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AN OVERVIEW ON POLYMER GRAFTING

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ABSTRACT
Polymers play a major role in pharmaceutical science as it constitutes an important class of materials by providing suitable substitute for conventional materials. Polymer grafting is a versatile method to modify the polymers in where monomers are covalently bonded to polymer. Recently, this approach open a new opening to pharmaceutical formulation. There are different techniques such as crosslinking, grafting, blending and composite formation techniques are used to modify the polymer. But the selection of proper polymer is a very important step for the formulation of the dosage form. Polymer used in pharmaceutical formulation determine the stability of formulation and drug itself, rate of drug release as well as its mechanism. Natural polymer and fibers are of large use for the mankind. Now a days the whole world has concentrated attention of its activity towards renewable and sustainable resources because of environment as well as health concerns. The use of grafted polymer provide many applications in terms of physicochemical properties as well as drug carrying capacity based on dosage form modifications. This review highlights the basic concept of polymer grafting and its various techniques such as chemical grafting, radiation grafting etc. are discussed with their significant pharmaceutical applications.

KEYWORDS: Polymer, Monomer, Fiber, Grafting, Modification.

INRODUCTION
Natural polymer and fibers are of large use for the mankind. Now a days the whole world has concentrated attention of its activity towards renewable and sustainable resources because of environment as well as health concerns. During last few years, the new fiber and polymer from renewable raw materials has been increased in comparison to artificial fibres. Different natural fibers like flax, pine needle, jute and ramie are the most suitable reinforcement materials because of their relatively high strength and stiffness in industries. The main constituents of natural fibers are cellulose, hemicelluloses, pectin and lignin with a small quantity of the extractives. The properties involved in bio-fibers mainly depend upon their origin, age, climatic conditions and extraction techniques. The presence of hydroxyl groups (polar group) in various constituents of lingo-cellulosic fiber reduces the usefulness in many applications. There are various techniques like graft copolymerization, chemical treatment (mercerization, acetylation, benzoylation etc.,) and treatment with various coupling agent can be used in order to improve its adhesion. Generally polymers used in the pharmaceutical industries due of their unique properties. But, pharmaceutical medication are suffered from disadvantage such as short half-lives, poor bioavailability, and physical and chemical instability.[1] Chemical instability of drugs involves some chemical reaction like hydrolysis, oxidation, deamidation and racemization and sometimes physical instability also involves alteration of highly ordered protein structure, leading to undesirable processes such as aggregation, denaturation and precipitation. Moreover, at a specific concentration for a specific time, the delivery of drug to the specific target site can achieved by using of proper polymer and also the selection of suitable polymer system is an important step involved in formulation of drug into dosage form. The incorporation of polymer in formulation design decides the stability of formulation and drug itself, mechanism, and rate of drug release.

Polymers are macromolecules which are composed of monomers linked covalently. These are the substance obtained from different sources i.e plant source, microbial source and synthetic sources which are used as binder, diluents, disintegrates in tablets, protective colloids in suspension, gelling agent in gels, thickeners in oral liquids in pharmaceutical applications.[2] Furthermore, with the help of modification of chemical functional groups of polymer, wide range of favorable properties can be imparted to polymer and unfavorable one can be diminished.

To overcome disadvantages associated with natural gums and synthetic polymers, gums can be modified through different ways or to modulate the site of drug release and

it's kinetic and also to makes them superior to their counterparts.[3]

Concept of Polymer Grafting

Polymer grafting is a versatile method to modify the natural polymer. The main purpose of a surface modification are improving the wettability, biocompatibility, mechanical properties etc of a surface polymer. Graft polymers are segmented copolymers which possess mechanical properties, solution properties different than linear polymers due to branched nature of the polymer as a result of grafted chain. The given picture labelled of "graft polymer" shows how two or more monomers polymerized together, i.e polymer species A are bonded with the grafted chain of B species. Grafting is one polymer modification technique in which a polymer is linked to the backbone of a parent polymer, the substrate, by chemical linkage. Generally, the component of the side chains are structurally different from the main chain and this grafted polymers are used as different application like compatibilizers, impact resistant materials or as a thermoplastic elastomers.[4]

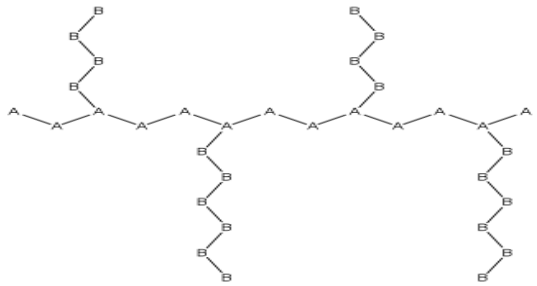

Fig. The graft copolymer consists of a main polymer chain or backbone (A) covalently bonded to one or more side chains (B).

