO_2) nanoparticles (0.02 wt.%) were sourced from Sigma Aldrich. The PMMA-TiO_2 nanocomposite films were fabricated using the casting technique. The resulting mixtures were poured into glass petri dishes, and after the solvent had fully evaporated, the films were left to dry at room temperature before being carefully removed. A digital micron thickness gauge with a precision of 0.001 mm was used to measure the film thickness. The sample preparation process was carried out by my supervisor."

2.2 Irradiation Method

The PMMA-TiO_2 nanocomposite films were placed in polyethylene sachets, and the irradiation was carried out with ^{60}Co Gamma source at a dose rate of 3.5 kGy/h at NCRRT, Atomic Energy Authority, Cairo, Egypt. The samples were irradiated at different times to obtain the desired doses (30 to 90 kGy). Irradiation of samples was carried out by my supervisor

2.3 Characterization techniques

2.3.1 UV-Visible Spectrophotometer

The optical spectra for pure PMMA and gamma irradiated PMMA-TiO_2 samples were obtained in the wavelength range from 200 to 1000 nm using the UV-Visible II-Beam Spectrophotometer (Hitachi, Model U-2000) and keeping the air as the reference.

2.3.2 AC conductivity Measurements

The electrical characteristics of both pure PMMA and gamma-irradiated PMMA-TiO_2 samples were analyzed at room temperature using an LCR Bridge (Model Z Hioki-3531, Japan), by my supervisor. The device was properly grounded, with all connecting cables shielded and earthed to minimize external interference. Silver paint was applied to both surfaces of each polymer specimen to ensure proper conductivity, and the samples were positioned between the electrodes of the measuring cell. This LCR bridge is capable of measuring resistance (R), across a frequency range of 50 Hz to 5 MHz at ambient conditions. The AC conductivity, (σ) was calculated using the flowing relation [23]:

$$\sigma = \frac{t}{RA} (\Omega^{-1} m^{-1}) \tag{2.1}$$

Where *t* is the thickness of polymer sample, *A* is the area of electrode plates.

2.3.3Surface Roughness measurements

A roughness tester was utilized to measure the surface roughness of the prepared films. This tester depends on a moving sensor on the film surface to recognize a roughness profile curve and immediately record the roughness parameters. The arithmetic average roughness (Ra) is defined as the mean of the absolute deviations of the surface profile from the central mean line over a defined evaluation length (L), and is mathematically expressed as [24]:

$$Ra = (\frac{1}{L}) \int_0^L |Z(x)| \, dx \tag{2.2}$$

where Z(x) represents the profile ordinates of roughness profile, [24]. The root mean square roughness (Rq) represents the square root of the average of the squared deviations from the mean line [24]:

$$Rq = \sqrt{\left[\frac{1}{L} \int_0^L (Z(x)^2) dx\right]} \tag{2.3}$$

The third parameter, Rz, quantifies the total height variation and is calculated as the sum of the maximum peak height (Rp) and the maximum valley depth (Rv) as shown in Fig (2.1) [24]:

$$Rz = Rp + Rv \tag{2.4}$$

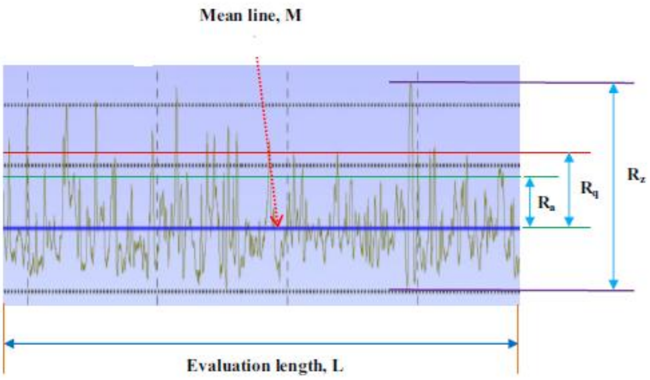


Figure2.1: a Two-dimensional roughness profiles.

