

GREEN GRAFTING

INNOVATIONS IN POLYMER FUNCTIONALIZATION FOR
SUSTAINABLE SOLUTIONS IN THE PHARMACEUTICAL
AND HEALTHCARE INDUSTRY

PART 1



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**Green Grafting: Innovations in
Polymer Functionalization for
Sustainable Solutions in
Pharmaceutical and Healthcare
Industry**

(Part 1)

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PREFACE

The first part of *Green Grafting: Innovations in Polymer Functionalization for Sustainable Solutions in the Pharmaceutical and Healthcare Industry* marks a significant step forward in promoting sustainability within polymer science, drug delivery, and healthcare materials. This part serves as a comprehensive introduction to the fundamental principles of green grafting, integrating concepts of polymer chemistry, eco-friendly synthesis, and material functionalization with the overarching goals of environmental stewardship and technological advancement.

The chapters in this volume establish the core theoretical foundation for understanding how grafting techniques can be adapted to meet the tenets of green chemistry, focusing on minimizing hazardous substances, utilizing renewable feedstocks, and enhancing biodegradability. The content encompasses the basic mechanisms, methods, and characterization techniques of polymer grafting while illustrating their relevance to pharmaceutical and healthcare innovations.

In addition, Part 1 explores the relationship between chemistry and sustainability, showcasing how the fusion of polymer science and green chemistry principles enables the creation of safer, more efficient, and environmentally responsible materials. The authors highlight pioneering work in renewable resources, eco-friendly solvents, and sustainable grafting methods that not only improve product performance but also reduce environmental impact.

This first part serves as the foundation for advanced exploration in Part 2, where the focus shifts toward specialized applications, industrial scalability, and future prospects. Together, both parts form a unified and forward-looking resource that embodies innovation, responsibility, and interdisciplinary collaboration in sustainable polymer research.

We extend our sincere gratitude to all the contributors, reviewers, and the Bentham Books editorial team for their invaluable contributions and support throughout the preparation of this volume. Their collective efforts have helped shape this book into a meaningful scientific reference for academicians, researchers, and industry professionals striving toward a more sustainable and innovative future.

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Introduction to Green Grafting

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Abstract: Green grafting is an innovative approach in the realm of polymer functionalization, focusing on the integration of eco-friendly processes and sustainable materials to advance the pharmaceutical and healthcare industries. This introductory chapter provides a comprehensive overview of green grafting, outlining its principles, methods, and applications. Emphasis is placed on the environmental and economic benefits of adopting green grafting techniques, such as reduced carbon footprint, enhanced material efficiency, and minimized use of hazardous chemicals. The chapter delves into the chemistry of green grafting, exploring various green solvents, catalysts, and renewable resources employed in the functionalization of polymers. Key advancements in the field, including the development of biodegradable polymers and biobased grafting techniques, are thoroughly discussed. Furthermore, the chapter highlights the significant role of green grafting in enhancing drug delivery systems, medical devices, and tissue engineering. Through a series of case studies and real-world applications, the transformative impact of green grafting on sustainability in the pharmaceutical and healthcare sectors is demonstrated. The chapter concludes with a discussion on future directions and potential challenges, emphasizing the need for continued innovation and interdisciplinary collaboration to fully realize the benefits of green grafting in creating sustainable solutions.

Keywords: Biodegradable polymers, Drug delivery systems, Green chemistry, Polymer functionalization, Sustainable solutions.

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INTRODUCTION

Overview of Green Grafting

Green grafting refers to the integration of green chemistry principles into the process of grafting, which involves the attachment of one molecular fragment (graft) onto a main polymer chain (backbone) or substrate. The concept of grafting has been extensively used in material sciences and biotechnology to alter or enhance the properties of substrates, such as improving their chemical resistance, mechanical properties, or biocompatibility [1].

Traditional grafting methods often involve the use of toxic chemicals, solvents, and energy-intensive processes that pose significant environmental risks. These concerns have driven research towards more sustainable practices, giving rise to green grafting methods. Green grafting adopts the principles of green chemistry to reduce the environmental impact of the grafting process. It focuses on using environmentally benign chemicals, reducing hazardous waste, and minimizing energy consumption during synthesis. Green grafting offers a sustainable alternative to traditional methods by reducing environmental risks and energy consumption while using safer chemicals. Table 1 provides a comparative overview of traditional and green grafting approaches, detailing the types of chemicals used, health risks, energy demands, and techniques applied. As shown, green grafting utilizes eco-friendly solvents and catalysts, significantly lowering the environmental impact and health hazards associated with traditional grafting methods.

Table 1. Traditional vs. green grafting [3, 4].

Aspects	Traditional Grafting	Green Grafting
Chemicals Used	Hazardous chemicals like benzene, toluene, and heavy metals	Safer alternatives like water-based solvents or bio-based catalysts
Environmental/Health Risks	Significant risks due to toxic chemicals and heavy metals	Reduced risks with eco-friendly chemicals
Energy Consumption	High temperatures and prolonged reaction times	Reduced, using milder conditions
Techniques Used	Free radical polymerization, atom transfer radical polymerization (ATRP)	Optimized methods using microwaves, enzymes, or catalytic systems
Reaction Conditions	Requires high temperatures, leading to greater energy demand	Milder conditions with reduced energy demands
Catalysts/Solvents	Solvents like benzene and toluene, contribute to environmental hazards	Bio-based catalysts and water-based solvents

The shift to green grafting aligns with global efforts to promote sustainability and reduce industrial pollution. It has also opened new avenues for the development of biocompatible materials in industries such as pharmaceuticals, biotechnology, and healthcare, where there is a growing demand for materials that are not only functional but also environmentally friendly [2].

Importance of Green Grafting in the Pharmaceutical and Healthcare Industries

Green grafting plays a crucial role in the pharmaceutical and healthcare industries, where the need for sustainable practices is growing in response to stricter regulations and increasing public awareness about environmental issues. The adoption of green grafting techniques provides a means to develop more sustainable materials for drug delivery systems, medical devices, and tissue engineering applications [3].

Sustainable Drug Delivery Systems

One of the significant applications of green grafting in the pharmaceutical industry is the development of advanced drug delivery systems. Polymers and other biomaterials used in drug delivery must meet stringent safety and biocompatibility standards. Green grafting allows for the synthesis of materials that degrade safely within the body, reducing toxic byproducts and lowering the overall environmental footprint. Grafted polymers can improve the solubility, stability, and targeted release of drugs, enhancing their therapeutic efficacy. By incorporating green chemistry principles, pharmaceutical companies can manufacture drug delivery systems that are not only effective but also aligned with sustainable production goals [4].

For instance, hydrogels and nanoparticles have been explored as carriers for controlled drug release. Through green grafting, researchers can design hydrogels that are synthesized using non-toxic, bio-based solvents and biodegradable polymers. This ensures that the materials break down into harmless byproducts after fulfilling their function in the body.

Green Grafting in Medical Devices

Green grafting is also pivotal in the development of medical devices such as catheters, implants, and wound dressings. These devices often require surface modifications to enhance their biocompatibility, reduce infection risks, or promote tissue integration. Traditional surface grafting techniques used in medical devices can leave residual toxic substances that are detrimental to patient health [5].

