Chapter I
Introduction

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1.1 Biodegradable Polymers

Currently, conventional synthetic polymeric materials are being consumed worldwide in nearly all horizons of routine life. However, the nature of such fabricated materials being non-biodegradable because produced from petrochemicals. The production amount of synthetic non-biodegradable polymers in the range of million metric tons is used either for short or long term purposes and cause environmental pollution. Physical recycling of non-biodegradable polymer is undesirable and impractical due to an immense amount of water and electrical energy consumption. Also, disposal, recycling, and storage of such materials after used raise the challenges against waste management and ecologist to cultivate cost-effective and eco-friendly solid waste disposal. Concerning the adverse environmental impact of conventional polymeric materials, it is being necessitated to exploit ecological, biodegradable, and renewable resource-based materials. Hence, the development and implication of *Biodegradable Polymers* in different sectors are quite obligating due to minimal environmental impact as well as exhibiting bioactive degradation or decomposition by bacteria, fungi, and algae microorganisms via the enzymatic process. Also, biodegradable polymers are sustainably recycled into natural substances, CH_4, CO_2, biomass, water etc. via biological routes [1]. Hence, the scientific and industrial inventions concern captivation pursuit and objectives associating the biodegradable polymers.

1.1.1 Classification of Biodegradable Polymers

As per ASTM standard D-5488-94d and European norm EN 13432, "biodegradable" means "capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds, and biomass". Biodegradable polymers classified into two categories as shown in Figure 1.1 by considering their origin as (i) Natural Biodegradable Polymers (ii) Synthetic Biodegradable Polymers [2]. Among all these biodegradable polymers, polysaccharides are macromolecules exist in entirely alive organisms in the biosphere. They are optimistic biomass with versatile features like renewable, availability, biocompatible, innocuous, photoresistive, and hydrophilic. They can acquire from massive class natural origins and are composed of

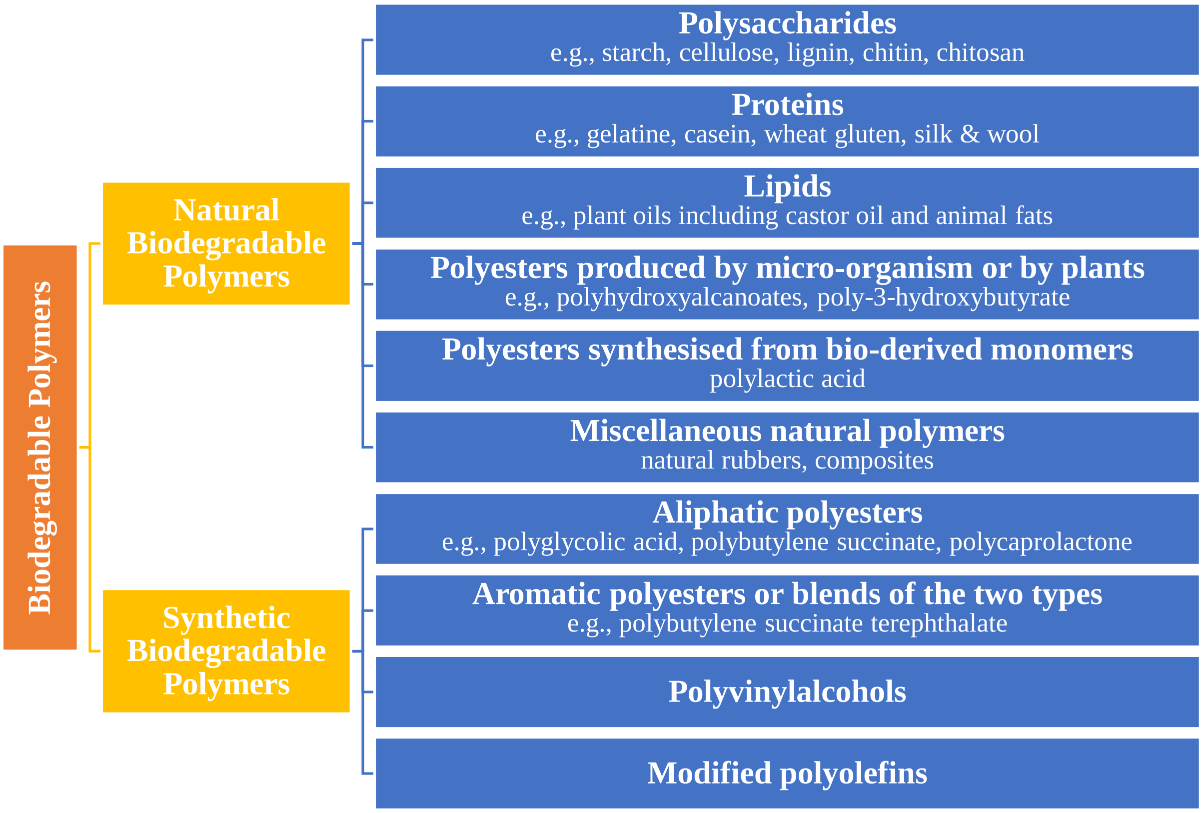

Figure 1.1 Classification of biodegradable polymer as per origin.