Chapter3

3. Result and discussion

3.1 UV–Vis Optical spectra Analysis

The optical spectra of pure PMMA and gamma irradiated PMMA-TiO_2 nanocomposite were investigated in the wavelength range of 200–800 nm. The results from Fig. (3.1) showed a significant increase in absorbance upon the addition of TiO_2 to pure PMMA, particularly in the ultraviolet (200–400 nm) region, demonstrating TiO_2's ability to absorb the UV-light. Conversely, a decrease in transmittance was observed in Fig. (3.2) in the same range, indicating a reduced ability of the material to transmit light. When the samples were exposed to gamma radiation at doses of 30, 60, and 90 kGy, a further increase in absorbance was noted, especially in the ultraviolet region. These changes may be attributed to the bond rupturing, which leads to the degradation of the polymer chain and/or cross-linking process. Simultaneously, transmittance decreased significantly, indicating a further reduction in the material's ability to transmit light. On the other hand, the pure PMMA sample (without TiO_2) exhibited the lowest absorbance, and the highest transmittance compared to the other samples. This can be attributed to its transparent nature, allowing greater light transmission and less absorption. These changes highlight the significant effect of TiO_2 incorporation and gamma radiation exposure on the optical properties of PMMA, opening new possibilities for their application in fields requiring precise control over light absorption and transmission, such as UV protection and optical applications[24].

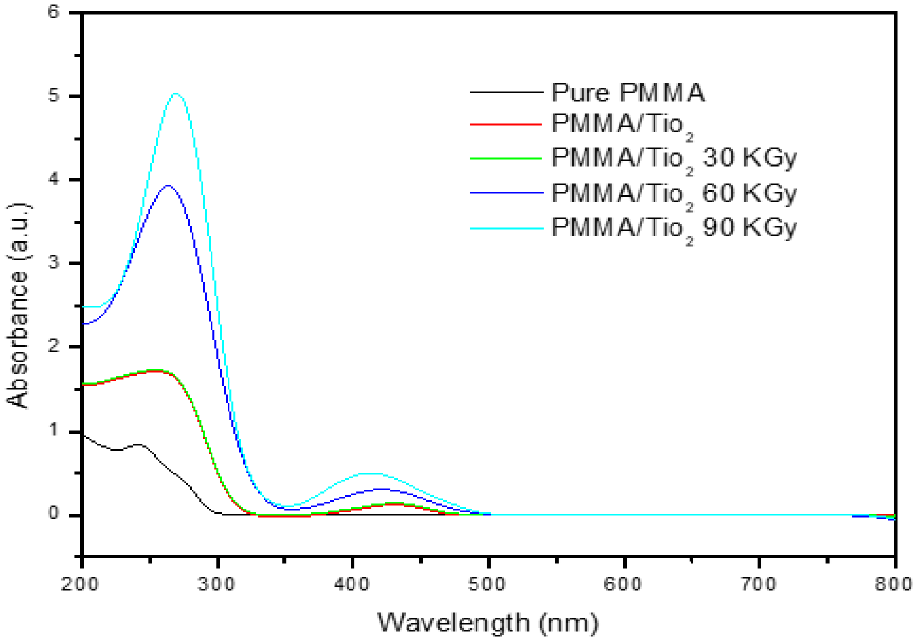


Figure3.1: UV−Vis absorption spectra of pure PMMA and PMMA-TiO₂ nanocomposites irradiated at different gamma doses