CHAPTER 2

Fundamentals of Polymer Grafting: Basics and Techniques

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Abstract: Polymers are gaining more attention due to a diverse range of applications. Crosslinking, co-polymerization, curing, mixing, and blending are various methods of polymer modification. However, the most effective and appealing method for enhancing the morphology, chemical composition, and physical properties of polymers is polymer grafting. Grafting permits modification of the parent structure, which enhances physicochemical properties, compatibility, thermal stability, multiphase response, flexibility, and reactivity of the parent polymer. Grafting includes the insertion of a functional group into the polymer backbone, grafting a sidechain to the polymer backbone, and combining one or more monomers on the polymer with or without an initiator by employing a variety of chemical, biological, and physical activators. The different technique employed in polymer grafting involves ionic grafting, radical generation using free radical polymerization (FRP), reversible addition-fragmentation chain transfer (RAFT), and nitroxide-mediated polymerization (NMP), as well as physical methods like plasma irradiation, UV radiation, photochemical grafting, and biological methods like enzymatic grafting. Polymers functionalized using the grafting technique can be employed in various fields like pharmaceuticals, drug delivery applications, wastewater treatment, tissue engineering, diagnosis, the textile industry, biotechnology, and other fields.

Keywords: Enzymatic polymerization, Free radical polymerization, Grafting polymer, Initiator, Plasma irradiation.

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INTRODUCTION

Polymers are made up of chemically identical units called monomers. Modified polymers have been gaining greater attention in pharmaceuticals, material sciences, textiles, and electronic fields due to their unique applications. Often, polymers are modified by altering their surfaces or by introducing end-terminal functional groups. There are various methods for altering polymer properties, including copolymer synthesis, crosslinking, polymer blending, polymer interpenetrating networks, and grafting. Among these methods, the grafting technique is widely used to alter the physicochemical properties of a polymer. When two or more different monomers are combined to form a polymer, it is called a copolymer, whereas a graft copolymer is created by the process of connecting one or more homopolymer blocks as branches to a primary polymer chain. As a consequence, a branched configuration is formed, where the main backbone is connected to separate homopolymers that serve as side chains [1]. When a graft copolymer has only one branch, it is referred to as a *miktoarm* star copolymer. These graft copolymers might be heteropolymers, which have distinct chemical structures, or homopolymers, which have the same chemical composition as the main polymer chains [2, 3]. Whereas when it is composed of two or more branches, it is referred to as a multi-arm star-shaped copolymer [4]. Grafting is a desirable method for adding different functional groups to a polymer [5]. Therefore, numerous techniques have been demonstrated to enhance the fundamental properties of the polymer backbone under specific conditions [6]. Graft copolymers are primarily utilized for altering polymer characteristics due to their distinct mechanical and thermal properties [2, 3]. Graft polymerization modifies the parent polymer, enabling the adjustment of specific properties without altering its core structure. This technique is commonly applied to both natural and synthetic polymers. Grafted polymers provide a simple method for introducing new properties while maintaining the original qualities of the base polymer. As a result, these polymers play a vital role in modifying physicochemical properties. This chapter discusses various approaches to graft polymerization, key parameters for controlling graft reactions, and recent advancements in the process, with relevant examples provided in each section.

POLYMER GRAFTING APPROACHES

Grafting of polymers is carried out using three main approaches: “grafting through,” “grafting on,” and “grafting from”. The following section covers the details of grafting approaches using the diagrammatic representation illustrated in Fig. (1).

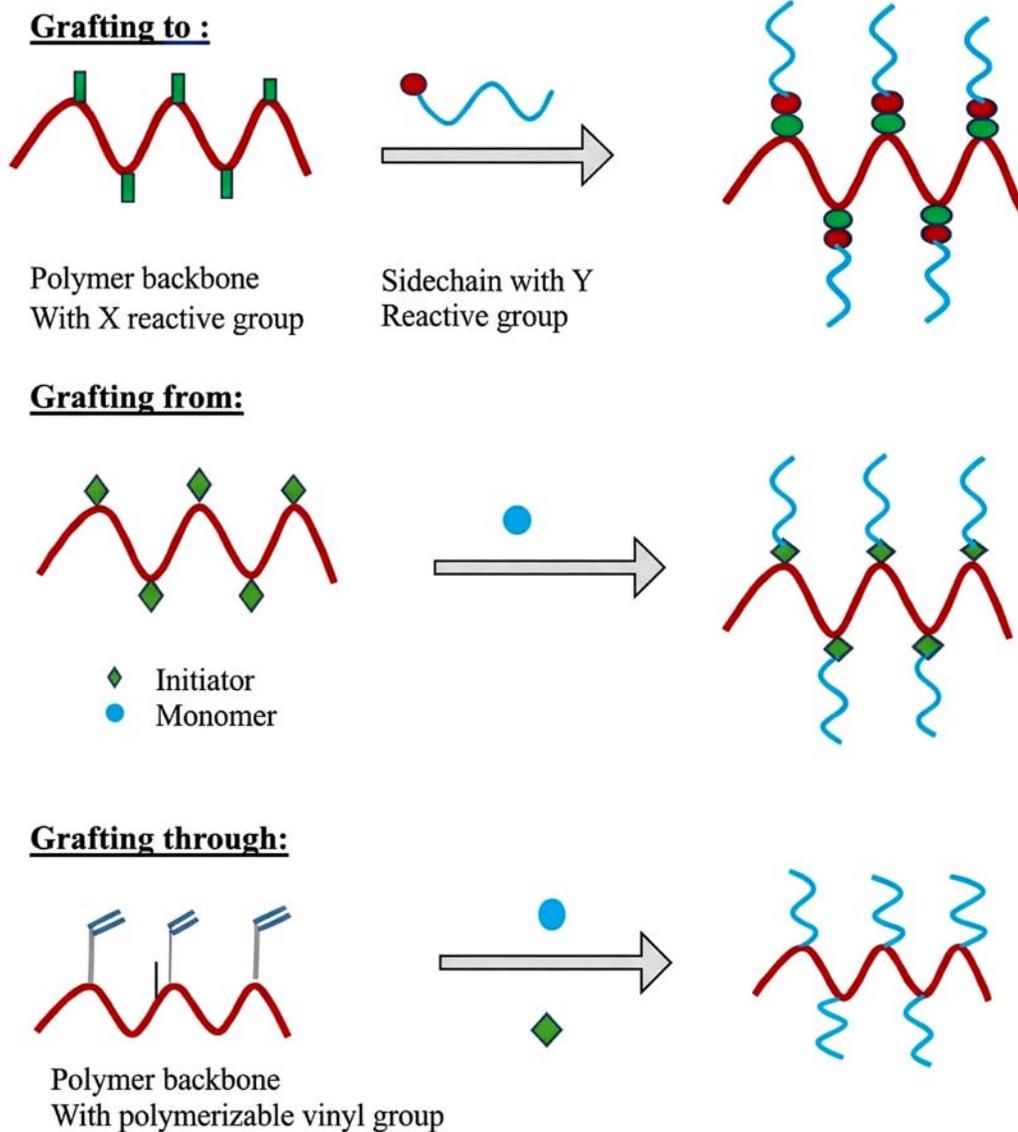


Fig. (1). Illustration of polymer grafting approaches.