monosaccharide units linked collectively by glycosidic bonds. Even with the structural similarities between different polysaccharides, they can be characterized by molecular weight, composition, and stereochemistry and/or site of the glycosidic bond. Depending on repeating monosaccharides, polysaccharides are categorized as homopolysaccharides having a single type of monosaccharides and heteropolysaccharides having more than one type of monosaccharide. Among the existing polysaccharides, chitin and its derivative chitosan, cellulose, and starch are being exclusively studied biopolymers for the fabrication of a wide spectrum of functional/hybrid materials [3]. The physicochemical behavior of these materials are entirely diverse due to different functional groups present in each saccharides unit viz. cellulose and starch associating OH group, while chitin and chitosan associating $NHC(=O)CH_3$, NH_2 functional groups respectively [3]. The functional group of polysaccharides along with naturally existing hydroxyl group provide the reactive sites to obtain the tailor-made functional materials for wide span applications in diverse fields.

1.1.2 Chitosan

Chitosan (pronounced ky-toe-san) is an amino-polysaccharide bio-polymer with advantages of biodegradability, biocompatibility, non-toxicity, and bio-renewability. It is derivative by deacetylation from chitin, which is the second most abundant polymer on the biosphere extracted from the shells of crabs, shrimp, prawns, and other crustaceans. Chitin was first discovered by Branconnot in 1811, however, it could not attain much research concern in comparison with alike cellulose due to structural rigidity and impregnable to common solvents. Later on in 1859, the French physiologist Charles Rouget discovered the chitosan from chitosan by stripping acetyl down. Chitosan (CS) is being used in diverse fields due to its excellent film-forming ability, cost-effectiveness, abundant availability, and potentials of being processable into various forms like microparticles, nanoparticles, membranes, gels, nanofibers, beads, and scaffolds [4]. Also, an advantage of ensuring dilution in diluted aqueous acidic solvents below pH 6.3 through the protonation of amine groups of chitosan macromolecule [5].

Presently, chitosan being used in numerous utilisations as a color removing agent from the waste of textile productions strong affinity of protonated amine group to trace the negatively charged dye molecules [6]. Chitosan is also used in wastewater treatment for the elimination of heavy metal owing to an excellent chelating capability [7]. It is exclusively used in medical, pharmaceutical, cosmetic, and bioengineering fields due to excellent biological properties such as biodegradable, biocompatible, and loading efficiency of organic and/or inorganic materials [8]. The chitosan-based films have attained huge growth in food packaging applications as barrier films, antibacterial films, and sensing films [9]. Chitosan is used as high-performing and low-priced membrane materials for proton exchange membrane fuel cells [10]. Chitosan is being utilized as a polymeric host matrix in recent advancements and innovations in electrochemical, energy storage, and electronic equipment insisted tractability, ultrathin, low-weight, and ecological multifunctional materials [11]. However, the glass transition temperature of pure chitosan is higher (203 °C) [12] indicting rigid and brittleness nature resulted in low electrical conductivity substantially limited its utilization as a host matrix. Additionally, chitosan matrix exhibits considerably lower intrinsic conductivity due to inadequate protonation of weak alkaline groups, i.e. $NH_2 + H_2O \leftrightarrows \mathrm{N}H_3^+ + OH^-$ [10]. The versatile functionalization of chitosan-based materials is becoming quite fascinating to resolve its particular shortcoming by various approaches in different fields drawn immense attention from the research and development communities [4–9,11,12]. Modification of pseudo-natural polycationic chitosan is feasible due to the amenable and reactive functional amine (–NH_2) group plus primary and secondary hydroxyl (–OH) groups [4,6,7,9–11,13,14]. Modification of chitosan altered its physicochemical, optical, biological, surface, and dielectric responses.

1.2 Modification of Chitosan

The prompt progress in the modification of chitosan implies wide span perceptions of the modified chitosan. Chitosan, in an acidic medium, behaves as a natural electrolyte thanks to protonation of –NH_2 groups belong to chitosan macromolecule. The presence of two chemically active groups of chitosan provided a diverse route to enhance its characteristics or to obtain novel desired properties.

1.2.1 Chemical Modification

Chemical modification of chitosan is a complex phenomenon affecting the structural prospects of vital groups by introducing the functional molecule. The chemical modification is achieved by grafting functional molecules, which is possible due to a longer polymeric chain of chitosan concerning designed molecules. The chemical modification of chitosan being reviewed by many authors emphasizing several aspects [8,14–16].