Methods of polymer grafting: Graft polymers are frequently prepared by using different polymerization approaches. There are mainly two types of grafting which are.

i. Grafting with a single monomer and
ii. Grafting with a mixture of two or more than two monomers.

Moreover, grafting copolymers can be obtained by using mainly three mechanism known as grafting to, grafting from and grafting through.

Grafting to: The grafting to method is the one of the simplest method to synthesize the grafted copolymer. Grafting to is resulted by reacting the substrate with using suitable method for creation of immobilized initiators followed by polymerization. This method involves coupling reaction between the functional group and the end groups of the branches.[5] In this method, a polymer chain which has a functional group at the end diffuses through the surface which can be reacted and therefore chain will be grafted to the polymer surface.[6] It has to be mentioned that due to the stereo chemical hindrance, density of grafting in this method is not high. This method often utilize different kind of techniques like free-radical polymerization, anionic polymerization, living polymerization techniques for the synthesis of graft copolymer.

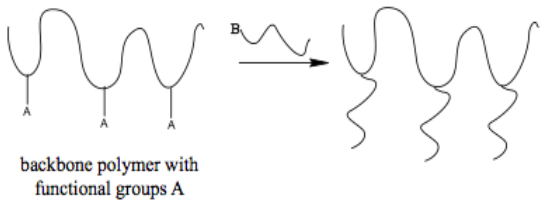

Figure 1: Grafting to approach of polymer modification.

Grafting from: Grafting from is the another most useful grafting approach which is used in the different techniques like cationic grafting, anionic grafting, free radical polymerization techniques and atom-transfer radical polymerization for the formation of grafting from copolymers. In this method, the macromolecular backbone is chemically modified to introducing the active sites which forms by copolymerization, and it can be incorporated in a part of the polymer or in a post-polymerization reaction.[5,6] This active sites are more capable of initiating functionality. The number of active sites with polymeric backbone helps to form the branches and it influences the number of grafted chain.

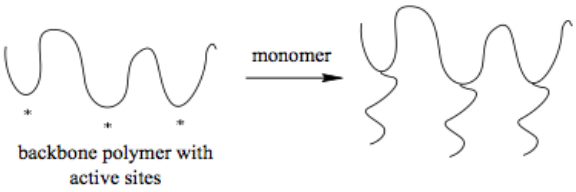

Figure 2: Grafting from approach of polymer modification

Grafting through: It is one of the simplest way to synthesize a graft polymer with distinct side chain, which is also called as macro monomer method. In the grafting through method, the polymerization represents copolymerization of free monomers in solution and polymerizable units bound to a substrate or is copolymerized with free radicals and with acrylate functionalized macro monomer.[7] Free polymer chains are formed initially in solution which can incorporate the monomer. Thereby, it get covalently bonded to the surface during polymerization process. The number of grafted chains are determined by the ratio of concentration of monomer or macromonomer as well as their behaviour of copolymerization. The graft copolymers are form when reaction process proceeds by

placement of polymer branches. The grafting through method allows for branches to be added homogenously or heterogeneously on the macromolecular to the monomer based on the reactivity ratio of the terminal functional group. The difference involved in the graft distribution has some specific effect on the physical properties of grafted copolymer. Different well known techniques like polymerization technique, living polymerization technique are used in this grafting through method.

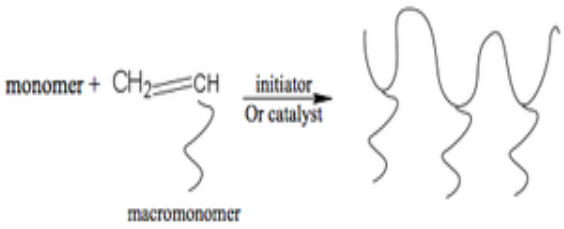

Figure 3: Grafting through approach of polymer modification.

Different Techniques Involved in Polymer Grafting.

1. Chemical grafting
A) Free radical grafting
B) Ionic grafting
2. Living polymerization grafting
3. Photochemical grafting
4. Enzymatic grafting
5. Plasma radiation technique
6. Radiation grafting.[8]

Chemical grafting method

Chemical grafting is a method, in which the using of initiator is very important. It is further classified into two types.