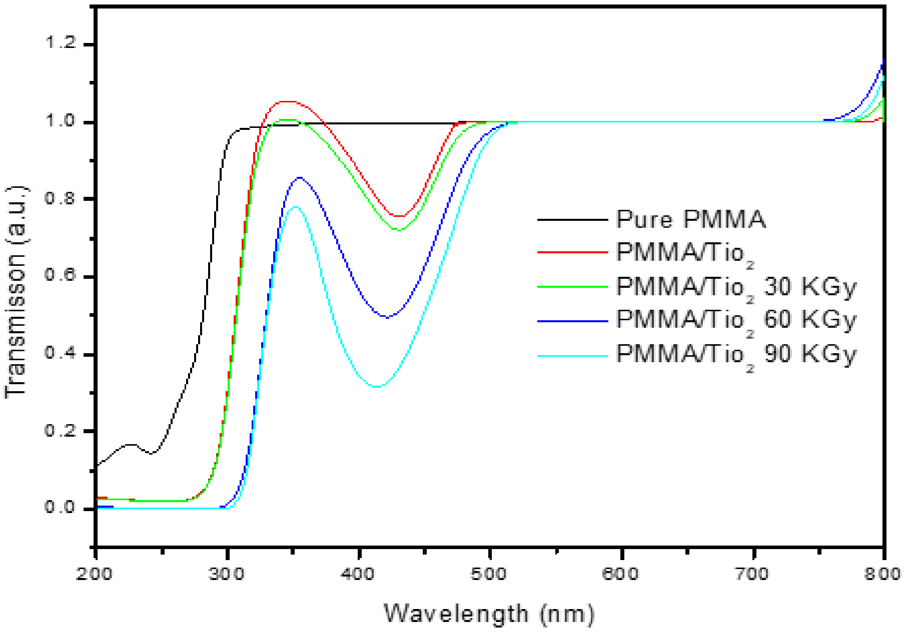


Figure3.2: Transmission spectra of pure PMMA and PMMA-TiO₂ nanocomposites irradiated at different gamma doses

3.2 Optical band gap energy study

The values of optical band gap of pure PMMA and irradiated PMM- TiO_2 samples were determined from Tauc' relation[25]:

$$(\alpha hv) = B(hv - Eg)^n \tag{3.1}$$

where α is the absorption coefficient and, $\boldsymbol{hv}$ is the energy of the incident photons, Eg is the value of the optical energy gap between the valence band and the conduction band, and n denotes the type of electronic transition[25], whether it is direct or indirect during the absorption process in the K-space. The index n can take the values 1/2, and 2 for direct allowed and indirect allowed, respectively. Factor B is a material-dependent constant. The optical absorption coefficient, $\boldsymbol{\alpha(hv)}$, was calculated from the measured absorbance, (A) [2]:

$$\alpha = \frac{(A\times 2.303)}{d} \tag{3.2}$$

where d is the sample thickness in cm. Figs (3.3) and (3.4) show the plots of $\boldsymbol{(\alpha hv)^2}$ and $\boldsymbol{(\alpha hv)^{1/2}}$ versus photon energy (hν), for direct and indirect transitions, respectively. The band gap was calculated by extrapolating the linear region of the plot to intercept the energy axis. The values of direct and indirect band gaps for samples have been calculated and listed in table (3-1) and (3-2), respectively. It is noticed that the values of direct and indirect band gap decrease with both the incorporation of TiO_2 nanoparticles and exposure to gamma radiation. The addition of TiO_2 introduced structural disorder at the polymer–nanoparticle interface, giving rise to extended localized states known as Urbach tails, characterized by Urbach energy (Eu). These tails emerge due to lattice distortions, which contribute to band gap narrowing by forming sub-band states near the band edges [25].

Gamma irradiation further influenced the optical behavior by generating localized defect states within the band gap. At lower doses, the breaking of hydrogen bonds in PMMA chains led to the formation of free radicals and intermediate energy levels that enhanced electronic transitions. As the irradiation dose increased to 60 and 90 kGy, the density of these defect states grew significantly, increasing the likelihood of photon-induced transitions and leading to further band gap reduction. This behavior was most evident at 90 kGy due to the accumulation of structural defects and bond scissions, which also resulted in the formation of unsaturated carbon bonds such as C=C and C≡C, and possibly new C–C bonds between chains that contributed to structural rearrangement[24].

