Industrial Engineering Journal
ISSN: 0970-2555
Volume : 54, Issue 8, No.1, August : 2025

HIGH ENERGY RADIATION EFFECTS ON PMMA, PVC AND THEIR SHIELDING FOR INDUSTRIAL APPLICATIONS – A SHORT REVIEW

Vijay V. Soman, Physics Department, Shri Mathuradas Mohota College of Science, Nagpur, India
Leena C. Joshi, Physics Department, St. Xavier's College, Mumbai, India
Vaishali V. Soman, Applied Physics Department, Priyadarshini College of Engineering, Nagpur
Email: vvsoman@gmail.com

ABSTRACT

As the polymers exhibit an extraordinary range of properties, they have plenty of industrial applications. There is an ever-demanding requirement for newer and newer polymers with improved functional properties. One of the methods to modify and improve the polymer properties is to irradiate the polymers with high-energy radiation. However, due to the ionizing nature of the high-energy radiation, the molecular structure of the polymers is changed, leading to some adverse effects on their properties. PMMA, PVC, and their blend systems are among the most extensively studied polymers with many industrial applications. Therefore, in this short review, the effects of radiation, the mechanisms of radiation damage and the effects of the addition of stabilizers, antioxidants to synthesize radiation-resistant polymer composites are discussed so as to make them sustainable in industrial applications.

Keywords:
PMMA, PVC, high energy radiation, gamma irradiation, electron irradiation, stabilizers

I. Introduction:

Polymeric materials have an extraordinary range of properties. They are extensively used in sectors like automobile, construction, electronics, aerospace, defense, healthcare, pharmaceutical industries, etc. [1]. Therefore, there is an ever-increasing demand to get newer and newer polymeric materials with improved and desired properties. To fulfill this ever-increasing demand, research and development in the area of polymer and polymer composites is increasing at a phenomenal rate.

There are many techniques used in the polymer industry to meet specific performance requirements, like copolymerization, grafting, crosslinking, plasticization, blending, etc. Among these methods, blending is a smart way to get a new polymer using commercially available polymers, wherein a new polymer called a 'polymer-blend' is obtained from the mixing of two polymers. The blends may be miscible or immiscible. 'Although most polymer pairs are immiscible or only partially miscible, several combinations have good mechanical, thermal, or other properties, which are useful in certain applications; such blends are often termed compatible' [2]. As the blends show different properties from those of the neat polymers, blends can be redefined as a "*modified polymer*".

Other methods to tailor the polymer properties are achieved through crosslinking and grafting by exposing the polymers to high-energy radiations like electron beam, γ-irradiation, etc. of desired energy levels. Such 'radiation processed' polymers, their blends, and even composites have enhanced utility and have several applications in biomedical, pharmaceutical sciences, electrical, coating processes, aerospace, membrane technology, textile, and many more areas of day-to-day interests and applications [1]. For example, gamma radiation-induced graft polymerization of acrylamide onto different substrates such as low-density polyethylene (LDPE) [3], poly(tetrafluoroethylene) (PTFE)[4], nylon-6 [5], silicone rubber [6], cotton fabric [7], etc. has been carried out by many researchers. Nesar et al. [8] have successfully grafted acrylamide onto polyvinylchloride (PVC) films using gamma radiation. The use of radiation-grafted copolymers as membranes also has a lot of applications in membrane technology. Sevil et al. [9] studied the dose response of polyaniline (PANI) samples blended with PVC and chlorinated poly(propylene)(PPCl) by measuring the high frequency conductance of these blends irradiated to different doses of gamma radiations and studied the electrical

conductivity in the frequency range of 1 kHz to 1 MHz to find out the most sensitive evaluation conditions.

Among the many polymers, polymethylmethacrylate (PMMA), polypropylene (PP), PVC, polyurethane (PU), polycarbonate (PC), etc., have biomedical applications due to their biocompatible nature. For example, since PMMA has no adverse reaction with human tissue, intraocular lenses have been implanted worldwide, and the majority of them are made from PMMA. PVC is widely used in a variety of medical devices, including blood bags, IV sets, etc. When the polymers are used for biomedical applications, they need to be sterilized. The use of γ-radiations for sterilization is a very convenient and most widely accepted method. The γ-radiations disrupt the DNA sequence of bacteria, and the material gets sterilized. The acceptable dose of sterilization is 2.5 Mrad. [3].

Due to the ionizing nature of the high-energy radiations, there are some adverse effects on polymer properties like: loss of flexibility, elongation, discoloration or yellowing, reduction in tensile strength and impact resistance, embrittlement and even major structural changes in polymers.

It is well reported that, on one hand, exposure of polymers to high-energy radiation is essential, in some situations inevitable [10], while on the other hand, the exposure can initiate degradation or deterioration in the required properties. It is therefore essential to add stabilizers and antioxidants to synthesize radiation-resistant polymer or develop polymer composites or provide optimal irradiation doses to strike a balance of beneficial effects with minimal degradation. PMMA, PVC, and their blend systems are among the most extensively studied polymers with many industrial applications. Therefore, the mechanisms of radiation damage and the possible methods for modifying these polymeric materials suited for extreme environmental conditions are reviewed in this article, along with their industrial applications.