1.2.1.1 N-Substitution

The reactive sites for the designed molecules belong to the amino group of chitosan is called *N-substitution*. Thanks to the immense reactivity of amino groups, the N-substitution approach to modify the chitosan become a suitable and promising one. This approach is generally attributed to the rupture of stronger inter and intra-molecular hydrogen linkages [8]. As a result, the solubility of chitosan improved at neutral or high pH solvents as well as in distilled water and organic solvents [16].

1.2.1.2 O-Substitution

The reactive sites for the designed molecules belong to the hydroxyl group of chitosan is called *O-substitution*. Since the hydroxyl groups have lower reactivity concerning the amino groups, designed molecules for O-substitution can also react with the amino groups of chitosan as well

[17]. Hence, this kind of reaction becomes complex and performed in a constrained condition with well-defined parameters able to control the activity between designed molecules and amino groups.

1.2.1.3 Free Radical Graft Copolymerization

The chemical modification of chitosan is achieved by a designed synthetic macromolecular chain linked with chitosan as side chain(s) called *free radical graft copolymerization* [8,15]. This kind of reaction is initiated by generating free radical sites on the chitosan chain whereby synthetic monomer of the synthetic polymer can react with the radical to transmit into a new polymer chain that is covalently linked to the chitosan polymer [18]. Grafting of chitosan being implemented through diverse approaches viz. chemical, gamma rays and plasma-induced, photochemical and enzymatic grafting [14]. This approach of modification emphasizing the opportunities of developing novel polymer matrix possess permanently united properties of both polymeric chains [8,14,15,18].

1.2.2 Physical Modification

Physical modification of chitosan is a straightforward approach involving the physical mixing of organic and/or inorganic composites interacting with the fundamental functional groups of chitosan macromolecules. Plenty of research communities used this methodology owing to facile, timesaving, efficient, and cost-effective route. According to the chemical nature of additive, classified into two categories (i) organics (ii) inorganic [19]. The additive based on organic includes natural polymers, synthetic polymers, carbon, and graphite. The additive based on inorganic takes account of oxides, hydroxides, silicates, metals, and salts. Based on additive, distinctive methodologies are being instigated to improve the properties and veracities of the chitosan in various filed as per preferred necessities.

1.2.2.1 Blending and Crosslinking

A route of instigating chitosan with another natural/synthetic polymer(s) with/without any chemical linkages is called *blending*. Polymer blending is an efficient way to achieve physical modification [14]. Chitosan as a blend component in chitosan/polymer blends, facilitate efficient physicochemical, dielectric, mechanical, and thermal properties, high strength, low density, processability, morphological, and biological properties [8,11,20]. The miscibility or compatibility of the blend matrix depends on intrinsic groups of involved polymers, polymer composition, molecular weight, and additives level as well as method and condition used for preparation [21]. Incompatibility between two polymers may be elevated due to feeble interfacial adhesion, different polarities, particular group interactions, and the difference in molecular weight [22]. Chitosan-based blends being a common theme in several reports by concerning performance and processability to obtain superior and unique matrix [14,20–22]. The advantages of blending are economical, time-saving, and engineered easily as per strategy by varying ratios of starting materials.

The modification of chitosan by the formation of chemical linking between monomers of the chitosan or with a molecular chain of different polymer to form a stronger three-dimensional network is called *crosslinking* [23,24]. The crosslinking of polymeric materials achieved through crosslinking agents, which can be classified as chemical, physical, enzymatical [25]. Moreover, the physical crosslinking of polymer observed upon radiation treatments. The crosslinker being surged during the formation of the assembly to bestow novel properties and functions at one stage as well as can be used afterward the formation process.

1.2.2.2 **Composites**

Materials that comprise of at least two physically and chemically different phases detached by a distinct interface is referred to as composites [19]. In the composites, the constituents remain identifiable, while that of in the blend matrix may not. Composites are combinations of materials differing in composition, where the individual constituents retain their separate identities [26]. As an additive, organics and inorganics materials being incorporated with the chitosan matrix. Chitosan matrix composites depend on the orientation and shape of embedding additive as well as the extent of interfacial adhesion. The functional groups of chitosan, particularly the protonated amine group, provided good possibilities of tailor-made composite owing to substantial electrostatic interaction with metals, salt, ceramic, hydroxides, silicates, etc. As per the size of filler, classified as macro-composites, micro-composites, and nano-composites. Particularly, within this quickly growing field, the emergence of nanocomposites found to be outstanding to bestow advance properties and functions of chitosan in the field of biosensors, catalysts, food packaging, medical and pharmaceutical applications, electro-optical devices, electrochemical devices, electronic devices, and as the electrolyte in the battery, capacitor, fuel cell [11,14,27,28].

