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POLYMER GRAFTING AND ITS APPLICATIONS: A REVIEW

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ABSTRACT: Grafting polymerization is a process in which polymer chains are covalently bonded (grafted) onto a backbone polymer, leading to the formation of a new material with enhanced properties or functionalities. This process involves the attachment of polymer chains (known as "graft chains" or "grafts") onto the surface or within the bulk of the substrate material. Polysaccharides have numerous applications in various industries, including food, pharmaceuticals, cosmetics, and biotechnology. They are used as thickeners, stabilizers, emulsifiers, gelling agents, and drug delivery systems due to their biocompatibility, biodegradability, and functional properties. Flavonoids are a group of polyphenolic secondary metabolites found in plants, fruits, and vegetables. They show a wide range of health benefits. They have gained interest recently due to their possible benefits for human health, especially their antioxidant, antiviral, antiallergic, anti-inflammatory, and anticancer characteristics. Flavonoid-grafted polysaccharide-form complexes generate synergistic effects, such as enhanced physical, chemical, and functional properties. Therefore, they show great potential for applications in food, cosmetics, and medicine. Structural characterization methods of the graft products, including FTIR, NMR, and DSC, are introduced.

INTRODUCTION: Polymers are macromolecules made up of monomers bonded together by covalent bonds. Jöns Jacob Berzelius D. was the one who originally used the term polymer[1]. Polymer segment branches covalently bonded to the leading polymer chains make graft copolymers. Graft copolymers with a single branch are called miktoarm star copolymers. Homo- or copolymers with different chemical compositions or topologies may make up the core and the branches [1].

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Polymer modification has received a lot of attention lately. One of the most promising methods for changing polymers is grafting. Graft co-polymerization is a promising method for adding different functional groups to a polymer [2]. The physicochemical characteristics of a polymer can be further modified by grafting.

Because they aim to preserve the extended conjugated structure in the parent chain while introducing and assimilating the features of the grafted components, grafting polymers are highly significant [3]. The synthesis of graft copolymers can be accomplished by three broad methods: "grafting through", "grafting to", and "grafting from" [1]. The reactions that occur when a reactive end-group macromolecule copolymerizes with a low

molecular weight second monomer are known as "grafting through", "grafting from" and "grafting to" respectively. In "grafting to," a reactive end-group polymer molecule interacts with the functional groups in the backbone. The most popular are the chemical processes of "grafting to" and "grafting from" polymer grafting [1].

Grafting Activators: Grafting activators, such as free-radical initiators, create grafting sites on the polymer backbone to start the grafting process. Polymer grafting activators fall into three categories: Physical, chemical, and biological [1].

Physical Activators: Electron-beam and γ-beam radiations are included in ionizing radiation, also called high-energy radiation. Three different avenues for radiation-induced grafting were pursued.

Irradiating the first polymer backbone in an inert gas or under vacuum produces free radicals during pre-irradiation. Subsequently, the monomer is placed onto the polymer substrate, exposed to radiation. The monomer can be a liquid, vapor or solution in a suitable solvent.

Air or oxygen is present during the peroxidation grafting process when the trunk polymer is subjected to high-energy radiation. Either hydroperoxides or peroxides are produced as a result depending on the kind of polymeric backbone and the radiation conditions. The stable peroxides break down into radicals after being treated with the monomer at a higher temperature, which initiates the grafting process.

The addition process in the mutual irradiation technique occurs when the polymer and the monomers are simultaneously exposed to radiation, producing free radicals.

Free electrons, ions and radicals combine to form plasma, a partially ionized gas. Depending on the gas used, this process may introduce an alternative functional group or generate free radicals on the backbones [4].

Microwave radiation causes rapid non-contact internal heating, quickening processes and boosting yields by directly interacting with polar molecules and ionic particles [5].

Chemical Activators: Chemical activators include, for example, backbone oxidant initiators and free radicals. Free radical initiators are compounds that demonstrate direct or indirect homolytic fission. In the first instance, the initiator functions alone; in the second, an extra environmental molecule is required to participate. Activation sites are formed when oxidant initiators directly react with functional groups in the backbone [2].

Biological Activators: These enzymes catalyze polymer modification reactions through functional groups at the chain ends, along the main chain or side branches, promoting highly selective nondestructive transformations on backbones under mild reaction conditions. Recent studies have demonstrated that lignin can be successfully grafted by oxidizing its phenolic components *via* laccase [6].