II. Effect of high-energy radiations in polymers:

It is observed that metals and ceramics are not much susceptible to the initiation of chemical reactions in them due to exposure to high-energy radiation. Whereas organic materials like polymers are very susceptible. Due to the ionizing nature of such high-energy radiations through the polymer, generations of ions, free electrons, and free radicals, and excitation of molecules take place. [1].

The high-energy photons cause ionisation events in polymeric materials that create peroxy radicals. In the presence of oxygen, these species can initiate degradation. “The radiation-initiated reactions in polymers can be basically of two types (i) cross-linking (gelling) and (ii) scission (degradation). Cross-linking involves cleavage of C-H bond on one polymer chain to form a hydrogen atom, which is accompanied by abstraction of a second hydrogen atom from a neighboring chain to produce a molecule of hydrogen. Thus, the two polymeric radicals that are adjacent combine to form a cross-link and the overall effect of cross-linking is that the molecular mass of the polymer goes on increasing gradually with the radiation dose. On the other hand, chain scission is opposite to cross-linking; such that a rupturing of C - C bonds takes place. Therefore, in the process of chain scission, there is a decrease in the average molecular weight [2]”. At modest levels, irradiation can lead to a decrease in the molecular weight of the polymer and a temporary colour change. Lee et al. [11] have reported that both cross-linking and chain scission may occur simultaneously during the irradiation of polymers but the relative ratio of cross-linking to scission depends upon the polymer structure. Two more radiation-induced processes observed in polymers are grafting and curing. "In the grafting process, monomers are introduced laterally onto the polymer chain. In the grafting process, covalent C–C bonds are formed. Whereas in the curing process, the rapid polymerization of an oligomer monomer mixture forms a coating that is essentially bonded by physical forces to the substance. In the curing process the bonding generally involves weak van der Waals’ or London dispersion forces” [12].

Like γ-radiation, electron irradiation, Sokhoreva et al. [L7] studied the effect of the high-energy alpha particles on the styrene accumulation kinetics and functional groups during the synthesis of proton-exchange membranes based on PVDF. They have reported that the ‘grafting styrene using alpha particles requires high doses of radiation, and the radicals initiated by α-particles persist for several

years, the degree of grafting and exchange capacity correlate with the absorbed dose and the proton conductivity measured at room temperature and 40% humidity ≥0.2 S/cm [13].'

Even though the polymers are susceptible to high-energy radiation, a wide variety of applications in the cosmetics, pharmaceutical, moulded products for medical applications (plastic syringes, surgical gloves, specimen containers, orthopedic implants, etc.) are sterilized using ionizing radiation before use where the sterilization dose is 25 kGy. In food preservation, sterilization is carried out at an irradiation dose of about 20-45 kGy, mostly with γ-photons [14].

Amongst the various high-energy radiations, the most common is the use of γ-photons. However, there are many studies where polymers are irradiated by other radiations like protons, α-particles [15], and electrons [16]. Tyutnev et al. [15] investigated the effect of 7.7 MeV protons and 20 MeV α-particles at room temperature on 14 polymers. The effect of 100 MeV proton irradiation on poly(ethyleneterephtalate) has been investigated by Briskman [17]. 'Radiation shielding in space missions is critical to protect astronauts, spacecraft, and payloads from radiation damage'[18]. Alloys are not suitable for space radiation shielding, whereas polymers, on the other hand, when suitably modified, provide sufficient radiation shielding function with lower weight and less secondary radiation generation [18]. Malawy et al. [19] in their study have reported "the induced defects and modifications enhanced by alpha particle on CdO and ZnSe-doped PMMA". They irradiated the samples with 4.5 MeV α-particle at a gradually increased fluence. They have reported that [19] 'α-particle caused interchangeable defects and cross-linking processes. The formation of C–H and O–H functional groups due to α-particle interactions and the filler–polymer interface has a great impact on the formed defects, which control the observed characteristics in the polymeric composite medium'.

It is to be noted that at times, the exposure of polymers to γ-radiations becomes a matter of concern in some of the applications as irradiation of polymers results in bond cleavage, giving free radicals, which in turn, in the presence of oxygen, react by a chain mechanism to form oxidation products, including the formation of hydroperoxides. The hydroperoxides are thermally labile, and the breakdown yields more free radicals, which can initiate new chain reactions with oxygen. This finally leads to chain scission and cross-linking" [12, 20-21]. The degradation has many disadvantages, such as decolorization, polymer becoming yellowish or brownish and also undesirable changes in physical properties like reduction in tensile strength and Youngs modulus. Therefore, the optimum exposure of the dose of the high-energy radiation has to be ensured.

In short, an extensive research work, conducted over the past few decades has shown that radiation-polymer interaction mainly involves chain scission or cross-linking or both, which leads to structural changes in the polymer under study. This causes changes in the bulk physical properties, including the mechanical, electrical, electronic, optical properties, etc. The stability of the polymer to withstand the environmental changes is also significantly affected due to structural changes caused due to radiation exposure.