1.2.2.3 Radiation Induced Modification

Ionizing radiation stands out as an advanced tool being enthusiastically pursued as an appealing methodology to modify the chitosan in a well-controlled manner. From the type of radiation viewpoint, chitosan is subjected to UV and gamma irradiation, electron beam as well as low and high energetic ion irradiation for expansion of functionalities [29]. The radiation treatment to modify the chitosan-based matrix can be facilitated in both ex-situ and in-situ approaches. Radiation yields irreversible changes during the interaction with the matter by depositing energy via various cascades and the impact of modification depends on radiation parameters. Upon UV and gamma irradiation, the molecular weight of chitosan considerably influences, and surface morphology also reform excepting the bulk properties. Plasma treatment is also used at low pressure with the specific setup to attain certain surface reform to fulfill the demand for particular relevance. Materials reformation and nature of defects created upon energetic ions irradiation was greatly different from UV, gamma, and electron beam irradiation. The ions with energy in the MeV range depositing tremendous energy in diminutive period yielding revolutions in the surface and bulk properties owing to the formation of low-molecular-weight free radical and ions, cross-linking, scission of bonds, carbonization along with the liberation of volatile gases and creation of color centres [30]. The structural rearrangement at macro-level yield modification in optical, structural, dielectric, surface, and thermal response of the chitosan matrix [29,30].

1.2.3 Concluding Remarks

The progression of polymer and polymer-based matrix embraces the invention and expansion of novel methodologies that provide functional applications. In the functionality domain, the chitosan-based matrix according to necessity is being predominantly modified via chemical and physical approaches. The chemical modification evolved a certain environment for reaction along with initiator, reactive agent, and catalyst, just to name a few. There is involvement of several steps along with the formation of stoichiometric waste after the reaction. Also, chemical modification involved many parameters that make the characterizations and explanations quite complex and difficult. Eventually, the central objective behind the exploitation of renewable-based resources loses its appealing goals as it may go through manipulations with non-renewable materials. Physical modification is a facile and mild route contrary to chemical one owing to the absence of involved chemicals and the purification process of the ultimate outcome. Physical modification belongs to additive either organic or inorganic, which can be implemented within the chitosan matrix. The addition of filler within the matrix can be possible up to a certain extent, thereafter, the matrix becomes irresponsive. Hence, it is being necessitated to modified the chitosan-based matrix via radiation treatments, particularly with MeV ions, which in terms, an advanced and multipurpose tool to modulate and enhance the optical, structural, and dielectric responses in a well-controlled and constrained environmental to expand the new era of chitosan-based material in a broad spectrum of the discipline.

1.3 Swift Heavy Ions Irradiation

All life has existed in a biosphere surrounded by radiation. Radiation, existed all along, classified as (i) non-ionizing and (ii) ionizing radiations in accordance with energy having an ability to ionize the matter. The radiation is a form of energy deposited during the passage through matter yield slight atomic vibration or shift in the molecule apart from knocking out the orbital electron referred to as *non-ionizing radiation*. It is originated from natural sources such as the sun and discharge of lightning as well as from man-made sources such as medical therapy, research and industrial development, and electronic appliances [31]. The radiation having abundant energy able to knock out the orbital electron of the atom and creating ions along its trajectory within the materials is referred to as *ionizing radiation*.

Ionizing radiation, viz. electromagnetic (e.g. UV, X-ray, or gamma-ray) as well as a particle (electron, neutron or charged species) during the interaction with any class of polymeric matrix yield modified materials owing to deposition of energy at macro-level. Specifically, the deposited localized energy density to the matrix by electromagnetic radiation is rather small and hence it may transform the materials up to a certain extent through photooxidative degradation. Swift heavy ions (SHIs) moving at a velocity comparable to the Bohr velocity of the electron [32] and depositing tremendously high localized energy density within a very small volume (~10^{-17} to 10^{-16} cm^3), in a very short time (~10^{-17} to 10^{-15} s) [33]. Moving SHIs of energy in order of MeV (>10 MeV) through the polymeric system forming nanometer-scale track shaped damage or molten cylindrical zones possess ions, electrons, radicals, and polymeric chains [33]. The essential inside the molten zones prominently depends on the ion beam parameters and yield engineered matrix. Consequently, as polymer matrix returns to its equilibrium solid form yielding macroscopic changes viz. optical, structural, dielectric, surface, thermal properties, etc. Therefore, by governing the informed choice of the energy, mass, fluence, and ion species of the SHIs, one can functionalize the matrix of interest.