Different Techniques of Grafting:

1. Chemical grafting
    a. Free radical grafting
    b. Ionic grafting
2. Grafting through living polymerization
3. Photochemical grafting
4. Enzymatic grafting
5. Plasma radiation technique
6. Radiation grafting

Chemical Grafting: Since, it determines the direction of the grafting process, the initiator is essential to chemical grafting. It is further separated into two categories: free radical and ionization grafting.

Free Radical Grafting: The initiators create free radicals during the chemical reaction which are transported to the substrate and mixed with the monomer to produce the graft copolymers. In general, free radicals can be created through direct or indirect methods. Grafting: an adaptable way to change polymer methods, variables and uses

In free radical-initiated grafting, the following initiator systems are utilized [7]:

PDC: Potassium diperiodatocup rate

PPS: potassium persulfate

TCPB: Thiocarbonation potassium bromate

APS: ammonium persulfate

FAS: Ferrous ammonium persulfate

CAN: Ceric ammonium nitrate

The approach most frequently used to create flavonoid-grafted polysaccharides using free radical initiators is the ascorbic acid and hydrogen peroxide (H_2O_2) redox pair [8]. There are several advantages to initiating the grafting reaction with the Vc/H_2O_2 redox pair. First, reaction reagents are a less expensive way to generate free radicals than carbodiimides or enzymes. Second, compared to carbodiimide, Vc/H_2O_2 redox poses less risk. Natural polysaccharides like chitosan, starch, Inulin and pectin are grafted with certain polyphenols through the action of free radicals [8].

Ionic Grafting: Using ions created by high-energy irradiation, ionic grafting can be either anionic or cationic. The polymer is irradiated to produce the polymeric ion, which then reacts with the monomer to form the grafted copolymer. A high pace of reaction is one potential advantage of ionic grafting [2].

Curcio *et al.* established the ascorbic acid and H_2O_2 redox pair initially [9].

Grafting Through Living Polymerisation:

a) Szwarcet *et al.* indicate a "living polymer" as one that "retains their ability to propagate for a long time and grow to a desired maximum size while their degree of termination or chain transfer is still negligible [10].

b) In controlled free radical polymerization methods, ionic and conventional free radical polymerization features are integrated. Live polymerization produces polymers with minimum polydispersity and regulated molecular weights [11].

c) Since traditional radical polymerization lacks control over the molecular weight, molecular weight Distribution and architecture, one of its drawbacks is the difficulty of customizing its macroscopic properties. Live ionic polymerizations can yield copolymers with well-defined structures, including regulated molecular weights and restricted molecular weight dispersion, as well as specified copolymer compositions, Branching and end-group functionalities.

d) Stable free radical polymerization (SFRP) produces a stable free radical by introducing an active radical site into the polymerization process and reversibly cleaving a dormant chain end through homolytic cleavage. Although styrene, acrylates and acrylamides were the main substances for which SFRP was employed. Styrene monomers were given the most excellent attention in the literature [12].

e) Dithiocarbonyl compounds, which work as efficient RAFT agents, must be present during free radical polymerization to achieve reversible addition-fragmentation chain transfer (RAFT) [13].

f) Dormant chains of Atom Transfer Radical Addition (ATRP) are capped by halogen atoms, which are reversibly transferred to metal complexes in lower oxidation states. This generates the transient rising radicals and complexes of the higher oxidation state. The primary response of ATRP is the activation-deactivation dynamic equilibrium mechanism [13].

Photochemical Grafting:

1. A macromolecule's chromophore absorbs light and transitions into an excited state, where it may split into reactive free radicals, which initiates the grafting process. There are two ways to start the grafting process: with and without a sensitizer [2].

2. Without sensitizer: The core mechanism generates free radicals, which join forces with the free radicals from the monomer to form the grafted copolymer.

3. Using a sensitizer: The sensitizer removes hydrogen atoms from the base polymer to

produce free radicals that can diffuse and establish the radical sites required for grafting.

Enzymatic Grafting: The underlying idea is that a chemical or electrochemical process can be started with the aid of an enzyme [14]. Recently, there has been a lot of interest in the enzymatic synthesis of flavonoid-grafted polysaccharides due to the enzymes high catalytic activity and substrate specificity. As an alternative to the risky, non-specific and ecologically unfriendly chemical coupling method, grafting flavonoids in to polysaccharides has been achieved up to this point utilizing several enzymes, including laccase, tyrosinase, horseradish peroxidase, and chloroperoxidase [8].