III. Effect of high-energy radiation on PMMA, PVC and their blends

It all started around 1930 when PMMA was used as a material for denture bases in dentistry, and since then, due to the biocompatibility, ease of manipulation, and low toxicity PMMA has been extensively used in other dental devices, orthopedic implants. In 1949, Ridley used PMMA-based intraocular lenses (IOLs) for the first time by implanting IOL into a 42-year-old woman [1]. As all medical implants require sterilization, the use of gamma irradiation for this purpose was most popular due to many reasons. The gamma radiation disrupts the DNA sequences of bacteria, leading to their eradication. However at high doses, irradiation of PMMA in particular can cause a permanent change in colour, production of a large amount of volatiles, surface crazing, cracking and embrittlement, eventually reducing it to dust. Indeed, PMMA has been used to monitor exposure to ionising radiation by use of spectrophotometry. (PMMA3)"

The PVC products are extensively used in hospitals, especially for single-use items like IV bags, catheters, blood bags, etc. The medical-grade PVC formulations are developed to reduce the risks of plasticizer leakage and improve compatibility with blood and tissue [1].

Researchers have shown that "scission and cross-linking depended not only upon polymer structure but also upon the energy deposited per unit track length or linear energy transfer (LET, eV/nm/ion)" [11]. "PMMA was considered to be a degrading type polymer under most irradiation conditions; it can behave as a cross-linking type under high LET conditions, thus changing a positive photo-resist to a negative type. High LET irradiation conditions can be achieved by a proper choice of ion species and energies." [11].

Optical and microstructural studies on electron-irradiated PMMA with positron annihilation study were carried out by Ismayil et al. [22]. The authors have observed that "PMMA films when irradiated with 8 MeV electron beam and the corresponding induced microstructural changes were investigated. The FTIR result indicates that the irradiation causes chain-scission and creates a C=C bond within PMMA, which in turn affects the optical properties of the film".

In an interesting study, structural modification of PMMA due to electron irradiation with varying energies was studied by Tiwari et al. [23]. The induced micro-structural changes were investigated. The authors have reported that 'the irradiation caused chain scission and creates C=C bond within PMMA, the amount of all of the functional groups decreases as a function of dose, corresponding to the energy loss of the incident electrons, appearance at 2357 cm^{-1} and 667 cm^{-1} in the FTIR spectra, corresponding to CO_2, due to trapped gas evolved during irradiation, implying breaking of carbonyl bonds'. In another study, Kudoh et al. [20] observed "the radiation-induced gas evolution analyzed after gamma-irradiation at 77K and room temperature" in PMMA and glass fiber reinforced plastic (GFRP). It is reported by the authors that "the yield of H_2 does not have much dependence on irradiation temperature. The yields of CO, CO_2, and CH_4, on the other hand, have large irradiation temperature dependencies which are consistent with changes in flexural strength, molecular weight, and network destruction. For both materials, the irradiation temperature dependence of degradation reflects the mobility of the main chain and methyl and ester groups" [20].

The effect of gamma radiation on semi-crystalline polyvinyl chloride polymer for low-voltage cable insulator was studied by Hutagol et al. [24] where, PVC was exposed to high gamma radiation exposure at doses of 25, 50, 100, 200, 400, and 800 kGy. The authors reported that "a gamma dose of 25 kGy increases the percentage of crystallinity, indicating the occurrence of crosslinking, while other doses exhibit a decrease of crystallinity with increasing radiation dose. Tensile stress significantly dropped up to 400 kGy but increased at 800 kGy. Elongation at break (EAB) decreased with higher gamma radiation doses. Overall, materials up to 800 kGy remained non-brittle, serving as effective insulators and demonstrating thermal stability within high gamma radiation exposure conditions".

Kudoh et al. [20] have reported the evolution of various gases when PMMA is exposed to γ photons at room temperature and even at -196° C (77 K). These authors have made an extensive study of the irradiation temperature dependence of the mobility of main chain and methyl and ester groups. They have also reported the changes in flexural strength, molecular weight and network destruction. Ishikawa et al. [25] have reported the degradation mechanism of PMMA using intensive ESR study. Shultz [26] has reported the predominance of cross linking of polymer chains in irradiated polyacrylates.

Oxygen consumption and gas evolution, analyzed by gas chromatography, was carried out by Zahran et al. [27]. These authors have reported the following observations: "(i) the total gas evolution and HCI dehydrochlorination increase with irradiation doses up to 0.3 MGy, and they tend to level off at higher doses, (ii) H_2 and CH_4 evolution continue to increase with the irradiation doses, but they are the minor gases from the total (iii) HCI is the main product during the irradiation of rigid PVC films under vacuum" [27]. The T_g for PVC is 81° C and has a melting point around 310° C [1]. PVC is thermally not very stable, and beyond 200° C it degrades. It is reported that the degradation of PVC,

the formation of a conjugated double bond structure, is responsible for the pink or yellow color of the degraded polymer.

"PVC irradiated under aerobic condition are different. ESR spectra have shown that peroxyl radicals are formed. Propagating reactions from peroxyl radicals are mainly composed by β-scission reactions. These β-scission reactions involved the decrease of average molecular weight and the formation of aldehydes, acids chloride and/or carboxylic acids. From all these results, anaerobic and aerobic mechanisms of degradation by PVC radiolysis are proposed [28]".

