CHAPTER 1
INTRODUCTION
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This chapter deals with the general introduction of polysaccharide-based hydrogel materials and their utilization in various fields. The aim and objectives of the present research work are also given at the end of this chapter.

1.1 Polysaccharide-based Hydrogels

The terms gels and hydrogels are used interchangeably by food and biomaterials Scientists to describe polymeric cross-linked network structures. The term hydrogel describes three-dimensional network structures having high-molecular weight and composed of a polymer backbone, grafted chains, water molecules and a crosslinking agent. These are polymeric materials that do not dissolve in water at physiological temperature and pH but they swell considerably in an aqueous medium and demonstrate extraordinary capacity (>20%) for imbibing water into the network structure (Peppas et al., 2000). The hydrogel structure is created by the hydrophilic groups or domains present in a polymeric network upon the hydration in an aqueous environment. The high-water content inside of the hydrogel fills up the polymer mesh (or porous space) and allows selective diffusion of solutes through the hydrogel polymeric matrix. These characteristics allow hydrogels to be used in a membrane separation process (Bell and Peppas, 1995). The three forces; polymer-water interactions, electrostatic and osmosis expand the hydrogels network. Hydrogels have many potential applications and it is well known that these applications are closely related to the intrinsic properties of the polymeric networks (Langer and Peppas, 2003; Hennink and Van Nostrum, 2002).

Hydrogels have emerged since the early 1950s as important materials in biomedical fields (Ulijin et al., 2007). They can be prepared by simultaneous copolymerization and cross-linking of one or more monofunctional and multifunctional monomer or by cross-linking of homopolymer or copolymer in solution. Semi-interpenetrating polymer networks (semi-IPN) is a way of blending two polymers where only one is crosslinked in the presence of another to produce an additional non-covalent interaction between the two polymers (Sperling, 1981). Semi-IPNs have been
developed as a convenient technique of preparing multi-component polymer materials and provided a convenient route to modify the properties of natural polymer-based hydrogels. Because of their exceptional properties like biocompatibility, biodegradability, renewability and non-toxicity, the natural backbone based hydrogels are playing an important role in diversified fields. In addition to graft co-polymerization, further development in this area involves the formulation of interpenetrating network (IPN) structure to impart additional rigidity to the matrix (Lee and Chen, 2001). One polymeric network swells in the network of another polymer and results in the formation of interpenetrating polymeric network. IPNs are three dimensional networks formed from homogeneous or heterogeneous polymers cross-linked in presence of one another (Ekici and Saraydin, 2004), and hence, combine the properties of each network. IPNs are one of the promising and versatile materials with enormous possibilities and potential. Hydrogels form the class of most biocompatible materials because they resemble natural tissues more than any other class of biomaterials. Moreover, they possess high water content, soft and rubbery consistency and low interfacial tension with water or biological fluids (Blanco et al., 1996). These polymers are coined with different names, based on their physical or chemical properties like, “stimuli-responsive polymers” (Jeong and Gutowska, 2002) or “smart polymers (SP)” (Hoffmann et al., 2000) or “intelligent polymers” (Kikuchi and Okano, 2002) or “environmental-sensitive” polymers (Qiu and Park, 2001). They form another important class of smart materials that are stimuli responsive and exhibit a phase transition in response to change in external conditions such as pH, ionic strength, temperature and electric currents (Bhardwaj et al., 2000). Smart hydrogels are very different from inert hydrogels in that they can ‘sense’ changes in environmental properties and respond by increasing or decreasing their degree of swelling.

Biopolymers, being renewable raw materials are gaining considerable importance because of the limiting existing quantities of fossil supplies and the recent environment conservative regulations (Clasen and Kulicke, 2001). Hybridization of the natural polymers with synthetic polymers is of great interest because of its application to biomedical and biodegradable materials. Grafting involves attachment of polymer chains to the back-bone polymer. The modification of polysaccharides to develop the biocompatible materials is a powerful tool, to control the interaction of
the drugs within the polymeric matrix in sustained drug delivery devices and to tailor the release profile of drugs and to enhance the load capability (Nishimura et al., 1993). Grafting and cross-linking of vinyl monomers are the common practices to modify and to improve the functional properties of polysaccharides and forms the three dimensional polymeric networks which swell quickly by imbibing a large amount of water (Mostafa and Morsy, 2004). Amount and type of polysaccharide backbone, monomer and crosslinker concentration affect the swelling ratio of the hydrogels (Mundargi et al., 2007; Mundargi et al., 2007; Zhang et al., 2005). Recently, many researchers have focused their attentions on the SAPs for developing new applications, such as conducting materials, biomaterials, sensors and release materials, wave-absorbing materials (Abd El- Rehim, 2005; Dispenza et al., 2006; Ito and Chuang, 2003; Omidian et al., 2005; Richter et al., 2004; Siddhanta and Gangopadhyay, 2005; Wada et al., 2004). They are useful in agriculture and horticulture, sensors, biomedical and pharmaceutical applications.