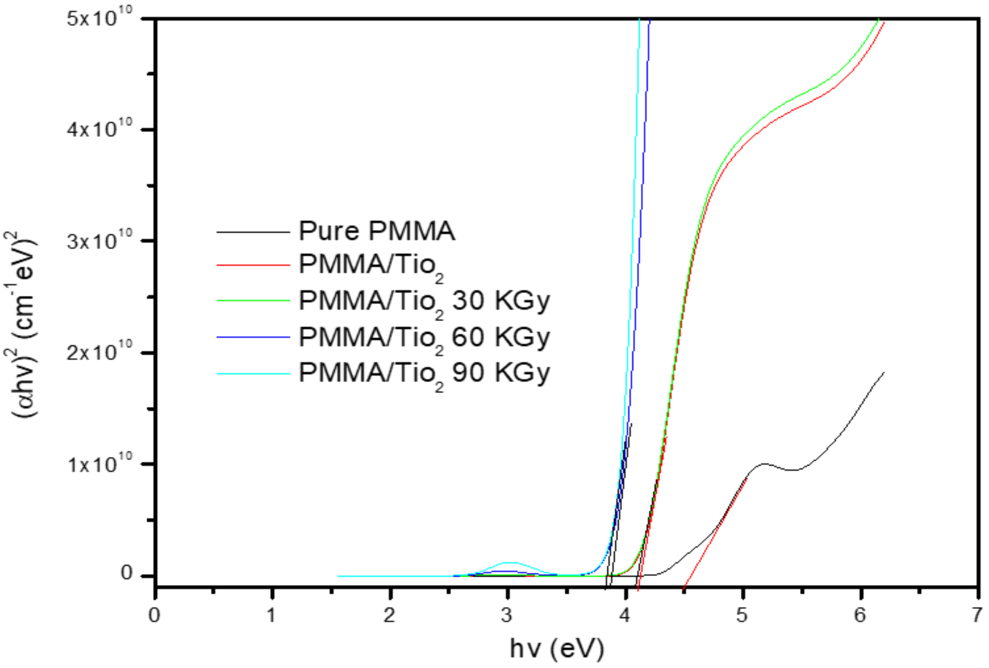


Figure3.3: (α h ν)^2 vs. photon energy for pure PMMA, PMMA–TiO₂, nanocomposites irradiated at different gamma doses

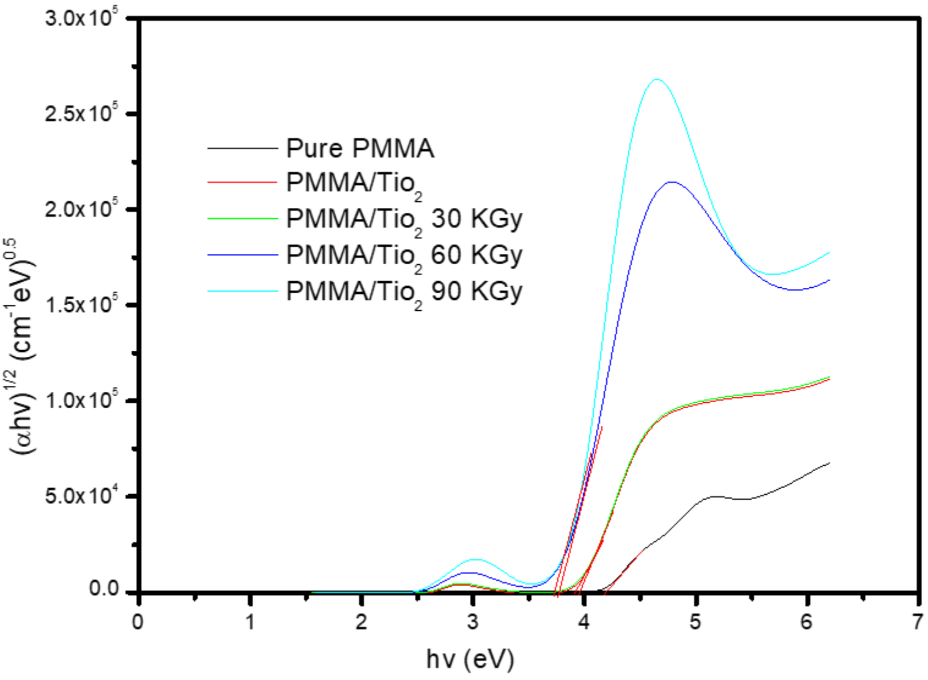


Figure3.4: (αhν)^(0.5) vs. photon energy for pure PMMA, PMMA–TiO₂, nanocomposites irradiated at different gamma doses

The direct band gap in pure PMMA decreased from 4.5 eV to 3.81 eV for the highest gamma dose. The indirect energy gap decreased from 4.18 eV for pure sample to 3.72 eV for highest gamma dose. The decrease in the energy gap implies an increase in the electrical conductivity of the samples [as reflected by the changes in band gap values (Tables 3.1 and3.2)].