Grafting onto (Grafting to)

In this approach, the polymer backbone is reacted with a single monomer. A monomer with a functional group is grafted to the single unit of polymer backbone that has a complementary functional group, which is suitable for attachment of the monomer [7]. A covalent bond is formed between the polymer backbone and monomer functional groups *via* chemical reaction. This approach is

CHAPTER 3

Principles of Green Chemistry in Grafting of Polymers

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Abstract: The polymer system and its chemistry have their roots in the systematic study of applied chemistry. Despite its origins in the last century's changes in climate and environmental pollution, polymer and green chemistry have become a hot topic for chemists. The polymer industry plays a significant role in applied chemistry as polymers have become omnipresent. Polymer grafting is a unique technique that enhances the chemical, morphological, biocompatibility, and physical properties, thereby improving the potential of polymers in terms of conduction and various properties beyond charge transport. A polymer's base activity can be enhanced by further conjugation with copolymers or by grafting. The grafting procedure can enhance the desired properties of the parent polymer and the activity of natural or synthetic polymers without altering their core nature. By this technique, the polymer backbone gains new properties from grafting different monomers like improved elasticity, ion exchange, hydrophobic/hydrophilic character, heat resistance, absorption of water, chemosensitivity, pH sensitivity, antibacterial effect, dye adsorption capabilities, *etc.* This chapter also covers the effectiveness and advantages of the polymer grafting approaches with their various applications in different fields. For the environment's safety, the solutions used in the solution polymerisation technique often face issues due to their viscosity and heat transfer. The central issue faced is removing solvent from the polymer, which requires intensive energy consumption methods like distillation. Since not all polymerization techniques can be performed using greener solvents, chemists are working to find alternative routes and safer solvents to minimize waste and help save the environment for such polymers.

Keywords: Biocompatibility, Grafting, Green chemistry, Monomers, Pollution, Polymer.

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INTRODUCTION

Overview of Green Chemistry

As the world has expanded its reach in science and technology, this has significantly boosted the economy and development, yet also led to environmental degradation [1]. Such sudden progress has manifested a high risk of climate change, ozone holes, and the accumulation of harmful, destructive organic pollutants in the biospheres [2]. Considering all these aspects, it is necessary to balance using natural resources and conserving the environment for a better future for the next generations [3]. Since green chemistry has already been practised over the last two decades, the environment has benefited a lot, and the harmful gas evolution rate has decreased over these years [4]. Due to this fact, new rules and regulations have been put forth to enhance the protection of the ecosystem from harmful chemicals and the synthesis of new compounds or moieties using much greener solvents and reagents. This is a step towards green chemistry [5].

Green synthesis/chemistry is a new branch of chemistry that involves using techniques or developing methods to help chemical engineers create chemical compounds and their synthetic routes in a much more straightforward manner, thereby eliminating harmful chemicals. This step towards eco-friendly and much more efficient products will lead to a brighter future for this ecosystem. Green chemistry has become a crucial tool in the fields of synthetic and applied chemistry [6].

Definition and Goals

According to the Environmental Protection Agency, green chemistry is defined as a chemistry that designs chemical products and processes that are environmentally harmless. Chemical products should be formulated in a manner that ensures they do not persist in the environment after application and break down into components that are harmless to the environment.

Historical Context and Development

Green chemistry was introduced by Poul T. Anastas in 1991 at the US Environmental Protection Agency's particular program launching event to provide a roadmap to a sustainable development method in chemistry, for industries working on chemical technology, academia, and government. In 1995, the annual US Presidential Green Chemistry Challenge was broadcast to the public. In 1996, the International Union of Pure and Applied Chemistry created a separate working party. In 1990, the first book and journal concerning green chemistry were published by the Royal Society of Chemistry [7].

The goals concerning green chemistry include:

- Clean chemistry
- Environmentally benign chemistry
- Atom economy

To reduce the use of dangerous or harmful substances in synthetic and applied chemistry, Paul Anastas developed twelve principles of green chemistry. However, when designing any reaction, it is very difficult to follow all twelve principles of the process simultaneously; however, it is recommended to apply as many principles as possible while carrying out synthesis.

Introduction to Polymer Grafting

Polymer grafting is used to enhance the polymer's shape, chemical composition, and physical characteristics. The current conduction and non-charge characteristics of polymers could be enhanced by this method. Transport improves the solubility of nano-dimensional traits such as morphology, biocompatibility, and biocommunication, and others of the parent polymer as illustrated in Fig. (1). The physicochemical characteristics of a polymer can be altered, considerably more by grafting or copolymerising with another polymer.

The significance of various chemical methods for polymer grafting—such as alkylation, click reactions, amide production, and free radical polymerization—has been addressed here, along with the process's significance and a thorough scientific justification. The efficiency of graft-to techniques and their use in a variety of domains are also covered in this review, which will give the learner a glimpse of polymer grafting [8]

Definition and Significance

Graft polymers are segmented copolymers comprising one composite's linear backbone and another composite's randomly distributed branches. The “graft polymer” in Fig. (2) illustrates the covalent link between the grafted chains of species B and polymer species A. Despite their structural differences, the individual grafted chains can be either homopolymers or copolymers. For the creation of stable blends or alloys, graft polymers, which have been manufactured for many years, are particularly utilized as impact-resistant materials, compatibilizers, thermoplastic elastomers, or emulsifiers. High-impact polystyrene, which has grafted polybutadiene chains over a polystyrene backbone, is one of the more well-known examples of a graft polymer [8].

Renewable Resources for Green Grafting: Types, Benefits, and Challenges

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Abstract: The pharmaceutical sector has been using renewable energy solutions more in recent years as part of its environmental stewardship and sustainability efforts. This development reflects an increasing understanding of the necessity of lowering carbon emissions, lessening the effects of climate change, and minimizing the environmental impact of pharmaceutical production processes. Globally, hospitals and health systems are making investments in clean, renewable energy to safeguard the health of their patients. Hospitals can continue to operate amid severe weather conditions or other disruptions by combining renewable energy with power storage. The EPA defines renewable energy as those sources that depend on non-depleting fuel sources that replenish themselves over brief periods. In reality, wind and solar energy provide the majority of renewable electricity generated in the United States since they are affordable, easily accessible, and clean. Compared to electricity, thermal energy (such as steam, heat, and hot water) presents greater challenges. Many healthcare facilities employ biomass-powered combined heat and power plants, although concerns exist regarding their impact on local health, carbon emissions, and sustainable forestry practices. Though they will need to grow in size before they can be economically utilized for healthcare, emerging technologies like green hydrogen may be useful in decarbonizing thermal energy. Green electrospinning is a promising field for sustainable nanomaterial production, offering eco-efficient methods and reducing environmental impacts. Biological nanofibers, which control drug administration and environmental cleanup, utilize strategies such as solvent removal, integration of renewable energy sources, and waste utilization. Additional investigation is required in the areas of materials engineering, scaling up procedures, achieving multifunctionality, and evaluating entire life cycle sustainability. Research on natural gums and mucilages could be used for drug delivery systems. This study examines the integration of renewable energy sources in pharmaceutical production processes, focusing on both the challenges and benefits.