A) Free radical grafting

One of the commonly used method for the modification of polymer is chemical grafting. This method involves that the free radicals obtain from the initiator are transferred to the substrate, which are react with monomer to form the graft copolymers. Different types of initiator are used in free radical grafting as initiator systems are as follows.[9]

- FAS: Ferrous ammonium sulphate.
- APS: Ammonium persulfate.
- CAN: Cerric ammonium nitrate.
- PPS: Potassium persulfate.
- TCPB: Thiocarbonation potassium bromate.
- PDC: Potassium diperioadtocuprate.

For determination of grafting percentage, initiator plays an important role on grafting. The grafting of vinyl monomers onto cellulose or cellulose derivatives was performed by chemical initiators. Generally, Redox initiators can be used at low temperatures, that they can react only with them amorphous region of cellulose. The reason involved in this system is that the latter are more reactive than the crystalline phase.

Ionic grafting

In this method the grafting can proceed through ionic mode and an anionic mechanism is involved where alkoxide of alkali metals used as initiators (such as sodium methoxide) or by cationic mechanism where alkaline metals salts are used as alkyl ammonium.[10]

Anionic grafting

Anionic grafting is also known as anionic grafting polymerization grafting. Hossein *et al.* performed the modification of a polysaccharide, sodium hyaluronate, by graft copolymerization of acrylic acid. Using the anionic initiator ammonium persulfate can initiated this graft copolymerization. After extraction of homopolymer, increasing in the molecular mass of sodium hyaluronate which was considered as the end point of grafting and also the basis for the determination of the grafting parameters. In this study, effect of concentration of sodium hyaluronate, acrylic acid, and ammonium persulfate as well as grafting temperature on grafting process was evaluated.[11]

Cationic grafting

Yoshikawa et al. have modified the chitosan with cationic living polymers like poly (isobutyl vinyl ether) and poly (2-methyl-2oxazoline). Analysis of the effect of molecular weight of living polymer cation on the mole number of grafted polymer was done in this study also it was found that viscosity of the resulting polymer was increased with increasing the grafting percentage in the process of grafting. This grafted polymer was also found to be soluble in water.[12]

Living polymerization grafting method

Transfer and termination reactions of the process are controlled than the conventional radical grafting method. In living polymerization, results in living polymers with regulated molecular weights and low polydispersities. Controlled free radical polymerization may be effectively achieved through atom transfer radical polymerization (ATRP). It proceeds until all monomers have been consumed and further addition leads to polymerization reaction. Szwarc et al. define the living polymerization grafting as “living polymer” is “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. Sometimes, a conventional radical polymerization undergoes disadvantage like it does not possess control over the molecular weight, molecular weight distribution, and architecture of the polymer, making its macroscopic properties very difficult to be tailored.[13-16]

a. Stable free radicle polymerization (SFRP)

SFRP generally applied for acrylamides and styrenics, still major attention in literature was on styrenic

monomers. Reversible homolytic cleavage of a dormant chain end to form a stable free radical site was applied to the polymerization.[17]

b. Reversible addition

Fragmentation chain transfer (RAFT) is achieved by performing a free radical polymerization in the presence of dithio compounds, which act as efficient RAFT agents.[18]

c. Atom transfer radical addition (ATRP)

Dormant chains are capped by halogen atoms which are reversibly transferred to metal complexes in the lower oxidation states. The key reaction of ATRP is the activation-deactivation dynamic equilibrium process.[19,20] Sonmez *et al.* reported the grafting of acrylamide by ATRP method and the initiation appears to take place through radical formation in a redox reaction of N – Chlorosulfonamide groups with CuBr.[21]

Photochemical Grafting

Photochemical grafting is another most important method for the modification of monomers onto polymers. Photochemical grafting can be achieved through sensitizer or in the absence of sensitizer. In this process, grafting occur due to the absorption of light by the chromophore, moves to the excited state, where it get dissociated into reactive free radicals. If the free radicals are not formed through bond rupture, the process can be initiated by the addition of photosensitizers such as benzoin ethyl ether, dyes etc. Then the free radicals react with monomer to form grafted polymer.[22-24]

Enzymatic grafting

The main principle involved in this process is based on an enzyme which can be used to initiates the chemical as well electrochemical grafting reaction. In this grafting techniques, the using of enzyme can offer a green approach by eliminating the use of reactive reagents with respect to safety, economy and efficacy. Furthermore, the application of enzymes specificity may offer the potential for tailoring macromolecular properties to desired ones in a precise manner. *Chen et al.* studied tyrosinase initiated the grafting of peptides onto the amine-containing polysaccharide chitosan.[25]