Table (3-1): Direct band gap values for the studied PMMA–TiO_2, nanocomposites irradiated at different gamma doses

Sample	Eg(ev)
Pure PMMA	4.5
PMMA- TiO_2	4.1
30KGy	4.05
60KGy	3.86
90KGy	3.81

Table (3-2): Indirect band gap values for the studied PMMA–TiO_2, nanocomposites irradiated at different gamma doses

Sample	Eg(ev)
Pure PMMA	4.18
PMMA- TiO_2	3.95
30KGy	3.89
60KGy	3.76
90KGy	3.72

3.3 Electrical Conductivity study

The AC electrical conductivity (σ_{ac}) of PMMA-TiO_2 nanocomposites was investigated across a wide range of frequencies and under various gamma irradiation doses (0, 30, 60, and 90 kGy). The experimental results revealed a slow increase in conductivity at low frequencies and a rapid increase at higher ones for all samples. At lower frequencies, the electrical response is significantly influenced by interfacial polarization due to charge accumulation at the boundaries between the insulating PMMA matrix and the conductive TiO_2 nanoparticles, but some charge carriers due to the thermal excitation overcome the potential barrier and thus produce a small conductivity. As the frequency increases, the influence of interfacial polarization diminishes, charge carriers get sufficient energy to overcome the potential barrier, and hence a rapid rise in conductivity exhibits at a high frequency [23], [26].

The incorporation of TiO_2 nanoparticles significantly improves conductivity of PMMA by introducing additional active sites and providing alternative pathways for charge transport. Furthermore, gamma irradiation introduces structural modifications such as polymer chain scission, localized oxidation, and vacancy formation, which result in the generation of free electrons and holes as mobile charge carriers. These carriers gain higher mobility within the polymer segments and can move between the defect states induced by irradiation, thereby contributing to the enhancement of AC conductivity [24].

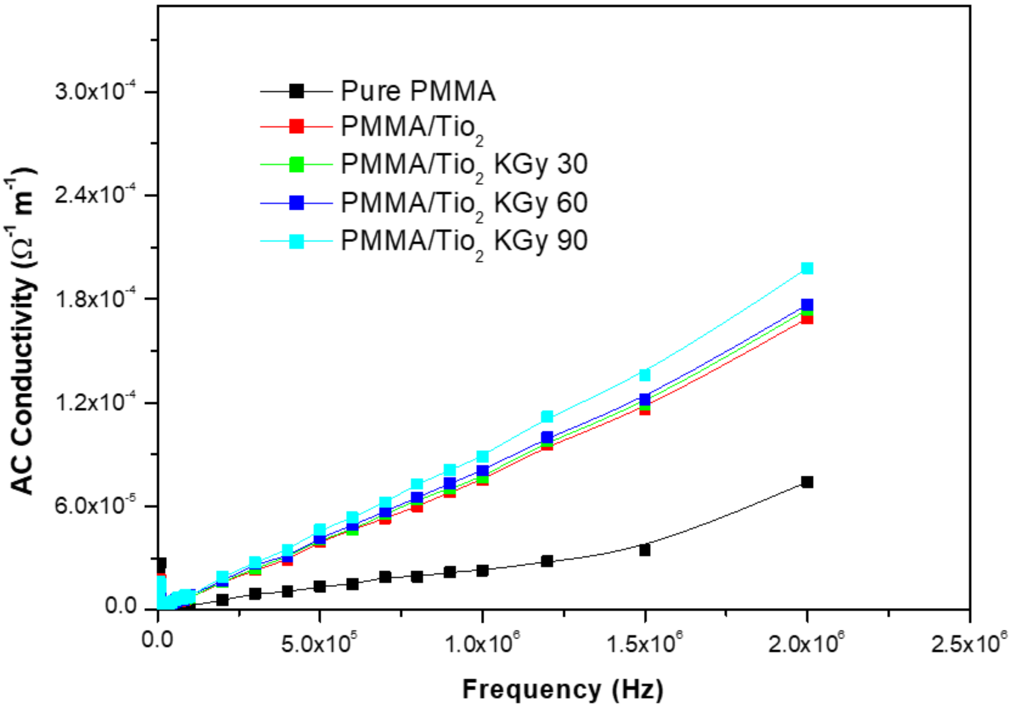


Figure3.5: Frequency-dependent electrical conductivity (σ) of PMMA–TiO₂ nanocomposites irradiated at different gamma doses

3.4 Surface roughness study

To gain deeper insight into the structural surface changes of polymeric films exposed to gamma (γ) irradiation, surface roughness analysis was employed as a key diagnostic tool. Three classical roughness parameters: Ra, Rq, and Rz were investigated to characterize the topographical evolution of the films.