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Keywords: Eco-friendly, Green grafting, Green electrospinning, Gums, Nanofibers, Renewable energy, Sustainable.

INTRODUCTION

The surrounding environment has bestowed upon humans a vast array of resources for directly or indirectly balancing the health of all living creatures. The pharmaceutical industry is compliant in using the majority of polymers in different dosage forms. Particularly polymers obtained from natural sources, such as various gums and mucilages, are extensively used as resources from nature for both novel and established drug delivery systems. Short half-lives, low bioavailability, and chemical and physical instability are among the drawbacks of pharmaceutical and biological therapies. The primary cause of physical instability is the modification of highly organized protein structures, which can result in unfavorable processes such as breakdown, aggregation, and precipitation. The drug's chemical instability is a result of various chemical processes, including oxidation, deamination, hydrolysis, and racemization [1]. Due to their numerous pharmaceutical uses, including binders, solvents, disintegrating agents in tablets, stabilizers for colloidal particles in suspension, thickening agents in oral solutions, bases in suppositories, gelling agents in gels, and polymers derived from plant sources, these substances have garnered remarkable attention in recent years. Polymers are also used in colorants, textiles, paper manufacturing, and cosmetics.

It is possible to successfully deliver medications to a targeted location at a particular level for a specific amount of time by using the right polymer or polymers. Easy production, a single dosage for prolonged release of the combined medication, enhanced stability, and maintenance of the intended therapeutic concentration are key advantages of using polymers with the appropriate properties in drug delivery systems. Therefore, selecting the appropriate copolymer system is a crucial step in preparing the drug for dosage form formulation. The drug's mechanism of action, degree of discharge, and stability are primarily dictated by the type of polymers utilized in the formulation. Macromolecules called polymers are made up of monomers bonded together covalently. Jöns Jacob Berzelius was the one who originally used the term "polymer" [2]. Due to their numerous pharmaceutical uses as binding agents, solvents, fillers in tablets, protective colloidal particles in a suspended form, gelling components in gels, thickening agents in oral preparations and bases in suppositories, polymers derived from microbial, marine, plant, and synthetic sources have garnered immense attention in recent years [3]. However, not all of the qualities required must be present in the polymers; formulation scientists may find that certain traits are missing from the polymers that are now on the market. This highlighted the importance of polymer grafting in the formulation

development process. A wide range of advantageous qualities can be added to polymers and their undesirable ones reduced by altering their chemical functional groups.

Gums can be altered or substituted with desired chemicals by various methods to address the shortcomings of both natural and synthetic gums. This allows gums to be comparable to their counterparts while also modulating the exact location of drug release and its kinetics—specific requirements designed for the intended uses. Reactive functional compounds, such as carboxylic acids, amino groups, hydroxyl groups, and thiol groups, show potential locations for grafting or chemical alteration in the chemical composition of polymers. In the era of polymers, it is crucial to tailor a polymer's characteristics to meet custom requirements tailored for specific uses. Polymer characteristics can be altered through various methods, including mixing, blending, and curing [4].

Natural polymers, known as biopolymers, are present in living organisms. A biological polymer is a molecule with a lengthy chain composed of monomeric units joined by covalent bonds to form a biodegradable molecule. Biopolymers primarily originate from natural sources, including bacteria, plants, and trees. Synthetic polymers are more random and simpler than biopolymers, which are complex molecules with well-defined three-dimensional geometries [5]. Renewable resources are utilized to produce a range of biopolymer materials with diverse chemical and physical properties. Nature contains lignin, cellulose, starches, hemicelluloses, and a wide variety of other biopolymers [6]. Future production for biopolymers will place high expectations on suppliers of innovative materials. Nonetheless, the material's cost-effectiveness must increase because they are being donated specifically for sustainable development. These polymer properties are utilized in new material applications, and goods are made with those characteristics in mind. Recent research has focused on developing new recyclable polymers with strong mechanical and skeletal properties. Massive amounts of biopolymers derived from living things have been produced. The existence of specific microorganisms and enzymes with unique degradable characteristics has been linked to the biological degradation of biopolymers [7]. Because the skeletal backbone of biopolymers contains nitrogen and oxygen atoms, they biodegrade readily. In the process of biodegradation, a biopolymer breaks down into carbon dioxide, liquid water, biomass, and various other natural elements, including damp water. Numerous bioengineering applications, including the engineering of tissues, systems for drug delivery, and wound dressings, are possible using biodegradable polymers [8]. Biopolymers thicken and solidify more successfully in abrasive pool settings due to their distinctive helical form, stiffness, charge-free chains, and strong resilience to cold and salt [9].

Types of Green Solvents in Grafting Processes

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Abstract: The desire for more ecologically friendly and sustainable synthetic techniques is driving an increasing amount of interest in the use of green solvents in grafting operations. Green solvents are safer and more environmentally friendly than standard solvents like toluene, since they are renewable, biodegradable, and non-toxic.

The creation of organic-inorganic hybrid materials, which have a wide range of uses in many industries, requires specialized grafting procedures. In these reactions, the solvent selection is crucial since it affects the process's efficiency, safety, and environmental sustainability. Although they are often utilized, traditional solvents like toluene carry serious dangers to human health and the environment. Investigating green solvents that are non-toxic, renewable, and biodegradable is therefore becoming more and more important.

The several kinds of green solvents that can be utilized in grafting procedures are highlighted in this abstract, including:

Bio-sourced Solvents: A sustainable substitute for conventional solvents, these solvents come from renewable biomass sources. Dimethyl carbonate, (+)-limonene, (–)-β-pinene, (+)-α-pinene, and 2-methyltetrahydrofuran (MeTHF) are a few examples.

Ionic Liquids: Ionic liquids are a family of low-volatility solvents made completely of ions. They may be employed in a wide variety of pressures and temperatures and are quite successful in grafting reactions.

Deep Eutectic Solvents: These solvents are created by combining two or more low-melting-point substances. They are a sustainable substitute for conventional solvents and are very successful in grafting reactions.

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Supercritical Fluids: Gases that are above their critical temperature and pressure are known as supercritical fluids. They provide a sustainable substitute for conventional solvents and can be utilized as solvents in grafting reactions.

Green Synthetic Organic Solvents: These biodegradable solvents come from sustainable resources. Solvents such as 2-methyltetrahydrofuran (MeTHF) and dimethyl carbonate are examples. These green solvents can be used in various grafting techniques, including:

Free Radical Grafting: In order to start the grafting reaction, free radicals are used in this procedure. It has been demonstrated that green solvents such as MeTHF and (+)- α -pinene work well with this method.

Ionic Grafting: This method transfers organic functionalities onto inorganic substrates by using ionic liquids as solvents.

“Click” Chemistry Grafting: This method transfers organic functionalities onto inorganic substrates by use of click chemistry processes. It has been demonstrated that green solvents such as dimethyl carbonate and MeTHF work well in this method.