Plasma radiation-induced grafting

In the method of plasma radiation grafting the process is initiated by using plasma. In this method, electrons are accelerated from the plasma have adequate energy to induce cleavage of the chemical bond of the polymer, ends in the formation radicals to initiate the graft co-polymerization. This method can be carried out without adding any photosensitizer. But this method is restricted to surface grafting.[26,27]

Radiation grafting

Radiation grafting is the most widely used grafting method which helps to functionalize the surface of the polymer. Irradiation grafting is the most commonly used methods for the modifying of the surface and bulk properties of the polymeric material is to graft monomers onto them and this technique is known as radiation induced grafting. This technique has the advantages such as low cost, simplicity, control over process and adjustment of the materials composition and structure. In addition, this method makes assure that the grafting of monomers that are difficult to polymerize by conventional methods without residues of initiators and catalyst.1 Radiation-induced grafting method is simply based on the irradiation of a base polymer either in the presence of a monomer (simultaneous radiation grafting) or without a monomer (pre-irradiation grafting) to create active sites.[28]

Ultraviolet radiation (UV), Electron beam (EB) radiation and gamma rays can be used for generating the active sites (free radicals) on a polymeric surface which can react with the vinyl monomer to form a graft copolymer. Generally the active sites (free radicals) easily reacts with the proper functional monomer to form covalent bond and as a consequences, growth of a macromolecules and all of these without use of chemical initiators.

The grafting of vinyl monomers onto natural fibres have also performed by radiation or microwave irradiation. The use of microwave irradiation was used to reduce reaction times as compare to traditional thermal initiated reactions. Kaith et al. (2007) has investigated the improvement in chemical resistant behaviour of methylmethacrylate (MMA) grafted flax fibre under the influence of microwave radiation (MWR).[29]

Free radical grafting

Free radical polymerization is one method of polymerization by which a polymer forms by the successive addition of the free radical building blocks. Free radical may be formed by different mechanisms usually involving separate initiator molecules. In this method, for obtaining a wide variety of different kinds of polymer and material composites, the free radical polymerization is a key synthesis. The irradiation of macromolecules can cause homolytic fission and thus `it forms free radicals on the polymer. The presence of an initiator is not essential in this free radical technique. In this case the medium is important e.g if irradiation is carried out in air then peroxide may be formed on the polymer. The grafting is proceed in three different ways and these are.[30-33]

a. Pre irradiation: the process of pre radiation involved the following steps.

• In the presence of air or inert atmospheric condition the polymer substrates are irradiated to form the stable active radical sites.

• Initiation of monomer reaction occurs with irradiated polymeric substrate.

b. Peroxidation

c. Mutual irradiation technique.

i. Radiation grafting through anionic mode
Radiation grafting process can also proceed with the help of an anionic mode and this method mainly involves the generation of ion through irradiated high energy, the ionic grafting is of two types which are cationic and anionic. To form the ionic polymer, the polymers are irradiated. Then this polymeric ion is reacted with monomer to form grafting copolymer.

Type of Polymer
Different grafting method including radiation grafting method which are used to modify the natural polymer as well as synthetic polymers. In this method different materials are used which should have the specific characteristics since the chemical structure and grafted morphology that can affect the degree of grafting property. Generally high irradiation dose is not recommended for pre-irradiation method. The amount of the radicals can influenced the grafting process in the polymeric irradiated substrate. Different analytical techniques such as Electron paramagnetic resonance (EPR) spectroscopy are used for identification and tracking the conversation of formation of radiation paramagnetic species and also EPR techniques can helps to monitor the radicals present in the sample. The comparison of amount of radicals in polymers are done by this method and it is also helpful to predict the radiation induced grafting behaviour. Different types of polymer for e.g. polystyrene and polyethylene can be irradiated by using ionization radiation grafting method.[34-36]

Type of monomer
The radiation grafting degree is a function of the reactivity of the consumed monomer. The reactivity property of monomer mainly depends on the chemical structure, polarity and also depends on energy of bonds. The concentration of monomer and type of different solvent used in the grafting techniques can influenced the property of grafting. The reactivity of monomer are also depended on diffusion of the reactant to the surface of polymer, which can affects the rate as well as efficiency of grafting process. Generally, with increasing monomer concentration, the degree of grafting increases. However, using too high concentration of monomer may enhance homopolymerization and decrease the degree of grafting. For every grafting system, the monomer concentration should be adjusted to avoid this undesired homopolymerization of the monomer. There are different kinds of monomers which are most frequently used in the grafting polymerization process are acrylic acid, acrylamide, methacrylate, methyl methacrylate, *N*-isopropyl acrylamide etc.[37]