1.3.1 SHIs Interaction with Matter

Particular revolutionary inventions initiated with SHIs associating different energy before one or two decades, now become a giant tree with fruitful applications in material science such as synthesis, modification, and characterizations. Fundamental of SHIs interaction with matter depends on projectile energy ranging from few eV to hundreds of MeV, accordingly applied as a vital and advanced tool to engineer the material shown in Fig 1.2. SHIs as a tool to engineer the properties of the material obliges substantial changes in the materials' responses such as optical, structural and dielectric, etc. Generally, the modification of material in highly controlled mode evolved approach of soft engineering and can be fulfilled by varying beam parameters. To engineer the materials, the SHIs with higher energy use with an appropriate range of ion fluence vary from 10^6 to 10^{13} ions/cm^2 or even further can be achieved with a

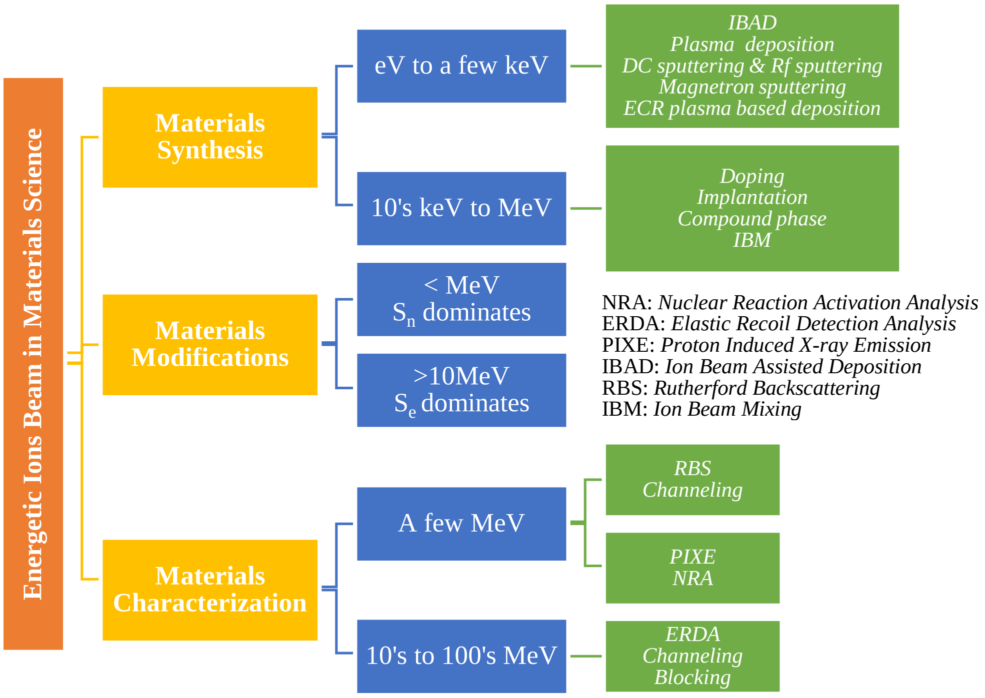

Figure 1.2 A schematic of the role of ion beam in materials science.
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beam current of few pnA. Fundamentally, SHIs, all the way through the material, continuously losing energy through elastic and inelastic collisions with atoms in the target materials. The energy of SHIs along with its trajectory in matter losses mainly through excitation and ionization of atom plus nuclear collisions [34].

1.3.1.1 Excitation and Ionization

SHIs at higher velocities, fundamentally transmit energy to the electrons of the target atoms during transit through material yielding excitation and ionization of target atoms is referred to as *electronic energy loss or inelastic energy loss* [$(-dE/dx)_e$ or S_e] [32,34]. As per Bohr approach, the charge state of the ion estimated by using the equation [35]:

$$\left(\frac{q}{Z}\right) = \left(\frac{v}{v_0\, Z^{2/3}}\right)$$

Where q is charge state, Z is a projectile atomic number, v_0 is Bohr velocity of the atomic electrons (2.188×10^8 cm/s). For $v < v_0 Z^{2/3}$, Z^* is less than Z and S_e subjected to velocity or energy of the projectile varied as per $S_e \propto v$ or $S_e \propto E^{1/2}$. As velocities increasing, the charge state of the projectile ion accordingly increases, and eventually, all the electron from the ion stripped off for the case of $v > v_0 Z^{2/3}$. Also, S_e depends on an atomic number of projectile ion along with velocity or energy as per $S_e \propto Z^2$ and $S_e \propto (1/v^2)$ or $S_e \propto (lnE/E)$, respectively [35].