IV. Reducing the damage of irradiated PMMA, PVC, and their blends for industrial applications:

There has been a considerable discrepancy in regard to the interpretation of the mechanisms of scission and cross-linking for irradiated polymers. The decomposition of polymers during technological operations needs to be prevented by the addition of plasticizers, fillers, etc. To minimize the damage, researchers have added stabilizers, antioxidants and antirad materials to neutralize free radicals, and radiation-resistant polymer blends or composites, controlled irradiation doses to balance beneficial effects like sterilization with minimal degradation.

Sevil et al. [29] demonstrated that the electrical conductivity of PANI/PVC composite films can be drastically increased by exposure to γ-rays or UV radiation as a result of dehydrochlorination (loss of HCl) of PVC. In fact, dehydrochlorination of PVC is an unwanted process. However, Sevil et al. [29] made use of this undesired property of PVC, where "this solvent-free novel process has been put to use in several applications like dosimetry, radiation monitoring or on-off devices under irradiation environment".

Saleh et al. [30] have reported "the synergistic effects of Al doping and gamma radiation on the optical properties of PMMA composites. By systematically analyzing changes in optical parameters such as the absorption coefficient, optical band gap, refractive index, extinction coefficient, dielectric constants, and optical conductivity across varying Al concentrations and gamma radiation doses, this study contributes valuable insights into the optimization of PMMA/Al composites for advanced technological applications" [30].

Dorostkar et al. [31] have developed a PMMA-based polymer composite incorporating WO3 for gamma radiation shielding using synthesis and Monte Carlo simulation. The authors claim that "the composite retained high optical transparency at low filler concentrations, making it an ideal candidate for transparent radiation shielding applications such as protective windows, protective screens, medical barriers, industrial monitoring panels, and protective eyewear. These findings highlight the strong potential of PMMA-WO3 composites as effective, lightweight, and transparent gamma radiation shields".

Muisener [32] et al. developed radiation radiation-resistant composite of PMMA by adding 0.26 wt % single-walled carbon nanotube (SWNT) to PMMA. They observed that after a dose of 5.9 Mrad of γ-radiation, the Vickers hardness value and the modulus of the neat PMMA decreased. However, these properties remain unchanged after irradiation for PMMA / SWNT composite. On the other hand, Li et al. [33] investigated poly(methyl-methacrylate)/multi-walled carbon nanotube (PMMA/MWCNT) nanocomposite for proton radiation shielding applications. They observed that PMMA/MWCNT composites in terms of radiation shielding effectiveness, which "was experimentally evaluated by comparing the proton transmission properties and secondary neutron generation of the PMMA/MWCNT nanocomposite with pure PMMA and aluminum. The results showed that the addition of MWCNTs in PMMA matrix can further reduce the secondary neutron generation of the pure polymer, while no obvious change was found in the proton transmission property. On the other hand, both the pure PMMA and the nanocomposite were 18%–19% lighter in weight than aluminum for stopping the protons with the same energy and generated up to 5% fewer secondary neutrons. Furthermore, the use of MWCNTs showed enhanced thermal stability over the pure polymer, and thus

the overall reinforcement effects make MWCNT an effective filler material for applications in the space industry." [33].

The addition of antirad materials, such as, the effect of fullerence C_{60} on the properties of PMMA when exposed to ionizing radiations have been very interesting and reported by Zhogova et al. [34]. They have carried out the effect of fullerence C_{60} on thermal, mechanical and optical properties of PMMA after exposing it to ionizing radiations and observed that C_{60} behaves as an effective antirad with respect to PMMA. Fullerence C_{60} addition raises temperature of destruction for polymer subjected to electron radiation by 20-25°C and also improves strength properties of PMMA. Similarly, Muisener et al. [32] have suggested that single-walled carbon Nanotubes(SWNT) have a potential application for radiation-resistant composites. The authors have observed the radiation resistant effects in PMMA-SWNT (0.26 wt % of SWNT) composites.

The PMMA films containing a concentration of complexes 0.5% by weight were studied by Yousif et al. [35] for their photostabilization by new types of 2-thioacetic acid-5-phenyl-1,3,4-oxadiazole with Sn(II), Ni(II), Zn(II), and Cu(II) complexes was investigated. It is observed by these reaserchers that Ni based complex was most efficient in the photostabilization process.

Alyousef et al. [36] investigated and proposed the use of PMMA-Bi_2O_3 polymer composites at various diagnostic energies (20, 30, 40 and 60 keV) and possible replacement of the conventional concrete and gypsum by these polymer composites at these energies.

Many authors have studied the effect of different plasticizers on gamma-irradiated PVC [37]. Kimura [38] reported that lower phthalate plasticizers stabilize PVC against the effect of gamma radiation more effectively than higher homologs of aliphatic esters.