1.2 Polysaccharides

Polysaccharides are polymeric carbohydrate structures which are formed by repeating units joined together by glycosidic linkages and contain various degrees of branching. Polysaccharides have general formula Cₙ(H₂O)ᵣ where r ranges between 200 and 2500. In nature, polysaccharides have various resources like algal origin (alginate), plant origin (pectin and guar gum), microbial origin (dextran and xanthan gum) and animal origin (chitosan and chondroitin). Starch and glycogen are storage polysaccharides whereas cellulose and chitosan act as the structural materials. They provide mechanical strength to plants (Lapasin and Pricl, 1995) which make them fit for applications like fibers (Pillai et al., 2009), films (Bastos et al., 2009), adhesives (Haag et al., 2004), melt processing plastics (Shi et al., 2007), hydrogels (Reis et al., 2007), drug delivery agents (Liu et al., 2007) and emulsifiers (Nakauma et al., 2008). Polysaccharides are bio-based materials possessing unique combination of functional properties and environmental friendly features. They are non-toxic, biodegradable and renewable materials. Commercially available products include starch, cellulose and their derivatives e.g. cellulose acetate, carboxymethyl cellulose, methyl cellulose, sodium alginate, xanthan gum, dextrin, carrageenan and hydralouric acid. Presence of
polar functional groups, high molecular weight and relatively rigid backbone are the key features which directly affect the physical and chemical properties of polysaccharides. Due to high interchain cohesive forces, they have high melting and softening temperatures. The stiff backbone makes them brittle and has high degree of crystallinity leading to insolubility in water and common organic solvents. Hydroxyl groups in the naturally occurring polysaccharides provide the reactive sites for the modification and materials with new industrial properties can be obtained.

The polysaccharides are the most abundant natural organic materials and polysaccharide based graft copolymers are of great importance and widely used in the various fields. Natural polysaccharides have received more attention due to their advantages over the synthetic polymers as they are non-toxic, biodegradable and economically viable. Modification of polysaccharides through graft copolymerization improves the properties of natural polysaccharides. Grafting is known to improve the characteristic properties of the backbones. Such properties include water repellency, thermal stability, flame resistance, dye ability and resistance towards acid-base attack and abrasion.

Graft copolymers play an important role in the preparation of conducting hydrogels. These graft copolymers on subjecting both for composting and soil-burial biodegradation studies are found to be biodegradable in nature. Polysaccharides and their graft copolymers find extensive applications in diversified fields. Applications of modified polysaccharides include drug delivery devices, moisture retention study in different soil, controlled release of fungicides, selective water absorption from oil-water emulsions and purification of water.

1.3 Concept of Graft Copolymerization

Graft copolymers are composed of a main polymer chain (backbone) to which one or more side chains (branches) are chemically connected through covalent bonds. Stannett (1981) defined graft copolymers as “Graft copolymers consist of a polymer backbone with lateral covalently linked side chains”. Both the backbone and the side chain polymers can be homopolymers or copolymers. Graft copolymer is a polymer comprising of molecules with one or more blocks of species connected to the main
chain as side chains, having constitution or configurational features that differ from those in the main chain (Ring et al., 1985). A polymer is called copolymer when the repeating units are two different monomers. The sequence in which monomers attach themselves depends upon their relative reactivities. Copolymers can be random, alternate, block and graft copolymers. First three types of copolymers differ with respect to sequencing of monomers. In case of random copolymer monomer units are randomly placed, whereas, monomers are present in an ordered form in case of alternate copolymer. Block copolymer involves the segments of different monomers attached together at terminals. Graft copolymer has a preformed polymer acting as a backbone to which polymeric chains are attached at different sites. Thus, graft copolymer consists of a polymer backbone with lateral covalently linked side chains (Stannett, 1981). The side chains may consist of a single monomer or of binary mixture. The graft copolymerization involving single monomer usually occurs in a single step whereas, graft copolymerization in the presence of vinyl monomers binary mixtures may occur with the simultaneous or sequential addition of monomers. When two monomers are added side-by-side it is called mosaic grafting. First graft copolymer was synthesized by Alferay and Bandel in 1951 by polymerizing vinyl acetate in the presence of styrene and vinylidene chloride (Alferay and Bandel, 1951).