PMMA-TiO₂ nanocomposite films showed a more pronounced increase in surface roughness compared to pure PMMA. The embedded TiO₂ nanoparticles promote the formation of finer surface structures and nano-texturing, which leads to increased surface roughness [11]. PMMA-TiO₂ nanocomposite films were subjected to γ-ray doses ranging from 0 to 90 kGy. As the radiation dose increased, a clear enhancement in the values of Ra, Rq, and Rz was observed as shown in Fig.(3.6). This increase in surface roughness is primarily attributed to chain scission, a degradation mechanism in which covalent bonds within the polymer backbone are broken. This leads to a decrease in molecular weight and the formation of nanoscale surface defects and pits, contributing to increased roughness [11].

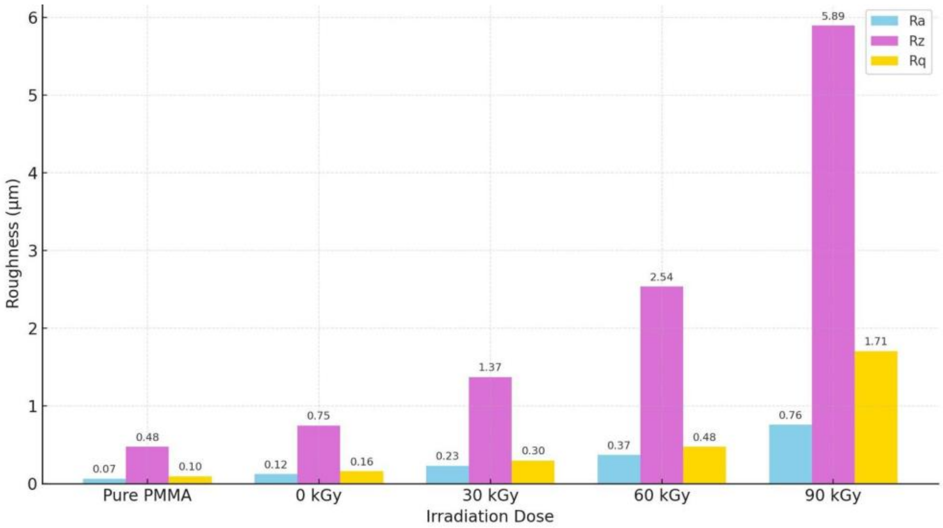


Figure3.6: Surface roughness parameters (Ra, Rq, Rz) of PMMA and PMMA/TiO_2 films as a function of γ-ray dose

Conclusion

In this context, the impact of gamma radiation on the optical properties, electrical conductivity and surface roughness of PMMA-TiO_2 nanocomposite films at different gamma doses were studied. UV–VIS spectra showed an increase in absorption with a marked decrease in transmittance after the addition of TiO2 and the increase of gamma dose. The direct band gap energy in irradiated PMMA-TiO2 nanocomposite films decreased to 4.5 eV to 3.81 compared to pure PMMA 4.5 eV. The indirect band gap energy in irradiated PMMA-TiO_2 nanocomposite films decreased to 4.1 eV compared to pure PMMA 4.5 eV. The reduction in the optical gap-band energy Eg indicates an improvement in the electrical conductivity of the nanocomposite polymers after gamma irradiation. This result was confirmed by measuring ac conductivity using LCR bridge. It observed that surface roughness increases Therefore, the results of this study demonstrate that the incorporation of TiO_2 nanoparticles into the PMMA matrix, with exposure to varying doses of gamma radiation, significantly enhances the material’s properties for use in various fields, including microelectronics, optical protection systems, and smart surface technologies.

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