1.3.1.2 Nuclear Collision

The projectile ion with energies lower than 1 MeV, fundamentally transmitted energy to the target nucleus by elastic collision, and consequently the target atom recoils is refer as *nuclear energy loss or elastic energy loss* [$(-dE/dx)_n$ or S_n] [32,34]. The ion tends to elastic collisions with the target nuclei, traveling with velocities, v, that of less than v_0. Also, ions surround their electrons and get neutralize via electron capture. If ion possesses energy greater than the certain threshold energy revealed atomic displacement, unless, the energy dissipates as atomic vibrations (i.e. phonons). During derivation of S_n, the interatomic potential between pair of the atom and the momentum transfer from ion to target taken into account. Hence, S_n influenced by ion velocity and charge state of two striking atoms. S_n attained higher magnitude at the end of the cylindrical track due to the fall of velocity [36].

1.4 Importance and Literature Review of Chitosan-based Matrices

1.4.1 Chitosan-based Polymeric Matrices

As discussed, pristine chitosan as well as its blend significantly being modified in various sectors for the fulfillment of certain requirements. The acetate or non-neutralized form of chitosan is favored in many fields due to the advantage of dilute acetic acid existing in the matrix. Chitosan is used in the pharmaceutical and medical field due to being natural antibacterial responses enhance in the acetate form [37]. Chitosan film in acetate form use in the technology of wearable electronics and as SPEs for battery and cells due to proton conductivity depends on the acetic acid concentration used for the preparation of film-forming solution [38]. This information may help develop flexible electronics, solid polymer electrolytes for fuel cells, and solid polymer batteries based on CS-acetate film. Also, the non-neutralized film revealed great potential of metal ions ($AgNO_3$, $CuNO_3$, $HAuCl_4$) reduction into size-dependent metallic nanoparticles particle distribution have an advance optical and electrical properties, its applications in wound dressing and drug, as catalysts and biosensor and electronic devices [39]. Also, owing to dilute acetic acids, exhibits the capability of ionic conductivity used as polymer electrolytes in electrochemical and electronic appliances.

Sionkowska et al. [40] modified the surface morphology of the chitosan matrix by UV irradiation and revealed alteration in surface free energy and the contact angle. Ulanski et al. investigated the gamma effect on chitosan in solid and aqueous states. After irradiation, a reduction in the molecular weight along with an increase in absorption is observed in the solid-state of chitosan [41]. Lim et al. [42] irradiated chitosan fibers and films by gamma-ray up to 25 kG and revealed a decrease in average molecular viscosity and a decrease in glass transition temperature with the main chain scissions upon irradiation. Ramnani et al. [43] exposed the chitosan in the presence of sensitizing CCl_4 by gamma radiation to acquire the crosslinked chitosan. Garcia et al. [44] examined momentous glycosidic bond cleavages without affecting the functional groups' altimetry yield chitosan with diminished molecular weight upon gamma irradiation at different doses. Gryczka et al. [45] discussed the degradation mechanism of chitosan upon gamma and electron beam irradiation.

Wanichapichart et al. studied the effects of low-energetic (15–30 keV) nitrogen ions on the filtering performance of the chitosan membrane. The outcomes of the experiment showed improved charge splitting for filtering excellence with enhanced hydraulic permeability and selectivity of negative ion. Kim et al. [46,47] reported controlled modification of molecular weight and later on its effect on the chemical, physical responses of chitosan upon proton irradiation (30–40 MeV). Prakrajang et al. [48] irradiated the chitosan membrane with Ar and N ions (15–25 keV) and consequent modification in surface morphology, contact angle, and electrical characteristics were carried out aiming the simulation of DNA transfer in the plant cells. Wanichapichart et al. [49] further explored the low energetic Ar and N ions (30 and 120 keV) influence on the chitosan membrane and observed surface modulation resulted in diminished pore area and permeate fluxes.

Moreover, a physically modified chitosan-based blend matrix with biocompatible and water-soluble PEO polymer being explored in many fields for different desired. Optically enhanced, flexible, and homogeneous self-sustained chitosan/PEO (CP) blend matrix obtained through effective interaction between proton donor amino group of chitosan and proton acceptor ether group of PEO. The existence of chitosan chains yields diminished crystallinity and also these matrix does not result in phase separation. Hence, the chitosan-based polymeric matrix with improved dielectric and optical responses can be emphasized in vast electrochemical applications owing to the amorphous state, which facilitates significant conductivity [27].

Zivanovic et al. [50] investigated the physical, mechanical, and antibacterial properties of the CP blend and concluded that the antibacterial response and tensile strength were subjected to chitosan composition. Li et al. [51] studied CP films performance concerning film thickness, the ratio of composition, and synthesis procedures. Shukur et al. [52] prepared CP blends incorporated with ammonium nitrate and concluded that it can be used as an electrolyte in advance of electrochemical devices. Cassani et al. [53] prepared a tailor-made electrodeposited biopolymer CP blend and explored its physicochemical and nano-mechanical properties as a function of constitute composition. Buraidah et al. [54] revealed CP blend embedded with ammonium iodide employed for plasmonic dye-sensitized solar cell because conductivity enhanced upon blending as a result of enriched flexibility and ions mobility.