Graft copolymerization of natural polymers with functional synthetic polymers gives modified products having wide range of applications. Graft copolymerization is an easy method to modify the structure of natural polymers and thus makes them suitable for various applications (Abdel-Halim et al., 2008a; 2008b; Abdel-Halim et al., 2010; Abdel-Halim et al., 2010). Modification of Guar gum by grafting of water-soluble vinyl monomers, results in the retention of desirable properties and incorporation of favorable properties. Grafting and crosslinking are common practice to improve the functional properties of polysaccharides and are carried out by chemical initiation or radiation initiation polymerization. In case of chemical initiated copolymerization, sometimes initiator and crosslinking agent left in the polymeric networks affect structural homogeneity, swelling behavior and mechanical properties of the hydrogels. In order to prepare the hydrogels for technologically important applications the network should be free from these impurities. In the years to come, there is going to be a continued interest in the natural gums and their modifications with the aim to have better materials for biomedical and pharmaceutical applications.
Recently, a lot of work have been reported mainly focusing on the applications of biopolymers based hydrogels in different fields like waste water treatment, superabsorbents, bio-medical applications and drug delivery applications (Peppas et al., 2000; Omidian et al., 2005; Kaith et al., 2012).

The presence of functional groups on the backbone is the basic requirement for the synthesis of graft copolymers. Graft copolymerization can be performed in homogeneous as well as in heterogeneous medium depending upon the solubility of monomer and the nature of solvent used for the reaction. Graft copolymerization proceeds either through “grafting from” or “grafting onto” method.

“Grafting from” method involves the generation of active sites on the polymer backbone which in turn initializes the monomer polymerization onto backbone and thereby resulting in the formation of graft copolymer (Fig. 1.1).

![Fig. 1.1: Schematic Representation of “Grafting from” Method](image1)

When a growing polymer chain (X₂) attacks another polymer X₁ the grafting is said to occur through “grafting onto” method (Fig. 1.2).

![Fig. 1.2: Schematic Representation of “Grafting onto” Method](image2)
Grafting method results in homogeneity in composition and molecular weight distribution. It provides a technique to incorporate special properties like dye ability, crease resistance, moisture and chemical resistance in the parent backbone polymer (Kaith et al., 2011; Basu et al., 1998; Mehta et al., 1994). Due to these characteristics a wide variety of natural and synthetic polymers have been modified through graft copolymerization. Such graft copolymers are called specialty polymers possessing branches of different chain lengths and resulting in desired properties.

1.4 Classifications of Hydrogels

Polysaccharide hydrogels can be classified on the basis of their synthesis, type of monomer involved and ionic charges.

1.4.1 On the basis of type of Monomer:

On this basis they can be classified into three categories:

(a) Homopolymer Hydrogels: These hydrogels possess single specie as basic unit and form three-dimensional network (Fig. 1.3) (Yang et al., 2002). The cross-linked network of homopolymer depends upon the nature of monomer and polymerization technique. The cross-linked networks are formed in the presence of crosslinking agent or without the presence of crosslinking agent. An example of homopolymer hydrogel is cellulose hydrogel and these were synthesized through one-step polymerization method in which cellulose was dissolved in urea/NaOH solution. On the addition of epichlorohydrin as cross-linker results in transparent hydrogel with macro porous structure (Zhou et al., 2007).

Fig. 1.3: Schematic Representation of Homopolymer
(b) Copolymer Hydrogels: These hydrogels possess two or more monomeric units in which at least one of the monomer is hydrophilic. Copolymer hydrogels have different arrangements like random, block or alternative with respect to main polymeric chain. The biodegradable triblock poly(ethylene glycol)-poly(ε-caprolactone)-poly(ethylene glycol) (PECE) co-polymeric hydrogel was used for the development of drug delivery system (Gong et al., 2009). A low molecular weight monomer is radically copolymerized with a (meth)acrylate functionalized macromonomer (Fig. 1.4) (Matyjaszewski and Tsarevsky, 2009).

![Fig. 1.4: Schematic Formation of Graft Copolymer](image)

(c) Interpenetrating Polymeric Hydrogels (IPN): These hydrogels involve two independent cross-linked networks (Fig. 1.5). The hydrogel in which one polymeric network swells in the network of another polymer results in the formation of IPN. These are called semi-IPN when one of the components is cross-linked, while the other component remains uncross-linked (Maolin et al. 2000).