In addition, green solvents are being used in solvothermal synthesis for the surface organosilylation of hierarchical nanozeolites. This approach offers a low-hazard and effective method for the synthesis of these materials, which have potential applications in various fields.

Overall, the use of green solvents in grafting processes is an emerging area of research, with significant potential for improving the sustainability and environmental impact of these reactions.

Keywords: Eco-friendly, Green solvents, Grafting, Organic solvents, Solvothermal synthesis.

TYPES OF GREEN SOLVENTS IN GRAFTING PROCESSES

In order to solubilize the organic reactant(s), the support particles are dispersed, the reaction's viscosity is reduced, and any exothermic reactions that may occur are controlled. The grafting reaction is often conducted with the use of a solvent. The solvent that is used is very important since it needs to be inert and considerate of both the organic molecules (which are typically very reactive) and the inorganic support's structural integrity. Examples of such compounds are APTS [1].

Furthermore, the solvent makes up a greater percentage of the reaction mass and has a significant effect on both the process's environmental impact and safety. Toluene is typically used in grafting techniques for these reasons [2, 3].

Because toluene has a manageable boiling point, the reaction mixture can be heated to 111 °C if needed, but it can then be readily extracted from the material. Toluene is also inexpensive and commonly accessible in the market. But toluene, which comes from the catalytic reforming of light petroleum fractions, is a nonrenewable solvent that poses a serious risk to human health [4, 5].

These days, finding more environmentally friendly solvents for the grafting process is a challenge toward more sustainable synthetic processes. In this paper, we examine the use of environmentally friendly and sustainable solvents for the grafting reaction as an alternative to toluene, examining the impact on the hybrid materials that are produced [6]. As shown in Fig. (1), there are 11 types of green solvents used for the purpose of green grafting techniques. Furthermore, green solvents are categorized into two broad classes, renewable and non-renewable solvents, as shown in Fig. (2).

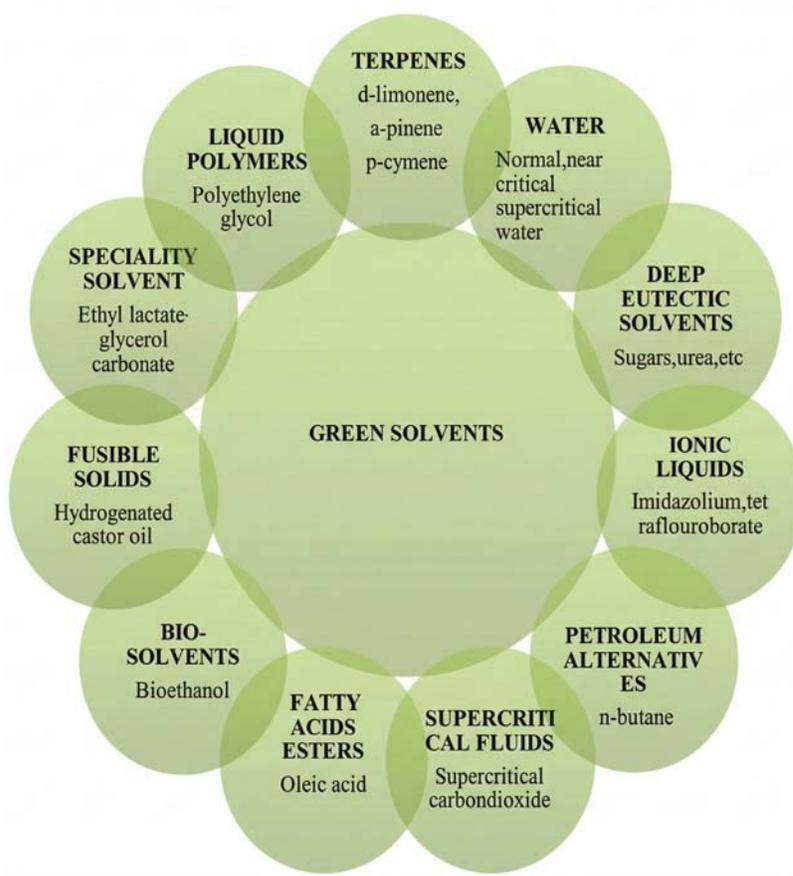


Fig. (1). Types of green solvents

CHAPTER 6

Radiation-induced Green Grafting: Mechanism, Applications and Benefits

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Abstract: The method for the creation of surface-grafting polymeric materials is gaining recognition because it makes it possible to create novel materials from well-known, commercially available polymers with desirable bulk properties like elasticity, permeability, and thermal stability, combined with advantageous, newly tailored surface properties like adhesion, biomimicry, and biocompatibility. Since it produces radicals on most substrates, ionizing radiation is one of the most effective techniques for creating graft copolymers. This process involves the use of radiation, such as UV, plasma, Electron Beam (EB), and γ -rays, to modify polymer substrates. The development of RIGG in pharmaceuticals focuses on the covalent immobilization of biocides to various polymer surfaces. Grafting can now be done under control to produce surfaces with specific and well-defined features. The application of radiation has entered a new era of grafting with the development of living free-radical polymerization techniques. The technique is applied to drug delivery systems, where grafted polymers provide controlled release profiles and targeted delivery, improving therapeutic efficacy and patient compliance. In biomedical applications, grafted polymers are utilized to create biocompatible surfaces for medical implants, ensuring reduced risk of infection and improved integration with biological tissues. Radiation-grafted wound dressings are developed for their enhanced antimicrobial activity and accelerated healing properties. The chapter delves into the scientific principles underlying RIGG, detailing the mechanisms by which radiation induces grafting and the factors influencing the process. The chapter then delves into the specific applications of radiation-induced green grafting in the pharmaceutical and healthcare industries.

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Keywords: Antimicrobial surfaces, Biomedical device, Green grafting, Healthcare products, Radiation-induced green grafting.

INTRODUCTION

Copolymers are polymeric materials that include two or more units of two distinct polymeric species bonded together in a specific configuration. Random, block, and graft copolymers are the three different kinds of copolymers. The two polymeric species are arranged differently in them. When the small structural units of two polymeric species appear in a random linear sequence, the copolymer is called a random copolymer. A linear copolymer including one or more continuous, lengthy sequences of each polymeric species is called a block copolymer. Graft copolymers are branching copolymers that have one or more side chains of one polymeric species linked to the “backbone” of another polymeric species. The surfaces of polymer forms can be functionalized in such a way that makes them suitable for a range of uses in the industrial, environmental, and biological domains through radiation-induced grafting [1]. Compared to other grafting processes, radiation-induced radical polymerization is widely applicable to a variety of polymeric material components and forms.

Graft polymerization with radiation-induced was thought of as a prospective method of modifying the surface of polymeric materials without changing the bulk material by chemically joining polar/nonpolar monomers with functional groups, such as H, -OH, -COOH, -NH₂, -SO₃, -OR, -R, and their derivatives. It preserves the physical characteristics and shape of the trunk polymer while allowing for the creation and development of new functionalities for polymer materials [2]. In addition, no unnecessary chemicals or catalysts are used when using RIG polymerization to add functional groups to polymers. Since this procedure does not require the use of a catalyst or other dangerous chemicals that could damage human skin or the environment, it can be considered both economical and environmentally friendly [3]. Graft polymerization can be started using four main methods: ultraviolet treatment, plasma treatment, electron beams, and gamma radiation.