During grafting procedures, employing enzymes rather than reactive reagents can offer a more ecologically friendly, economical, safe and effective solution. Furthermore, the ability of enzymes to precisely customize desired macromolecular properties may be made possible by their specificity [11].

Plasma Radiation: High-energy accelerated electrons from plasma are utilized to cause cleavage of the chemical bonds in the polymeric structure, which forms macromolecule radicals and starts graft copolymerization. These processes are known as electron-induced excitation, ionization and dissociation. The grafting probabilities provided by slow-discharge plasma radiations are comparable to those of ionizing radiation [15].

Radiation Grafting: Free radicals are produced when high-energy radiation is applied to the polymeric backbone. These radicals serve as active sites for the grafting and propagation of side-chain grafts. These radicals quickly react with appropriate functional monomers to establish covalent connections and ultimately the production of macromolecular chains, all without the requirement for chemical initiators [11, 16].

Characterization of Grafted Polymers Using Analytical Techniques: The assessment and characterization of grafted polymeric materials are conducted using the following analytical techniques: elemental analysis, Differential Scanning Calorimeter (DSC), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD) and Nuclear Magnetic Resonance (NMR) [17].

Fourier Transform Infrared Spectroscopy: Fourier transform infrared (FT-IR) spectroscopy is utilized as a characterization approach to determine the functional groups of organic compounds.

It can produce valuable information, such as the significant covalent bond and functional group composition and is mainly employed to investigate the composition of unknown organic compounds qualitatively. By comparing the changes in the FT-IR spectra of polysaccharides and grafted products, one can infer the structural characteristics of the polyphenol-polysaccharide conjugates [18, 19].

Nuclear Magnetic Resonance: Nuclear magnetic resonance (NMR) spectroscopy is the primary analytical technique to determine organic compounds' structure and biological macro-molecules. Using several analytical procedures can provide valuable structural information regarding the complete molecule. ^{1}H and ^{13}C in polysaccharides has been examined using their NMR spectra. Preparation, description, rheological characteristics, and antioxidant qualities of grafted ferulic acid was reported [20, 21].

X-Ray Diffraction: X-ray diffraction (XRD) is a scientific technique used to determine the composition, internal atomic structure, or shape of materials by analyzing their X-ray diffraction patterns [22]. X-ray diffraction (XRD) is an investigative method used to ascertain the materials' composition, internal atomic structure, or shape [19, 23].

Scanning Electron Microscopy: The FieldEmission Scanning Electron Microscopy (FE-SEM) provides accurate and highly three-dimensional data on the surface microstructure of the sample, whereas Scanning Electron Microscopy (SEM) may describe the microscopic morphology of substances. Currently, FE-SEM and SEM of polyphenol-polysaccharides are used to study surface morphology [24].

Differential Scanning Calorimetry: The thermal stability of grafted copolymers is frequently investigated using DSC technology [8].

Pharmaceutical Utilities of Grafted Polymers:

- To change the biological carrying capacity of a drug:
- To attain the intended features of the dose form
- To graft polymers to obtain specific physicochemical qualities
- To accomplish site-specific distribution by polymer grafting
- Active packaging films
- Hydrogels for regulated medication dispensing
- Micelles for the administration of oral medications
- Emulsions for the delivery of nutraceuticals [8, 11].

CONCLUSION: Polymer grafting involves attaching polymer chains to a backbone polymer, significantly enhancing or modifying its properties. This versatile technique allows for precise tailoring of polymers, leading to improved mechanical strength, thermal stability and chemical resistance. The applications of grafted polymers are vast, ranging from biomedical uses such as drug delivery systems and tissue engineering scaffolds to advanced materials in coatings, adhesives and composites. Additionally, they play a crucial role in environmental applications like water treatment and the development of biodegradable plastics, showcasing their potential in diverse industries. In order to confirm successful grafting of polymers, several instrumental methods, including FT-IR and NMR spectroscopy, SEM, DSC and XRD are often used. Grafted polymers can be further developed into different forms (*e.g.*, films, hydrogels, micelles, and emulsions) with wide applications in the food and pharmaceutical industries. However, studies on the applications of grafted polymers are very limited.

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