![Fig. 1.5: Schematic Representation of Interpenetrating Network](image)
1.4.2 On the basis of Ionic Charges:

On this basis they can be classified into three categories:

(a) **Neutral Hydrogels:** These hydrogels have neutral monomeric units which cross-link to form three-dimensional networks (Fig. 1.6) and may be homopolymeric or copolymeric in nature. The copolymeric polysaccharide hydrogels with monomers like acrylamide, hydroxyalkyl methacrylates and N-vinyl pyrrolidone result in neutral hydrogels.

![Fig. 1.6: Neutral Hydrogel Network](image)

(b) **Ionic Hydrogels:** These hydrogels contain charged anionic and cationic monomeric species (Fig. 1.7). These may be formed by modifications in neutral hydrogels by partial hydrolysis or addition of excess of polyelectrolytes.

![Anionic Polymer](image) ![Cationic Polymer](image)

**Fig. 1.7: Ionic Hydrogels**

(c) **Ampholytic Hydrogels:** Hydrogels have polymeric networks having both cationic and anionic monomeric units (Fig. 1.8). The properties of ampholytic hydrogels depend upon the presence of ionic species along the polymer chain. Proteins below its
isoelectric point are positively charged and expected to associate with anionic hydrocolloids and form polyion complex hydrogels (complex coacervate) (Magnin et al., 2004).

Fig. 1.8: Formation of Polyion Complex Hydrogels

1.4.3 On the basis of Method of Synthesis:

On this basis they can be classified into two categories:

Gels are substantially dilute cross-linked systems and can be categorized principally as weak or strong depending on their flow behaviour in steady-state (Hoffman, 2002). Gelling polysaccharides are very common in food industries (Sabyasachi et al., 2010). They can further be divided into synthetic or natural polysaccharide based hydrogels (Rosiak and Yoshii, 1999). The hydrogel structure is created by the hydrophilic groups present in polymeric network. Gelation which corresponds to the cross-linking of macromolecular chains depends upon the structural conformation of the initial materials. The mixture of such polydisperse soluble branched polymer is called ‘sol’. Continuation of the linking process results in increased branched polymer chains with decreasing solubility. Thus, the ‘infinite polymer’ is called the ‘gel’ or ‘network’ and is permeated with finite branched chains. Gelation or sol-gel transition can take place either by physical cross-linking (physical gelation) or by chemical cross-linking (chemical gelation). Physical gels can be sub categorised as strong gels and weak gels (Scheme 1.1).

(a) Permanent / Chemically Cross-linked Gels: The hydrogels with covalent bonding exhibiting more stable behaviour are known as permanent or chemical gels (Fig. 1.9) (Hennink and Nostrum, 2002). Such hydrogels attain an equilibrium
swelling state which depends on the polymer-water interaction parameter and the crosslink density (Rosiak and Yoshii, 1999).

(b) **Reversible / Physically Cross-linked Gels**: Hydrogels held together by molecular entanglements, and/or secondary forces including ionic, hydrogen bonding or hydrophobic interactions are known as reversible or physical gels (Fig. 1.9). In physically cross-linked gels, dissolution is prevented by physical interactions, which exist between different polymer chains (Hennink and Nostrum, 2002). Such interactions are reversible and can be disrupted by changes in physical conditions or application of stress (Rosiak and Yoshii, 1999). Cross-linking may be achieved by different techniques depending upon involvement of physical or chemical cross-linking.

![Diagram of gelation mechanisms](image)

**Fig. 1.9: Chemically Cross-linked and Physically Cross-linked Hydrogels**

**Scheme 1.1: Classification of Gelation Mechanism**

- Physical
  - Strong
    - e.g. elastomer, gelatin
  - Weak
    - e.g. Xanthan, matured acacia gum

- Chemical
  - Condensation
    - e.g. polyeaster gel
  - Addition
    - e.g. CMC-g-acrylic acid
  - Cross-linking
    - e.g. polydimethylsiloxane
1.5 Methods of Graft Copolymerization

Basic principle that lies behind the synthesis of graft copolymerization is the generation of active sites, in the form of free radicals or a functional group, on the backbone. Polymerization of monomers onto active sites results in graft copolymerization. Several methods have been proposed for the generation of graft copolymers or for the generation of active sites on the polymeric backbones and are classified as:

(a) Physical Methods
(b) Chemical Methods
(c) Enzymatic Grafting
(d) Plasma-Initiated Grafting
(e) Radiation-Induced Grafting

Among these different methods of graft copolymerization, chemical methods and radiation-induced grafting methods are extensively studied.