In case of PVC, a polyhalogenated chain with chlorine atoms is covalently linked to atoms of carbon, thus providing many points of dipole interactions along its chain which gives rise to strong inter-chain interactions and consequent rigidity to the polymeric material. PVC is therefore a stiff and inflexible material. Therefore, to make it a flexible and an elastic material, PVC is plasticized. Furthermore, to prevent its decomposition both during technological operations and in service, stabilizers are added. Therefore, aiming at the improvement in the stability of PVC, many classes of stabilizers are known. They are organo-tin stabilizers and fully organic stabilizers [39-41]. 'The different methods of using these stabilizers are either addition to the polymer or chemical modification of the polymer to displace the labile sites by more stable stabilizer moieties' [42, 43]. Grafting copolymerization [44] or blending with other polymers of high thermal stability [12] are the two most recent methods. These two methods possess the advantage that the stabilizing moieties are polymeric in nature which help the compatibility between the polymer and the stabilizer moieties as well as the improvement of the mechanical properties. Kong et al. [45] have proposed a new radiation stabilizer, trans-stilbene oxide (StO). StO showed a significant improvement of gamma radiation resistance for the plasticized PVC. The possible mechanism can be explained on the basis that an epoxy functional group effectively stabilizes the process of dehydrogenation, the formation of hydroperoxides, the formation of oxygen-containing groups and the synergetic effects of an epoxy compound and thus the presence of StO is more notable for the prevention of radiation oxidation in the presence of an aromatic group. Many more authors have studied the effect of different plasticizers on γ-irradiated PVC. Tritolyl phosphate was also reported as an effective radiation protective agent. Allyl Esters, which can be used as ordinary plasticizer were reported as radiation sensitizers for cross-linking of PVC [46].

Sagheer et al. [47] has observed that the addition of a "very small amount of PMMA in PVC increases its first and second thermal decomposition temperature and drastically lowers the evolution of harmful pyrolysis products like HCl and other volatile aromatic products. The stabilizing effect is found to be the most significant with 10 wt.% PMMA in the PVC matrix. Such blends can be very useful to avoid the evolution of hazardous chemicals like HCl and other chlorinated hydrocarbons."

In an interesting study, Avcıoglu [48] developed 'all-in-one radiation protection materials since various forms of ionizing radiation, such as neutrons and gamma rays, can occur simultaneously'. These researchers [48] examined the ability of transition metal borides to attenuate both photon and

particle radiation by synthesizing fourteen different transition metal borides. Further, it has been reported that 'SmB_6 and DyB_6 demonstrated exceptional neutron attenuation for thermal and fast neutrons due to the high neutron capture cross-sections of Sm, Dy, and B. The outcomes of this study reveal that transition metal borides can be suitable candidates for shielding against mixed neutron and gamma radiation [48].'

Charlesby [49] has proposed the use of high-energy radiation for crosslinking and degradation in industrial processing. This is because the 'high energy radiations can be considered as a means of producing copious radicals and ions i.e. chemically reactive species within the irradiated specimen. The main advantages proposed by this scientist about the gamma radiations as a source of radicals or ions over chemical catalysts are –large range of concentrations is possible, with simple control and accurate reproducibility, complete control of temperature, lack of catalyst residue, etc'. The author has further pointed out that "Of the many changes observed in irradiated polymers, crosslinking has been the most interesting from the point of applications. Crosslinking occurs when the side chains or even the H atoms are split off. The radicals formed on adjacent chains can react together to give a covalent bond, thereby linking the polymer molecules together. At first, this merely increases the average molecular weight and degree of branching. A point is soon reached at which an incipient closed network is formed, and this completely transforms the physical properties of the material. The advantages of the radiation technique include the complete control of density of crosslinking, the formation of crosslinks in the solid state, no need for catalysts or other additives, no heat treatment, and the ability to crosslink polymers, which, in the absence of unsaturated groups, are largely resistant to conventional chemical treatment.

Conclusions:

In order to tailor some of the polymer properties, it is essential to expose them to high-energy radiation; however, the associated drawback is that this exposure can initiate degradation or deterioration in some other properties. Further, due to their inherent properties like: non-toxic nature, cost-effectiveness, lightweight, processing performance, high corrosion resistance, flexibility, and thermal stability, etc. it is therefore essential to add stabilizers and antioxidants to synthesize radiation-resistant polymer or develop polymer composites. The polymer-nanoparticle composite matrix is also another effective method to develop radiation shields. With these outstanding advantages, the study of polymer composites has gained significant importance in radiation shielding applications as compared to other conventional radiation shielding materials.

REFRENCES:

[1] Gowarikar V. R., Viswanathan N. V., Sreedhar J. Polymer Science, New Age International (P) Limited, Publishers, New Delhi, (Eighteenth Reprint May 2001)
[2] Fekete E., Foldes E., Pukanszky B. Eur. Polym .J. **41** (2005) 727
[3] Postnikov, V. A.; Lukin, N. Ju.; Maslov, B. V.; Plat, N. A. *Polymer Bulletin* **1980**, *3-3* (1-2), 75–81. https://doi.org/10.1007/bf00263208.
[4] Hegazy, E. A.; N.B. El-Assy; Taher, N. H.; A.M. Dessouki. *International Journal of Radiation Applications and Instrumentation Part C Radiation Physics and Chemistry* **1989**, *33* (6), 539–543. https://doi.org/10.1016/1359-0197(89)90311-1.
[5] Huang, C.-N.; Wu, C.-M.; Lo, H.-W.; Lai, C.-C.; Teng, W.-F.; Liu, L.-C.; Chen, C.-M. *Polymers* **2019**, *11* (2), 386. https://doi.org/10.3390/polym11020386.
[6]Hoffman, A. S.; Ratner, B. D. The Radiation Grafting of Acrylamide to Polymer Substrates in the Presence of Cupric Ion — I. A Preliminary Study. *Radiation Physics and Chemistry (1977)* **1979**, *14* (3-6), 831–840. https://doi.org/10.1016/0146-5724(79)90118-3.
[7]Harper, R. J.; Mehta, P. Finishing Cotton-Wool Blends. *Textile Research Journal* **1985**, *55* (12), 761–766. https://doi.org/10.1177/004051758505501209.
[8]El-Nesr, E. M.; Dessouki, A. M.; Abdel-Bary, E. M. Gamma Radiation Induced Graft