IMPORTANCE OF RADIATION-INDUCED GREEN GRAFTING IN PHARMACEUTICALS

Sustainability of the Environment

The use of radiation, like gamma rays or electron beams, for the grafting process limited the use of chemical initiators, which led to the production of less hazardous waste. Chemicals and solvents used in traditional grafting methods have been proven to be harmful to the health of people and the environment.

Thus, grafting using the radiation technique aligns with the principle of green chemistry and proves to be advantageous.

Accuracy and Regulation

Accuracy is achieved through the radiation grafting polymerization technique as it controls variable factors and grafting parameters, such as dose, time of exposure, and rate, which precisely define grafting. Precise grafting is an important aspect in terms of pharmaceutical preparations, as it directly determines the characteristics of the formulation where targeted drug delivery must be achieved.

Improved Properties of the Material

Grafting with radiation improves the properties of materials, such as mechanical strength, hydrophilicity, biocompatibility, drug loading capacity, and swelling behavior for the preparation of different pharmaceutical formulations. The incorporation of functional groups aids in achieving improved characteristics, which makes it more feasible for use in pharmaceutical applications [4, 5].

Flexibility and Wide Range of Use

Radiation grafting methods have multiple applications and adaptability. A variety of polymers, ranging from natural to synthetic, like chitosan, cellulose, polyethylene, and polypropylene, can be modified using the radiation-induced grafting method, which increases their usage to a wide range of pharmaceutical applications, like the development of improved drug delivery systems, wound dressing, and scaffolds for tissue engineering.

Better Systems for Delivering Drugs

Targeted release and controlled release of drugs are the major concerns of pharmaceutical preparations, where safety and efficacy with effective drug therapy shall be delivered, such as in cancer therapy. With radiation grafting, cutting-edge medication can be developed as drug carriers that react to specific physiological variables, like temperature and pH, through the incorporation of specific functional groups.

Less Immunogenicity and Biocompatibility

To design an implant or medical device, the issue of biocompatibility should be considered. Radiation grafting is capable of enhancing biocompatibility by allowing for the incorporation of suitable polymer surfaces grafted until they integrate with surrounding tissues, and an immune system response is lower.

CHAPTER 7

Plasma-Assisted Green Grafting: Principles, Environmental Benefits, and Uses

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Abstract: In the field of medicine and pharmacology, PAGG (Plasma-Assisted Green Grafting) is a revolutionary method that uses green chemistry and non-thermal plasma to improve material surfaces in an ecologically friendly way. This novel method utilizes non-thermal plasma for the activation and modification of surface characteristics. This eliminates the need for hazardous chemicals or excessive heat during the grafting of functional groups or polymers. Significant environmental benefits result from this, including reduced energy consumption, lower environmental pollution, and a decrease in the use of hazardous chemicals. PAGG has demonstrated tremendous promise in the pharmaceutical and healthcare industries. By enhancing the biocompatibility of medical implants, PAGG ensures that the body will absorb these devices more easily, thereby reducing the likelihood of rejection and complications. Furthermore, PAGG enhances medication delivery mechanisms, enabling more effective and targeted therapeutic administration that can reduce adverse effects and improve treatment outcomes. Another important achievement that contributes to infection prevention and enhanced patient safety in clinical settings is the creation of antimicrobial surfaces made possible by PAGG. The technique provides an environmentally friendly alternative to conventional grafting procedures by enhancing the mechanical stability, antibacterial properties, and biocompatibility of implants, medical devices, and drug delivery systems. As a result, PAGG aligns perfectly with the growing demand for sustainable practices in the medical and pharmaceutical industries. By reducing the environmental footprint and improving the safety and efficacy of medical treatments, PAGG drives innovation and sustainability, offering

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substantial benefits for both patient care and environmental health. This technique exemplifies how cutting-edge technology can contribute to sustainable development in critical fields.

Keywords: Biocompatibility, Drug delivery system, Environmentally friendly, Non-thermal plasma, Plasma-assisted green grafting, Sustainability.

INTRODUCTION

The goal of the scientific discipline of “green chemistry” is to create chemical products and processes that minimize or completely do away with the need for dangerous materials. Green chemistry aims to develop more environmentally friendly and sustainable chemical processes by using waste reduction, energy conservation, and renewable resource utilization strategies. This strategy places a strong emphasis on enhancing safety and efficiency while minimizing the adverse environmental impacts of chemical manufacturing and use. Green chemistry aims to preserve the environmental and public health benefits of chemical advancements while promoting safer chemical development, utilizing benign solvents, and developing energy-efficient processes [1, 2]. Green grafting is a polymer grafting method that is environmentally friendly and aims to mitigate the pollution that polymer synthesis has historically caused. Through the attachment of side chains to a polymer backbone, this approach modifies the mechanical strength, solubility, and thermal stability of the polymer. The environmentally friendly feature of this process is highlighted by the substitution of sustainable monomers made from plant-based materials, natural oils, or sugars for conventional petroleum-based compounds [3]. In green grafting, green solvents are essential. These eco-friendly substitutes for traditional solvents are derived from plant- or bio-based resources that are replenishable [4]. Green solvents help reduce pollutants and greenhouse gas emissions during the grafting process, as they are less harmful to the environment, often biodegradable, and have a smaller environmental footprint. Green solvents ensure that the grafting procedure complies with green chemistry principles, in contrast to conventional solvents, which are typically petroleum-based and can cause significant environmental contamination [5]. Green grafting stresses energy efficiency by utilizing procedures that operate at lower pressures, temperatures, or energy inputs, in addition to employing green solvents. To reduce energy usage, technologies such as microwave or ultrasonic energy are utilized in place of conventional heating techniques [6]. Enzymes that are biocompatible, reusable, or non-toxic are also preferable catalysts, which further aligns the grafting process with green chemistry concepts. There are major health and environmental benefits when green solvents and green grafts are combined. For example, due to their decreased volatility and toxicity, green solvents are typically safer, as they expose users to

fewer hazardous compounds and reduce the risk of respiratory difficulties, skin irritation, and other health concerns associated with solvent usage. Contrarily, a lot of common solvents are combustible, volatile, and poisonous, which pose serious health hazards, including the possibility of long-term consequences like cancer or neurological damage. In terms of economics, green grafting techniques and solvents may occasionally incur higher upfront costs, but total expenditures may be lower due to lower waste disposal costs, safer handling, and less stringent regulations [7]. Moreover, implementing green practices can enhance a business's sustainability profile and potentially provide it with competitive advantages. On the other hand, traditional solvents may be quite expensive to handle, dispose of, and comply with environmental regulations, even if they are initially less expensive. In terms of performance, green solvents used in green grafting yield outcomes that are on par with or even better than those of conventional solvents in various applications, including coatings, cleaning products, and pharmaceuticals [8].