1.5.1 Chemical Method

Chemical method of graft copolymerization involves the use of chemicals which act as initiators to generate active sites on backbone (Fig. 1.10). The use of various redox initiator systems like Lewis acids, strong bases and metal carbonyls have been reported for chemical grafting. Grafting of vinyl monomers onto backbones has been accomplished by using a range of free radical initiators and redox systems like benzoyl peroxide, azoisobutynitrile, ceric ammonium nitrate, potassium persulphate, potassium permanganate and Fenton’s reagent (Shah et al., 1950; Gao et al., 1998; Hsu and Pan, 2007; Cho and Lee, 2002; Misra and Dogra, 1980; Chiang and Hu, 1996). Researchers are also developing new redox systems for the incorporation of desired properties into backbone. The potassium peroxydiphosphate-metal ion-cellulose thiocarbonate redox initiator system use for the graft copolymerization of methylmethacrylate onto cellulose in fabric form (Zehran and Mahmoud, 2003).

Atom transfer radical polymerization (ATRP) is a modern method to generate free radical sites on dormant chains. In this method halogen atoms are capped onto inactive sites which are reversibly transferred to metal complexes in lower states. A
large number of cross-linked hydrogels have been synthesized using grafting process (Hennink and Van Nostrum, 2002).

**Fig. 1.10: Formation of Graft Copolymer through Chemical Method**

### 1.5.2 Radiation-Induced Grafting

Radiation-induced grafting is the most convenient method for the graft copolymerization. When electromagnetic radiations pass through backbone it results in the formation of active sites for the reaction (Fig. 1.11). Radiation technique enables to maintain the purity of product as it is free from contamination. It allows to carry-out reaction at different depths of backbone which depends upon the penetrating power of the radiation used. Moreover, the molecular weight of polymer formed can be regulated in case of radiation induced grafting. The unique features of radiation method make it a preferred technique of graft copolymerization (Kaur *et al.*, 1998; Kaith and Kalia, 2008).

Grafting can proceed either by the use of low energy radiations or high energy radiations. Irradiation of backbone with low energy radiations like UV and Visible light results in the homolytic fission to generates free radicals on the backbone (Khan *et al.*, 2001; Hassan *et al.*, 2002; Mamun *et al.*, 2010; Zaman *et al.*, 2010). In presence of low energy radiations grafting may proceed with or without photoinitiator. The graft copolymer of partially carboxymethylated *Guar gum* (PCMGG) with methyl acrylate was synthesized by using ultraviolet radiation as an assisted initiation approach and cerium (IV) ammonium nitrate (CAN) as a photo-initiator (Thaker and Trivedi, 2005). The UV-initiation method shows higher graft ratio and graft efficiency than that without UV-initiation (Thaker and Trivedi, 2005).
Microwave radiation is another important energy source and is emerging as an effective tool for graft copolymerization. Microwave radiations can rapidly transfer the energy into bulk of reaction mixture which results in the rapid interaction of the material in the reaction mixture (Deshayes et al., 1999). Microwave-mediated synthesis routes are characterized by short reaction times with excellent yields. Polyacrylamide was graft copolymerized on chitosan under microwave radiations with reaction rate eight times higher than conventional heating (Singh et al., 2006). Grafting of ε-caprolactone (Fang et al., 2005) and acrylic acid (Huacai et al., 2006) onto chitosan has been studied under microwave radiations. Grafting of hydroxymethylacrylate onto wool fiber (Xu et al., 1996), methylmethacrylate onto flax fiber (Kaith et al., 2008), acrylic acid onto Artemisia seed gum (Zhang et al., 2007), polyacrylamide onto Xanthan (Kumar et al., 2008) and Guar gum (Singh et al., 2004) has been reported under microwave radiations. Cassia siamea seed gum has been found to undergo graft copolymerization under microwave radiations without the use of radical initiator (Singh and Tripathi, 2006).

Radiation induced grafting can proceed in three different manners:

(a) Mutual or direct method
(b) Preoxidation method
(c) Pre-irradiation method

Mutual method involves the simultaneous irradiation of backbone and monomer to generate free radicals (Fig. 1.12). The product formed is a mixture of homopolymer and graft copolymer. The schematic presentation can be as follows:

![Fig. 1.12: Grafting through Mutual Method](image-url)
Preoxidation method involves the irradiation of polymer in the presence of oxygen. The peroxides and hydroperoxides are formed which in subsequent steps initiate the polymerization of monomer resulting in formation of graft copolymers (Fig. 1.13).