Copolymerization of Acrylamide onto Poly(Vinyl Chloride) Films. *Polymer International* **1998**, *46* (2), 150–156. https://doi.org/10.1002/(sici)1097-0126(199806)46:2%3C150::aid-pi981%3E3.0.co;2-l.
[9]Sevil, U. A.; Güven, O.; Kovács, A.; Slezsák, I. Gamma and Electron Dose Response of the Electrical Conductivity of Polyaniline Based Polymer Composites. *Radiation Physics and Chemistry* **2003**, *67* (3-4), 575–580. https://doi.org/10.1016/s0969-806x(03)00108-7.
[10]Cherkashina, N. I.; Pavlenko, V. I.; Shkaplerov, A. N.; Popova, E. V.; Umnova, L. A.; Ivanova, O. A.; Kartashov, D. A.; Shurshakov, V. A. Testing a Radiation-Protective Polymer Composite on the ISS. *Advances in Space Research* **2024**, *74* (10), 5172–5178. https://doi.org/10.1016/j.asr.2024.07.029.
[11]Lee, E. H.; Rao, G. R.; Mansur, L. K. LET Effect on Cross-Linking and Scission Mechanisms of PMMA during Irradiation. *Radiation Physics and Chemistry*, **1999**, *55* (3), 293–305. https://doi.org/10.1016/s0969-806x(99)00184-x.
[12]Bhattacharya, A. Radiation and Industrial Polymers. *Progress in Polymer Science* **2000**, *25* (3), 371–401. https://doi.org/10.1016/s0079-6700(00)00009-5.
[13]Sokhoreva V.V. ;Koptsev M.; Lomov I.V. ; Mukhambetalin D.B. Study of the High-Energy Alpha Particles Influence on the Styrene Accumulation Kinetics and Functional Groups during the Synthesis of Proton-Exchange Membranes Based on PVDF. *Radiation Physics and Chemistry* **2024**, *221*, 111745–111745. https://doi.org/10.1016/j.radphyschem.2024.111745.
[14]Goulas, A. E.; Riganakos, K. A.; Kontominas, M. G. Effect of Ionizing Radiation on Physicochemical and Mechanical Properties of Commercial Monolayer and Multilayer Semirigid Plastics Packaging Materials. *Radiation Physics and Chemistry* **2004**, *69* (5), 411–417. https://doi.org/10.1016/j.radphyschem.2003.08.013.
[15]Tyutnev, A. P.; Boev, S. G.; Abramov, V. N.; Kuzmenkov, E. A.; Vannikov, A. V. Track Effects in Radiation Induced Conductivity of Polymers. *physica status solidi (a)* **1990**, *121* (1), 205–212. https://doi.org/10.1002/pssa.2211210124.
[16]Ratnam, C. T.; Nasir, M.; Baharin, A.; Zaman, K. Evidence of Irradiation-Induced Crosslinking in Miscible Blends of Poly(Vinyl Chloride)/Epoxidized Natural Rubber in Presence of Trimethylolpropane Triacrylate. *Journal of Applied Polymer Science* **2001**, *81* (8), 1914–1925. https://doi.org/10.1002/app.1624.abs.
[17]Briskman, B. A. Specificity of Proton Irradiation Effects on Polymers. *Nuclear Instruments and Methods in Physics Research Section B Beam Interactions with Materials and Atoms* **2007**, *265* (1), 72–75. https://doi.org/10.1016/j.nimb.2007.08.028.
[18]Li, Z.; Chen, S.; Nambiar, S.; Sun, Y.; Zhang, M.; Zheng, W.; Yeow, J. T. W. PMMA/MWCNT Nanocomposite for Proton Radiation Shielding Applications. *Nanotechnology* **2016**, *27* (23), 234001. https://doi.org/10.1088/0957-4484/27/23/234001.
[19]Doaa El-Malawy; Hassan, H. E.; M. El Ghazaly; S. Abdel Samad; M. Al-Abyad. Low-Energy α-Particle Irradiation of Polymeric-Based Nanofiller. ˜ *The œEuropean physical journal plus* **2023**, *138* (8). https://doi.org/10.1140/epjp/s13360-023-04300-x.
[20]Kudoh H.; Kasai, N.; T. Sasuga; T. Seguchi. Low Temperature Gamma-Ray Irradiation Effects on Polymer Materials—3. Gas Evolution and Change of Molecular Weight. *Radiation Physics and Chemistry* **1996**, *48* (1), 95–100. https://doi.org/10.1016/0969-806x(95)00433-x.
[21]Zahran, A. H.; F.M. Ezz Eldin. Radiation Effects on Poly(Vinyl Chloride). 2. Effect of Plasticizers on the Behaviour of PVC. *International journal of radiation applications and instrumentation, Part C, Radiation physics and chemistry/International journal of radiation, applications and instrumentation. Part C, Radiation physics and chemistry* **1986**, *27* (3), 175–183. https://doi.org/10.1016/1359-0197(86)90049-4.
[22]Ismayil; V. Ravindrachary; R.F. Bhajantri; S.D. Praveena; Boja Poojary; Dutta, D.; P.K. Pujari. Optical and Microstructural Studies on Electron Irradiated PMMA: A Positron Annihilation Study. *Polymer Degradation and Stability* **2010**, *95* (6), 1083–1091.