Recently, Kowalonek [55] discovered UV irradiation assisted photooxidation of CP blend. He concluded that the effects of radiation on surface and thermal characteristics are strongly subjected to blend composition. Kianfar et al. [56] investigated alteration in thermal, morphology, and water resistance behavior of the CP blend developed by the electrospinning technique upon UV treatment.

1.4.2 Chitosan-based Solid Polymer Electrolyte

At the beginning of 1970, the innovative and progress initialed in the field of glass, ceramic, and polymer electrolytes evolving solid-state materials. Due to being good ion conductivity, electrolyte materials found promising and immense utilization in various sectors. Polymer electrolyte firstly reported in 1973 by Fenton et al. and its advanced conducting attribute explored in 1975 by Wright et al. and later such kind of materials realized they are eventual in electrochemical devices [57]. Polymer electrolyte is a membrane/film bearing dissolved charged or chargeable groups of salts in a higher molecular weight polymeric matrix. As per origin, either natural or synthetic one used as a polymer electrolyte host matrix. Also, it is chiefly categorized according to the physical state and used composite materials as (i) solid polymer electrolytes (SPE$_S$) (ii) composites polymer electrolytes and (iii) gel polymer electrolytes. SPEs have certain advantages over liquid electrolytes such as no leakage and corrosion, flexibility, low weight, transparency, ease of processing, and operative at a higher temperature. SPEs have several functionalities belongs to electrochromic and electrochemical as well as in electronic devices, for instance, electrochromic windows, electrochemical sensors, batteries, solar and fuel cells, supercapacitors, etc. [27].

The chitosan biopolymer is being utilized as a solid polymer electrolytes (SPEs) host matrix. Due to functional groups with oxygen and nitrogen atoms possess a lone pair of electrons, facilitate chitosan to form complexes with the salt. Hence, they are being studied for technological development in the field of batteries, supercapacitors, sensing devices, fuel cells, electrochemical cells, etc. Chitosan-based SPEs predominantly reported on different salts with cations H^+, Li^+, N^+, K^+, Mg^{+2}, Cu^+, Ag^+, Au^+ and NH_4^+ etc. SPEs with Ag^+ ions are of specific concern owing to their unique optical and electrical characteristics. We are particularly interested in silver nitrate ($AgNO_3$) salt due to the advantage of good complexation with polymeric matrix, eco-friendly, low-toxic, and non-inflammable nature. Another reason for favoring the silver nitrate salt as it has been rarely investigated in the SPE system with chitosan as a host. Morni et al. [58] studied the functioning of silver nitrate doped chitosan-based electrochemical cells and concluded that it can be used as an electrolyte for the fabrication of solid-state batteries. Yulianti et al. [59] observed improvement in the electrical properties of chitosan-based polymer electrolytes synthesized via a low energetic ion implantation approach with Li, Cu, and Ag ions species.

1.4.3 Chitosan-based Polymer Nanocomposites

The discipline of nanotechnology and nanocomposites science are the prevalent sector for its novel applications and advancement in the discipline of polymer science. This field evolves strategy, synthesis methodology, characterization, and utilization of materials having dimensions in the nm range. The term *"nanocomposites"* first coined in 1970 by Theng and in the late 1980s, this sector gained attention and pursuit from industrial and academic aspects [60]. The term *"nanocomposite"* is used in a scientific report by Komarneni in 1992 and afterward universally used in routine [61]. As per the preferred assembly for the purpose of improvement through nanocomposites, it is mainly classified as polymer matrix composites, ceramic matrix composites, and metal matrix composites [62]. Progress in polymer science involved a broad spectrum of the topic along with the obvious implementation of nanotechnology. Polymer matrix nanocomposite is one of the promising candidates belongs to cultivating and novel field of advanced and hybrid materials with sophisticated chemistries. The multiphase assembly of a polymer matrix and an inorganic dispersive phase that has at least one dimension that is smaller than 100 nm referred to as polymer nanocomposites.