Type of solvent
Selection of solvent used in radiation technique is very important. The type of solvent mainly affects on homogeneity of the grafted chains and also affects on efficiency of grafting, which can be obtained using good swelling solvents. During the grafting process depending on the solvent, its properties and behavior during the grafting process, the degree of grafting for the same monomer, dose, atmosphere reaction, temperature, etc. can differ significantly. Water and alcohols are widely used for grafting of hydrophilic monomers. However for every grafting system, the solvent should be selected experimentally, especially for the RAFT-mediated grafting processes.[38]

Type of radiation
The different type of radiation (dose, dose rate) such as gamma radiation and electromagnetic radiation are frequently used in the radiation induced grafting process. Using a gamma source, a mutual method is involved in this radiation process in where electron beam radiation is the preferred radiation, as compare to the pre irradiation process. The dose rate i.e. delivery of dose is specific unit of time in radiation process. But in case of source of isotope, the dose rate is very low while the beam of electron radiation is relatively very high. Generally, the irradiation time in a gamma source is much longer as compare to using a high energy electron beam. This factor affects the degree of grafting. When the dose is higher, the greater the amount of radicals are formed in the polymeric material, which having the direct impact on the degree of polymeric grafting. The concentration and lifetime of radicals are affected by the dose rate and the oxidation and time after that the termination of the growth graft chains occurs. In the process of simultaneous grafting or mutual grafting, for the same dose, increase in the dose rate results in lower efficiency of grafting, because the high concentration of radicals increases their recombination leading to a rapid termination process and to more homopolymerization.[39,41]

Temperature
Irradiation temperature and grafting temperature are important parameters influencing the process of radiation-induced grafting.

Irradiation temperature
In the pre-irradiation method, the polymeric substrate are irradiated at sub-ambient temperatures which should be 0°C and lower and in order to restrain the combination of radicals generated during irradiation. Then, even after storage, the trapped radicals may be used to initiate graft polymerization in the process.

Different Analytical Techniques Used in Polymer Grafting: There are different analytical techniques are used to characterize as well as evaluate the grafted polymeric materials and these are given below.

Fourier transmission infrared, NMR, X-ray diffractometer, differential scanning calorimeter, Elemental analysis and MW analysis
i) Fourier transmission infrared (FTIR): FTIR helps to characterize specific functional groups added to blend as a result of grafting.

ii) NMR: 13C -solid state NMR are used for characterization of Hydrocarbon backbone.

iii) X-ray diffractometer (XRD): XRD is often used to identify new formed phases, define the degree to which starting materials have reacted and assess the level of amorphicity of the final products. The main purpose of XRD is to characterize the Polymorphism of polymers.

iv) Differential scanning calorimeter (DSC): Purity and melting point of polymers are characterize by using DSC technique.

v) Elemental analysis: Elemental analysis Elemental composition such as C, H, N content are characterized by element analysis techniques.

vi) MW analysis: This analysis techniques are performed to characterize the gain in molecular weight after grafting of polymer.

Applications

Grafted copolymers are used in various application which have got diversified properties. Generally, polymers are biodegradable, environment friendly, efficient and cost effective also and these after cross linking and graft copolymerization can be used for sustained release of drugs. Hydrogel used in oil industry are highly selective in nature which can remove saline from petroleum fraction and saline emulsion. So, such grafting polymer plays an important role in oil industry also. Sometimes, the characteristics of hydrogel faces the problem to trap the colloidal particles in their folds and force them to settle down at the bottom. Thus, modified polymers play an important role in the removal of colloidal particles from potable water. Grafting of synthetic polymers onto polysaccharides can further improve their properties like water repellency, acid–base resistance, thermal stability and increased mechanical strength. Moreover, the grafted polymers when used as reinforcing materials for the preparation of biodegradable composites are found to possess better compatibility with the matrix. Grafted copolymers are used in different pharmaceutical application such as Membranes for the separation of gases or liquids. It is also used as a drug deliver or as a polymeric emulsifier in the formulation of dosage forms.[42-44]

CONCLUSION

The using of different grafting techniques help to modify the property of polymer and therefore polymer grafting is a most wonderful new technique to give design in dosage form. Modification of polymer makes the polymer in higher quality to their natural as well as synthetic counterpart. Various grafting techniques such as conventional one chemical grafting, enzyme grafting, living polymerization, radiation-induced and recently introduced plasma radiation grafting are used to achieve the tailored properties of polymer. The grafted polymers can be characterized by using different analytical techniques such FTIR, NMR, and XRD. These different modern techniques also helps to analyse the grafting of polymers. Recently, there are a various number of industrialist should have to show great interest in the field of polymer grafting which are applicable in the pharmaceutical application.

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