https://doi.org/10.1016/j.polymdegradstab.2010.02.031.
[23]Tiwari, P.; Srivastava, A. K.; Khattak, B. Q.; Verma, S.; Upadhyay, A.; Sinha, A. K.; Ganguli, T.; Lodha, G. S.; Deb, S. K. Structural Modification of Poly (Methyl Methacrylate) due to Electron Irradiation. *Measurement* **2014**, *51*, 1–8. https://doi.org/10.1016/j.measurement.2014.01.017.
[24]Hutagaol, A. G.; Muhammad Ilham Bayquni; Setiawan, J.; Dwi Putranto; Usman Sudjadi; Sungkono Sungkono; Rosika Kriswarini; Masrukan Masrukan; Yunus, M. Y. Effect of Gamma Radiation on Semi-Crystalline Polyvinyl Chloride Polymer for Low-Voltage Cable Insulator. *Bulletin of Electrical Engineering and Informatics* **2025**, *14* (2), 823–832. https://doi.org/10.11591/eei.v14i2.7940.
[25]Ichikawa, T.; Yoshida, H. Mechanism of Radiation-Induced Degradation of Poly(Methyl Methacrylate) as Studied by ESR and Electron Spin Echo Methods. *Journal of Polymer Science Part A Polymer Chemistry* **1990**, *28* (5), 1185–1196. https://doi.org/10.1002/pola.1990.080280519.
[26]Shultz, A. R. High-Energy Radiation Effects on Polyacrylates and Polymethacrylates. *Journal of Polymer Science* **1959**, *35* (129), 369–379. https://doi.org/10.1002/pol.1959.1203512905.
[27]Zahran, A. H.; Hegazy, E. A.; Eldin, F. M. E. Radiation Effects on Poly (Vinyl Chloride)—I. Gas Evolution and Physical Properties of Rigid PVC Films. *Radiation Physics and Chemistry (1977)* **1985**, *26* (1), 25–32. https://doi.org/10.1016/0146-5724(85)90028-7.
[28]Colombani, J.; Véronique Labed; Christophe Joussot-Dubien; Alain Périchaud; Raffi, J.; Kister, J.; Rossi, C. High Doses Gamma Radiolysis of PVC: Mechanisms of Degradation. *Nuclear Instruments and Methods in Physics Research Section B Beam Interactions with Materials and Atoms*, **2007**, *265* (1), 238–244. https://doi.org/10.1016/j.nimb.2007.08.053.
[29]Sevil U. A.; Güven O.;Birer O.;Süzer S. Doping of 2-Cl-PANI/PVC Films by Exposure to UV, γ-Rays and E-Beams. *Synthetic Metals* **2000**, *110* (3), 175–179. https://doi.org/10.1016/s0379-6779(99)00266-0.
[30]Saleh, B. A. A.; Kraishan, A.; Elimat, Z. M.; Karaki, I. A.; Alzubi, R. I.; Juwhari, H. K. Effect of Gamma Radiation on the Optical Properties of PMMA Composites with Varying al Concentrations. *Radiation Physics and Chemistry* **2025**, *226*, 112342. https://doi.org/10.1016/j.radphyschem.2024.112342.
[31]Mahdieh Mokhtari Dorostkar; Saray, A. A. Development of PMMA Based Polymer Composite Incorporating WO3 for Gamma Radiation Shielding Using Synthesis and Monte Carlo Simulation. *Scientific Reports* **2025**, *15* (1). https://doi.org/10.1038/s41598-025-11155-y.
[32]Muisener, P. A. O.; Clayton, L.; D'Angelo, J.; Harmon, J. P.; Sikder, A. K.; Kumar, A.; Cassell, A. M.; Meyyappan, M. Effects of Gamma Radiation on Poly(Methyl Methacrylate)/Single-Wall Nanotube Composites. *Journal of Materials Research* **2002**, *17* (10), 2507–2513. https://doi.org/10.1557/jmr.2002.0365.
[33]Li, Z.; Chen, S.; Nambiar, S.; Sun, Y.; Zhang, M.; Zheng, W.; Yeow, J. T. W. PMMA/MWCNT Nanocomposite for Proton Radiation Shielding Applications. *Nanotechnology* **2016**, *27* (23), 234001. https://doi.org/10.1088/0957-4484/27/23/234001.
[34]Zhogova K.B. ; Davydov, I. A.; V.T. Punin; B.B. Troitskii; G.A. Domvachiev. Investigation of Fullerene C60 Effect on Properties of Polymethylmethacrylate Exposed to Ionizing Radiation. *European Polymer Journal* **2005**, *41* (6), 1260–1264. https://doi.org/10.1016/j.eurpolymj.2005.01.010.
[35]Yousif, E.; Hasan, A. Photostabilization of Poly(Vinyl Chloride) – Still on the Run. *Journal of Taibah University for Science* **2015**, *9* (4), 421–448. https://doi.org/10.1016/j.jtusci.2014.09.007.
[36]Alyousef, H. A.; Alotiby, M. F.; S.A. Tijani; Alotaibi, B. M. A Study on the Use of PMMA - Bi_2O_3 Polymer Composites as a Replacement for Concrete and Gypsum at Diagnostic Photon Energies. *Journal of Radiation Research and Applied Sciences* **2023**, *16* (4), 100707–100707. https://doi.org/10.1016/j.jrras.2023.100707.
[37]Gayatri Panthi; Rishikesh Bajagain; Dhiraj Kumar Chaudhary; Kim, P.-G.; Kwon, J.-H.; Hong, Y. The Release, Degradation, and Distribution of PVC Microplastic-Originated Phthalate and Non-