![Fig. 1.13: Grafting through Preoxidation Method](image)

Pre-irradiation technique involves the exposure of backbone to radiations in inert environment to form free radicals which when treated with monomers result in graft copolymerization (Fig. 1.14). Gamma-radiation-induced graft copolymerization of methyl methacrylate onto jute fiber was carried out by the preirradiation method in an aqueous medium by using octylphenoxy-polyethoxyethanol as an emulsifier. The different factors that influenced the graft copolymer reaction process have been investigated (Khan, 2005).

![Fig. 1.14: Grafting through Pre-irradiation Method](image)

### 1.6 Conducting Polymeric Hydrogels

The modifications of crosslinked hydrogels with conducting polymers (CPs) may lead to the preparation of multifunctional electrical conducting materials. A conducting hydrogel describes a polymer with combined properties of water absorption and conductivity. Conducting polymers (CPs) has the electronic and optical properties of semiconductors and the metals, in addition to the fascinating mechanical properties due to processing advantages of polymers. Since conducting polymers have combined
properties of polymers and metals, therefore, they have extensive applications in different fields like button size battery, electrochromic devices, electromagnetic shielding, sensor technology, nonlinear optics, molecular electronics and enzyme immobilization matrices (Malinauskas, 2001; Schwendeman et al., 2002; De Paoli et al., 1999; Dubois, 1989; Roncali et al., 1989; Salaneck, 1991; Cirpan et al., 2003; Alkan et al., 2001).

Polyaniline (PANI) identifies a rich family of electronically active, mutually converting, conjugated polymers (Kang et al., 1998). Among the conducting polymers (CPs), polyaniline (PANI) is a well-known versatile conducting material, which has found particular biological utility due to its easy synthesis, low cost, tunable conductivity and environmental stability (Malhotra et al., 1990; Tiwari et al., 2013). The electrical conductivity of PANI depends mainly on the dopant concentration, oxidant-to-monomer ratio, the rate of addition of oxidants, the nature of dopants, purity of monomer and polymerization time (Pron et al., 1988; Syed and Dinesan, 1991; Cortes and Sierra, 2006). It can be rapidly ‘switched’ with the addition of acids (protonation) and bases (deprotonation) (Prokes and Stejskal, 2004). The acid doped PANI yields conducting emeraldine salt and is dedoped to form the insulator emeraldine base (Han et al., 2002). Because of its rich chemistry, polyaniline is one of the most studied conducting polymers over the past 50 years (Yin and Ruckenstein, 2000). Polyaniline can exist in various oxidation states, differing in electrical, electrochemical and optical properties. The three major oxidation states are leucoemeraldine (white or clear and colourless), emeraldine (green for emeradine salt and blue for emeraldine base) and pernigraniline (blue or violet) (Fig. 1.15) (Feast et al., 1996).

Fig. 1.15: Main Polyaniline Structures n+m = 1, x = Degree of Polymerization

Among above three oxidation states, the fully reduced state is leucoemeraldine with n=1, m=0; consist of phenylene rings joined together by amine-type nitrogen atoms.
Pernigraniline is the fully oxidized state with n=0, m=1; consisted of phenylene and quinoid rings separated by imine nitrogens. The emeraldine (n=m=0.5) form of polyaniline is also referred to as emeraldine base (EB) and is neutral. On doping, it changes to emeraldine salt (ES) with the imine nitrogens protonated by an acid. Emeraldine base (EB) is considered to be the most useful form of aniline due to its high stability at room temperature (Feast et al., 1996; Ansari, 2006).

![Chemical Structure of Acid Doped Polyaniline](image)

Protonation by acids induces an insulator-to-conductor transition keeping the number of $\pi$ electrons in the chain constant (Fig. 1.16) (Ito et al., 1998).

In the pursuit of modified and improved properties of polysaccharides, recent research interest has focused towards the modification of cross-linked hydrogels with conducting polymers (CPs) via free radical polymerization, since this offers a simple technique to combine the superior properties of the CPs with the highly cross linked hydrogels (Ansari and Keivani, 2006). Various authors have synthesized electrically conducting hydrogels based on different polysaccharides and polyaniline through graft copolymerization (Tiwari, 2008; Tiwari, 2007). The materials produced have found applications in the areas of biosensors and gas sensors (Tiwari and Singh, 2007; Tiwari and Singh, 2008).