Green chemistry innovations continue to become increasingly effective and widely adopted. Green grafting techniques include, for example, grafting cellulose with biodegradable polymers such as Poly(Lactic Acid) (PLA) using green solvents and enzymatic catalysts, or grafting natural rubber with polymers derived from plant oils without the need for solvents. Grafting involves attaching polymer chains or side groups to an existing polymer and is achieved through methods such as free radical or living polymerization [9]. Polymer grafting has emerged as a promising alternative in response to the growing global demand for natural products and the depletion of available resources. By using this technique, it is possible to create segments of polymers that are covalently attached to the main chains of polymers, resulting in the development of copolymers and the integration of special properties from the grafted materials. Grafted polymers are extremely advantageous in a variety of applications because this method adds additional functions while maintaining the extended conjugated structure of the original chain, as shown in Fig. (1) [10].

Green grafting is a significant advancement in polymer chemistry, facilitated by the use of environmentally friendly solvents. This method offers a safer, more environmentally friendly, and often more cost-effective option for polymer grafting compared to older techniques, aligning with the growing emphasis on green chemistry [11]. Green grafting reduces the use and manufacture of harmful compounds by employing sustainable processes and green solvents, thereby promoting an industry that is more ecologically and health-conscious. Using different plasma systems, plasma-induced graft copolymerization is an appealing method for creating antibacterial and antifouling coatings. With the use of monomer precursors (silicon, hydrocarbons, and fluorocarbons) or polymerizable

Enzymatic Green Grafting: Role of Enzymes and their Sustainable Advantages

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Abstract: Enzymatic grafting of biopolymers has lately become a focus of green chemistry technologies due to increased environmental concerns and resulting legislative constraints. Over the past decade, polymer science has witnessed a surge in research on enzymes such as laccases and lipases. The goal of this research is to use these enzymes to graft multifunctional polymers for various applications. In this context, a number of bio-composites, such as bacterial cellulose (BC), poly-3-hydroxybutyrate grafted ethyl cellulose, and keratin-g-ethyl cellulose, were effectively synthesized using enzyme-based grafting, with laccase and lipase as model bio-catalysts. Wood preservative made by creating covalent connections between bioactive compounds and wood using the laccase enzyme. The free-radical polymerization of aromatic substances, including gallate esters and lignins, is catalyzed by horseradish peroxidase. To increase the hydrophobicity of the fibers, Dodecyl Gallate (DG) was grafted onto the surfaces of lignin-rich jute textiles using HRP-mediated oxidative polymerization. By using the laccase enzyme, cellulose grafting with ferulic acid is expected to enhance the mechanical properties of the resultant biocomposites. Moreover, the low molecular weight phenol and Pycnopus cinnabarinus laccase enzyme's ability to biomodify high-content cellulose fibre for use in making paper. These low-molecular-weight phenols, which are covalently bonded to flax fibers by laccase treatment, can function as antibacterial agents, resulting in antimicrobial handsheets. This economical and resilient method offers enormous potential in the production of cellulose-based functional polymers.

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Keywords: Covalent, Enzymatic grafting, Green chemistry, Laccase, Lipase, Polymerization.

INTRODUCTION

An inventive and eco-friendly method of surface or material modification is enzymatic green grafting, which involves attaching bioactive chemicals or polymers *via* enzymatic processes [1, 2]. Because this process can produce functionalized materials with improved qualities and a reduced environmental impact compared to typical chemical procedures, it offers significant potential in several sectors, including environmental science, biotechnology, materials science, and medicine [3]. Enzymatic green grafting is based on the concept of enzymatic catalysis, which utilizes enzymes as biocatalysts to accelerate specific chemical reactions [4, 5]. Due to their exceptional specificity in recognizing substrates and executing reactions, enzymes provide precise control over the modification process. Enzymatic green grafting operates under mild conditions, such as neutral pH and moderate temperatures, utilizing water as the solvent, which reduces energy consumption and waste generation [6, 7]. This is in contrast to conventional chemical grafting methods, which often require harsh conditions and organic solvents and produce hazardous waste. Grafting is the process of affixing molecules or polymers to a substrate surface in order to impart particular characteristics or functions [8]. The selection of both the enzyme and the substrate determines the type of alteration and final material qualities in enzymatic green grafting. This method can be used with a variety of substrates, including metals, ceramics, biomaterials, natural polymers (such as cellulose and chitosan), synthetic polymers (like polyethylene and polystyrene), and cellulose [9 - 11]. The selection of enzymes with high specificity for the intended substrate and reaction conditions is crucial to the effectiveness of enzymatic green grafting. Catalysts generated from biology, such as enzymes, accelerate chemical reactions without being consumed in the process [12]. Generally, these enzymes identify specific functional groups or chemical structures that are present on both the grafting molecule (also known as the “grafting agent”) and the substrate. For example, lipases and esterases are frequently utilized in grafting operations involving ester bonds, and proteases and peptidases are used to change proteins or peptides on surfaces [13, 14]. Similarly, carbohydrates are grafted onto substrates by glycosyltransferases. It is frequently necessary to prepare the substrate surface to expose reactive functional groups or create an environment conducive to enzyme activity before enzymatic grafting can occur [15, 16]. Pre-treatment procedures, such as cleaning, functionalization, or activation, may be necessary for this. Techniques for activation include chemical etching, plasma treatment, and surface functionalization using linker molecules that can communicate with both the grafting agent and the substrate. The molecule or polymer chain that will

be affixed to the substrate surface is known as the grafting agent. It is essential to consider factors such as the grafting agent's stability under grafting conditions, compatibility with the enzyme, and the desired features it imparts to the substrate when designing an efficient grafting agent [17, 18]. Small compounds, oligomers, or polymers containing specific functional groups that can participate in enzymatic activity and form covalent bonds with the substrate are known as grafting agents.

It is possible to apply enzymatic green grafting to modify the surfaces of various materials, thereby acquiring specific characteristics or functions. Typical methods encompass immobilization on polymers, bioconjugation, and functional coatings. Immobilization on polymer surfaces is a technology used to improve catalytic stability and efficiency [19, 20]. It includes immobilizing enzymes on polymer surfaces. This method is helpful in biomedical settings where tissue engineering, medication administration, and biosensing can all be accomplished with immobilized enzymes. Enzymes can be coupled with biomolecules (such as peptides or antibodies) in a process known as bioconjugation to produce functionalized surfaces for use in targeted drug delivery systems, biosensors, or diagnostic tests. The process of applying functional coatings to surfaces to enhance adhesion, antibacterial characteristics, or biocompatibility is known as enzymatic grafting [21 - 23]. To reduce the risk of infections, antimicrobial peptides, for example, can be grafted onto medical devices. Biopolymers modified by natural polymers, such as cellulose, chitosan, and starch, can be enzymatically modified to enhance their properties for various applications, including chitosan grafting and cellulose modification [24, 25]. Cellulases and hemicellulases can be utilized in cellulose modification to alter cellulose fibers for use in papermaking, textile applications, or biocomposite materials. Surface functionalization or degradation to change the mechanical characteristics is one type of modification. In contrast, chitosan grafting is a biopolymer derived from chitin that can be enzymatically grafted with molecules or polymers to enhance its antibacterial activity, biocompatibility, or drug delivery properties. Enzymatic modification of synthetic polymers, such as polyethylene, polypropylene, or polystyrene, can introduce particular functional groups or enhance their compatibility with other materials, a process known as polymer functionalization [26 - 28]. By inserting reactive groups, such as hydroxyl or carboxyl groups, enzymes like oxidases or peroxidases can be employed to activate polymer surfaces. Subsequent grafting reactions with functional compounds or polymers can be carried out on these activated surfaces. Moreover, enzymatic grafting can help mix polymers with various characteristics together by altering their interfacial interactions or surface chemistry. This method works well for combining polymers to create composite, coating, or packaging materials. The capacity of enzymatic green grafting to modify biomaterials with enhanced biocompatibility, bioactivity, or improved