Phthalate Plasticizers in Sediments. *Journal of hazardous materials* **2024**, *470*, 134167–134167. https://doi.org/10.1016/j.jhazmat.2024.134167.

[38]T. Kimura *Kobunshi Kagaku* **20** (1963) 65

[39] Yassin, A. A.; Sabaa, M. W.; Mohamed, N. A. Polymerization Products of P-Benzoquinone as Thermal Stabilizers for Rigid Poly(Vinyl Chloride): Part I—Preparation of the Stabilizer. *Polymer Degradation and Stability* **1985**, *13* (2), 167–181. https://doi.org/10.1016/0141-3910(85)90066-7.

[40]Yassin, A. A.; Sabaa, M. W.; Mohamed, N. A. Polymerization Products of P-Benzoquinone as Thermal Stabilizers for Rigid Poly(Vinyl Chloride). Part II—Evaluation of the Stabilizing Efficiency. *Polymer Degradation and Stability* **1985**, *13* (3), 225–247. https://doi.org/10.1016/0141-3910(85)90011-4.

[41]Yassin, A. A.; Sabaa, M. W.; Abdel-Naby, A. S. Cyanoguanidine and Its Complexes as Thermal Stabilizers for Rigid Poly(Vinyl Chloride). *Polymer Degradation and Stability* **1991**, *31* (2), 189–202. https://doi.org/10.1016/0141-3910(91)90074-2.

[42]Yassin, A. A.; Sabaa, M. W.; Abdel-Naby, A. S. Cyanoguanidine and Its Complexes as Thermal Stabilizers for Rigid Poly(Vinyl Chloride). Polymer Degradation and Stability 1991, 31 (2), 189–202. https://doi.org/10.1016/0141-3910(91)90074-2.

[43]Starnes, W. H.; Plitz, I. M. Chemical Stabilization of Poly(Vinyl Chloride) by Prior Reaction with Di(N-Butyl)Tin Bis(N-Dodecyl Mercaptide). Macromolecules 1976, 9 (4), 633–640. https://doi.org/10.1021/ma60052a021.

[44]Kelkar, D. S.; Balasubramanian, V.; Kurup, M. B. Electrical and Structural Properties of Ar+ Implanted Nylon-6 Films. *Polymer International* **1997**, *42* (4), 393–396. https://doi.org/10.1002/(sici)1097-0126(199704)42:4%3C393::aid-pi729%3E3.0.co;2-3.

[45]Kong, C.-S.; Yoon, G. H.; Khang, G.; Rhee, J. M.; Lee, H. B. Stabilization of Nontoxic PVC Formulation for Gamma Irradiation Sterilization, II. Effect of Antioxidants. *Bio-medical materials and engineering* **2002**, *12* (3), 211–224.

[46]PINNER, S. H. Enhancement of Radiation-Induced Cross-Linking of Polyvinyl Chloride. *Nature* **1959**, *183* (4668), 1108–1109. https://doi.org/10.1038/1831108a0.

[47]Fakhreia Al-Sagheer; Ahmad, Z. Stabilizing Poly(Vinyl Chloride) Using Its Blends with Poly(Methyl Methacarylate): Pyrolysis GC/MS Studies. *Journal of Hazardous Materials* **2014**, *278*, 584–591. https://doi.org/10.1016/j.jhazmat.2014.06.024.

[48]Avcıoğlu, C.; Avcıoğlu, S. Transition Metal Borides for All-In-One Radiation Shielding. *Materials* **2023**, *16* (19), 6496. https://doi.org/10.3390/ma16196496.

[49]Charlesby, A. Use of High Energy Radiation for Crosslinking and Degradation. *Radiation Physics and Chemistry (1977)* **1977**, *9* (1-3), 17–29. https://doi.org/10.1016/0146-5724(77)90070-x.