### 1.7 Biodegradability of Hydrogels

The overgrowing environmental pressure caused by the wide spread consumption of petroleum based polymers and plastics has hastened the development of biodegradable and environmentally acceptable materials. Biodegradability of polymers is a multifunctional property referring to end-of-life options of materials in different biological environments. During the last decade, biodegradable hydrogel has
been extensively studied due to their great biodegradability, biocompatibility and smart responsibility to environmental stimulus including chemical substances and changes in temperature, pH and electric field. Biodegradable plastics and polymers were first introduced in 1980s. Wang et al. (2003) grafted isocyanate-terminated poly(caprolactone monoacrylate) (NCO-PCLA) onto cellulose diacetate (CDA) and determined from the soil burial tests and active sludge tests that graft copolymers have good biodegradability in natural conditions. Natural polymers are available in large quantities from renewable sources, while synthetic polymers are produced from non renewable petroleum resources. Biodegradation takes place through the action of enzymes and/or chemical deterioration associated with living organisms. This event occurs in two steps. The first one is the fragmentation of the polymers into lower molecular mass species by means of either abiotic reactions, i.e. oxidation, photodegradation or hydrolysis, or biotic reactions, i.e. degradations by microorganisms. This is followed by bioassimilation of the polymer fragments by microorganisms and their mineralisation. Biodegradability depends not only on the origin of the polymer but also on its chemical structure and the environmental degrading conditions. The biodegradability of most supports relies on hydrolytic degradation (Pradny et al., 2006), spontaneous or enzyme catalyzed (Pradny et al., 1990). Several biopolymers were evaluated for their swelling behaviors, moisture retention and biodegradability.

1.8 Applications of Polysaccharide-based Hydrogels

Polysaccharide based hydrogels due to their dynamic structural properties have been employed for various potential applications. Hydrogels have been used in numerous biomedical applications like contact lenses and devices like sustained drug delivery systems, as agricultural applications like water storage granules and controlled release of pesticides and waste water treatment like heavy metal ions absorption. These hydrogels are also used in important industrial fields like electrophoresis, chromatography and protection of technical and electronic instruments, food industry, cosmetic industry and many more (Kaith and Kumar, 2007; Kaith and Kumar, 2008).
1.8.1 Agricultural Applications

Superabsorbent polymers (SAPs) are unique group of materials that can absorb liquid over hundred times their weight. Storage of water in different agriculture fields has remained a challenging task. Superabsorbents have been used as soil additives to increase the water retention of soils, which can replace the traditional moisture retention aid for soil (Barbucci et al., 2000). The crosslinked polymers with hydrophilic nature i.e. hydrogels have attracted much interest in agriculture area as they can improve water and fertilizer retention in soil and thus increase the growth of plants (Shahid et al., 2012). Because of the water absorption and retention capacity, hydrogels are very useful in horticulture and agriculture (Zohuriaan and Kabiri, 2008; Wang and Gregg, 1990; Yan et al., 2006). An increase in water holding capacity due to hydrogel significantly reduced the irrigation requirement of many plants (Agaba et al., 2011). The application of hydrogels is an important practice to assist plant growth by increased water retention by sandy soils and its availability to plants in dry regions. Therefore, superabsorbent polymers can be used as an effective water-saving material for agriculture and ecological recovery. Biodegradable polymers can be used for the controlled release of agricultural chemicals. The active agent can be dissolved, dispersed or encapsulated by the polymer matrix or coating, or is a part of the macromolecular backbone or pendent side chain. Carboxymethyl cellulose (CMC) available as sodium salt NaCMC is a polyelectrolyte showed good swelling capability and is used to improve soil quality through water retention (Sannino et al., 2009). The water absorption of the saponified cassava starch-graft-poly(acrylamide) and/or poly(acrylic acid) in salt and buffer solutions of different ionic strengths was measured, from which the superabsorbent properties are found to be pH sensitive (Kiatkamjornwong et al., 2000).