CHAPTER 9

Mechanochemical Green Grafting: Methods, Environmental Benefits, and Uses

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Abstract: Mechanochemistry has garnered considerable attention as a potent, long-lasting, efficient, eco-friendly, and economical synthesis technique for creating new functional materials. This method is based on physicochemical reactions that are accelerated by mechanical force using milling and grinding. Mechanochemical synthesis is described as a chemical reaction that occurs through the absorption of mechanical energy. To facilitate chemical reactivity, reactions are carried out by grinding the reagents using ball-mill devices, such as vibrating, planetary, tumbler ball-mills, or single-screw devices, which employ mechanical forces. This technique is reported for the practical, solvent-free synthesis of superhydrophobic surfaces using a mechanochemical approach. One-step mechanochemical grafting was employed to generate thiol-functionalized montmorillonite, resulting in covalent organic frameworks (COFs) with excellent iodine capture properties as adsorbents. MOFs comprise the following widely used structures: ZIF-8, HKUST-1, MIL-101, UiO-66, and MOF-5. These approaches are used to prepare bio-inspired metal-organic frameworks, novel metallopharmaceuticals and metallodrugs, phenol hydrazone derivatives, cyclodextrin nanosponges (CD-NS) polymers, copper oxide nanoparticles, and silver nanoparticles for antibacterial activity; to perform mechanoactivation of silicon to synthesize alkoxy silanes; to synthesize heterocyclic derivatives using a ball mill; to produce pharmaceutical cocrystals; and to synthesize catalysts. The distinguishing features of mechanochemical processes over solution-based chemistry include more selective reactions, which allow for simpler work-up procedures.

Keywords: Ball mill, COF, Green grafting, Mechanochemistry, MOF, Nanoparticles.

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INTRODUCTION

Mechanochemistry [1], which is well known in the fields of crystal engineering and polymorphism, is regaining popularity as an organic synthesis approach. While the technology is not new, it is developing beyond its original purpose of providing a solvent-free alternative. Despite numerous synthetic transformations having been recorded, those with reactivity differences from traditional solution-based reactions are likely the most fascinating. It is described as “a chemical reaction that is induced by the direct absorption of mechanical energy”. Therefore, it complements the traditional techniques of activation: heat, irradiation, and electrochemistry. It is also connected to tribochemistry [2, 3], which involves chemical interactions on the surface/boundary of distinct environments. Despite its recent renaissance, mechanochemistry remains considerably less studied and understood than traditional methods of energy input [3 - 6]. For example, pericyclic reactions behave differently depending on whether they are triggered by light or heat. The response outcome is foreseeable using the Woodward-Hoffmann rules. Interestingly, when ultrasound is employed as the input energy for a pericyclic reaction, unexpected products have been detected; in fact, it has been proposed that Woodward-Hoffmann laws should not be used to describe mechanochemical pericyclic reactions [7].

Mechanochemistry, therefore, offers the chance to investigate a unique chemical space of reactions. Mechanochemistry can describe the impact and pulling forces. This approach focuses on the influence of milling. Wilhelm Ostwald is credited with coining the term “mechanochemistry” in 1907, along with electrochemistry, photochemistry, and thermochemistry [8-10]. Matthew Carey Lea first proposed the idea that mechanochemical reactions could differ fundamentally from thermochemical ones in 1892 [11-13]. Subsequently, the area of mechanochemistry has grown steadily, from Staudinger's pioneering work on polymer mechanochemistry in the 1930s to various investigations into supramolecular mechanochemistry in the 1980s and solid-solid organic synthesis techniques in the 1990s [14]. Presently, the IUPAC defines a mechanochemical reaction as a chemical reaction caused by the direct absorption of mechanical energy [15]. Despite the rapid development of shearing- and grinding-induced mechanochemistry and the frequent publishing of novel synthetic processes for diverse products, the mechanism at the microscopic and molecular levels remains unknown [16]. Reactive extruders and high-speed ball mills are sometimes referred to as “black boxes” because the chemical processes they carry out are protected by enclosures, most of which are composed of metal or ceramic. This leads to one of the key challenges of mechanochemistry: the lack of a good theory that completely describes the current reactions while being universally applicable to varied synthetic methods [17]. Mechanochemistry now has three theories: the

hot-spot theory, the magma-plasma model, and the pseudo-fluid model, each of which may describe specific occurrences in distinct subdisciplines [18-20]. Mechanochemistry is a rapidly expanding field in chemistry. The efficient energy dispersion and mass movement caused by mechanical forces have permitted the removal of solvents, resulting in cleaner, quicker, and more straightforward chemical syntheses than conventional solvent-based processes. Mechanochemistry has established itself as a dependable synthesis technique, as evidenced by several reports. In particular, the use of mechanochemistry to synthesize molecules that are difficult or impossible to obtain using conventional methods has advanced many areas of chemistry, and mechanochemical activation is now recognized as a promising technique alongside thermal, photochemical, and electrochemical activation.

METHODS OF MECHANOCHEMICAL GREEN GRAFTING

Improving a surface polymer's wettability, biological compatibility, physical properties, etc., is the primary goal of surface modification. The different techniques of grafting include chemical grafting, free radical grafting, ionic grafting and photochemical grafting. By removing the need for reactive chemicals, enzyme application can provide a safer, more cost-effective, and environmentally friendly method of grafting procedures. Moreover, the specificity of enzymes may provide a possibility for precisely customizing desired macromolecular characteristics. Among them, it is predicated on the idea that the chemical/electrochemical grafting process may be started with the aid of an enzyme. By removing the need for reactive chemicals, enzyme application can provide a safer, more cost-effective, and environmentally friendly method of grafting procedures [21]. Moreover, the specificity of enzymes may provide a possibility for precisely customizing desired macromolecular characteristics. High expectations are placed on innovative materials by recent technology breakthroughs and the quest for new functionalities of designed solids, which are typically delivered by extremely complex procedures [22]. However, it is essential to create manufacturing methods that are straightforward, affordable, waste-free, high-yield, and scalable for both financial and environmental reasons [23]. Material synthesis has traditionally been dominated by wet chemistry procedures, which have been well-optimized throughout time to fulfill strict standards to limit waste creation. However, due to the inherent nature of solution processing, the production of solvent waste cannot be prevented. Furthermore, solution-based chemistries are linked with extensive treatment periods and post-synthesis drying procedures. Mechanochemistry has recently gained popularity as a viable method for carrying out chemical reactions and material synthesis under considerably gentler circumstances than solvothermal approaches. A noteworthy benefit of employing mechanochemistry is the ability to carry out the reactions

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