Due to growth strategies and approaches toward the implementation of eco-friendly and green polymeric materials in everyday life, global research communities devoted noteworthy efforts to overcome some challenges would now expand the horizon of innovations and applications of novel natural polymers based nanocomposites materials with desired responses. Chitosan is an excellent candidate as a host matrix for polymer nanocomposites membrane/film because the presence of the free electron doublet on the nitrogen of amino groups, and hydroxyl groups may also favor the interaction between polymer and nanocomposites. The reinforcement of nanoparticles quite superior to the filler of micro and macro size at equal additive loading. Polymer with nanocomposites exhibits better performance than pristine polymers owing to the substantial specific interfacial area between nanocomposites and polymeric matrix providing extensive binding, known as the "nano-effect" [63]. These effects are attributed to bonding energy at the interface through van der Waals and electrostatic interactions along with hydrogen and covalent bonding [64]. Chitosan-based nanocomposites are widely utilized in the field of electronics, environment, optics, medicine, wearable devices, capacitors, batteries, sensors, electromagnetic shielding etc.[3,4,9–11,21,27,28,38]. Also, this kind of material has advantages such as low-weighted, bendable, compact, eco-friendly, low-cost, and ease of processing. However, the dielectric permittivity of such polymer is moderately low for electronics utilizations. This constraint could be overcome by incorporating various types of filler viz. ferroelectric, ceramic or metallic nanoparticles (NPs) [65–67]. Chitosan has an excellent chelating mechanism that could interact with many metallic NPs such as gold, silver, platinum, and palladium [68]. Besides, Silver nanoparticles (Ag NPs) gain specific consideration due to unique optical, electrical, biological, and thermal properties subjected to size, shape, aspect ratio, surface chemistry, and distribution [69]. Hence, assembly of chitosan embedded with Ag NPs consequently yield a matrix with unique and curious responses. There are different methodologies being employed for synthesis of chitosan–Ag NPs matrices, namely, chemical reduction, green reduction, sol-gel reaction and UV, gamma, and microwave irradiation. There are diverse physical and chemical techniques being used and invented for the preparation of Ag NPs embedded chitosan matrices. In the chemical approach, Ag NPs formed by reduction of silver-based salts by employing reducing agents under certain environments. However, this approach may evolve toxic, and residual may affect the functional groups yields physicochemical and electric responses may violate eco-friendly and non-toxic purpose behind such materials. During the synthesis, chitosan itself acts as both reducing as well as capping agents in polymeric matrices [70].

González-Campos et al. [71] studied the relaxation process by means of thermal and dielectric behavior of chitosan-AgNPs as a function of NPs loading and moisture content. Prokhorov et al. [72] explored the conductivity of chitosan-AgNPs system concerning percolation mechanism as well as temperature dependant responses of the matrices. González-Campos et al. [73] carry out the correlated study of electrical properties to antibacterial activity of neutralized chitosan-AgNPs matrices as a function of additive level of AgNPs. Kumar-Krishnan et al. [74] investigated comparative responses of antibacterial and electrical of silver ions and silver nanocomposites within chitosan matrices.

Furthermore, the blend of chitosan with PEO, a biocompatible, and semicrystalline nature, has been studied by many researchers [50,51,75–77]. Depending on the composition ratio of chitosan and PEO, the blend matrix may either miscible or immiscible. The miscibility or compatibility of polymers depends on functional group, polymer composition, molecular weight, and additives level. Incompatibility between two polymers may exist due to feeble interfacial adhesion, different polarities, particular group interactions, and the difference in molecular weight [22]. Consequently, to prepare the polymeric blend with optimum responses, the different compatibilizing agent is being used viz. organic (i.e. block copolymers, plasticizer, reactance) and inorganic (i.e. layered silicate, metallic nanoparticles, carbon nanotubes) fillers. By dispersing the AgNPs in CP blend may interact with functional groups of individual polymer yielding the affinity of the polymers for each other. Hence, the structural, optical, and dielectric properties of the polymeric blend upon addition of NPs significantly changed as a function of additive level [77].

Bonardd et al. [77] prepared the CP blend with Au NPs matrices via solution casting approach. They concluded that the presence of gold nanoparticles enhance blend miscibility along with modification in structural, thermal, and surface morphology.

1.5 Objective

The self-standing biodegradable matrices based on chitosan have been prepared *via* solution casting approach. As per the constitutes of the prepared matrices, we have divided in three categories as (i) Chitosan-based Polymeric Matrices (ii) Chitosan-based Solid Polymer Electrolyte (iii) Chitosan-based Polymer Nanocomposites. To study the SHIs irradiation induced modification in prepared matrices as a function of beam parameters, explicitly, mass, energy, electronic energy loss, and fluence, two distinct C^{+5} (60 MeV) and Ni^{+7} (100 MeV) ions were selected for irradiation. As a consequence, the structural response of post irradiated matrices is discussed using XRD and FTIR spectroscopy. The change in optical characteristics is explored using UV-visible absorption spectroscopy. The polymeric surface in many disciplines is an imperative and key aspect altered upon energetic ions induced capably reconnoitered using SEM and AFM. The relaxation and conductivity mechanisms upon MeV ions irradiation radically affected and studied using different dielectric formalisms across broad frequency window in accordance with structural, morphological, and optical rearrangements and modifications. Inclusively, we aim to investigate the functionalized eco-friendly biodegradable polymeric matrices by well-controlled irradiation technique and are hence of prominence for applications in material and biomedical disciplines.

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