1.8.2 Water Purification

In the present scenario of industrialization and problems related to industrial wastewater treatment, managing world’s water resources has become more complex than ever. To remove organic or heavy metal pollutants from wastewaters, the development of novel sorbents, represents an intensive and popular research field during the last decades. Colored water and solutions containing toxic heavy metals
from many industries produce considerable polluted waters. The pollutants must be removed from wastewater before discharging it into the environment. Different dyes in water can affect plant life and is aesthetically unpleasant (Paulino et al., 2006; Uddin et al., 2009). These toxic heavy metal ions are highly soluble in the aquatic environment and are easily taken by the aquatic lives. Therefore, dye pollution in water stream is a major environmental problem. The methods of dye removal from industrial wastewaters could require many processes such as biological treatment, coagulation, electrochemical techniques, adsorption and oxidation. Among these methods, adsorption is considered an effective, simple design and economical method to remove dye contaminations from wastewaters (Kiani et al., 2011; Chiou and Li, 2003; Rauf et al., 2008; Mittal et al., 2010). The cellulose graft copolymers obtained by grafting of vinyl monomers with functional groups such as acrylamide (Bicak et al., 1999), acrylic acid (Lin et al., 2010; Guclu et al., 2003; Cavus et al., 2006; Wen et al., 2001), acrylonitrile and 2-acrylamidomethylpropane sulfonic acid (Guclu et al., 2003) have been used in the adsorption of hazardous contaminants such as heavy metals ions or dyes (Coskun and Temuz, 2005) from aqueous solutions (O’Connell et al., 2006; Liu and Sun, 2008). Carboxylic group and hydroxyl group grafted onto hydrogels also serve as donor in alkaline environment and responsible for adsorption of dye. In fact, it is known that charged hydrogels are able to absorb effectively from water oppositely charged organic and inorganic pollutants. The hydrogels are nontoxic, easy to handle and also their reusability makes them promising material for water purification.

1.8.3 Biomedical Applications

Functionalized hydrogels are used in biomedical applications. Hydrogels have porous structure. This porosity of hydrogels is helpful in drug release. Graft copolymers are cost effective, biodegradable, environment friendly and efficient therefore can be used for the sustained release of drugs after graft copolymerization and cross-linking. Poly(N-isopropylacrylamide-co-acrylic acid) hydrogel cages are synthesized for their use as drug carriers (Gu et al., 2007). Hydrogel possesses many remarkable properties such as immediate pain control effect, easy replacement, transparency, barrier against bacteria, good adhesion, easy handling, oxygen permeability, control of drug dosage,
absorption and prevention of loss of body fluids (Saha et al., 2008; Higa et al., 1999; Sen and Avci, 2005; Roy et al., 2010; Roy et al., 2010). Hydrogels are used in artificial muscles formation, wound-healing bioadhesives, artificial organ preparation like kidney membrane preparation, articular cartilage, artificial skin, sexual organ reconstruction materials and vocal cord replacement materials (Peppas, 1987). Smart hydrogels play an important role in drug delivery as they may dictate not only where a drug is delivered but also when and with which interval it is released (Soppimath et al., 2002). Synthetic extracellular matrix, implantable devices, biosensors, valve to control permeability across porous membrane and smart microfluidics are the other biomedical applications of polysaccharide based hydrogels.

1.9 Gums

Gums are important families of natural polymers derived from the seeds or tubers of plants (Deshmukh et al., 2012). In general, gums may be classified into three major classes, natural gums, chemically modified natural gums and chemically synthesized synthetic gums. Popular natural gums are Guar gum, Gum ghatti, Karaya, Tragacanth, Acacia, Arabica, and some are unidentified gums. The polysaccharide gums have different molecular structures and properties, but their common advantages such as renewable, biodegradable, nontoxic, biocompatibility make them found extensive applications as a commercial polymer in many areas (Ghorai et al., 2012; Ghosh et al., 2010; Rana et al., 2011). Plant gums are naturally occurring polysaccharide exudates from several species of plants or extracted from the endosperm of some seeds. They are polymers with a high molecular weight consisting of aldopentoses, aldohexoses and uronic acids joined together by a glycoside bond (Mills and White, 1999). Some plant gums have been widely used as paint media and sizing agents since the 3rd millennium BC (Mills and White, 1999; Newman and Serpico, 2000; Vallace, 1997; Pitthard et al., 2006; Pitthard et al., 2006; Mejanelle et al., 2002; Bleton et al., 1996; Schneider and Kenndler, 2001; Vallace et al., 1998). Natural gums are promising biodegradable, nontoxic, freely available and less expensive polymeric materials for use in drug delivery systems (Bhardwaj et al., 2000). However, these materials have certain drawbacks, like uncontrolled rate of hydration, thickening, drop in viscosity on storage, microbial contamination and
require functionalization/modification to overcome these problems (Tekade and Chaudhari, 2013). Gum exudes naturally, darkened often by non-carbohydrate contaminants and the dried product is separate out and ground in the usual manner. The polysaccharide gums represent one of the most abundant industrial raw materials and have been the subject of intensive research over comparable synthetic materials due to their sustainability, biodegradability and safety (Rana et al., 2011).

1.9.1 Guar Gum

*Guar gum* is a naturally occurring non-ionic branched polysaccharide which belongs to the group of galactomannan. It can be isolated from the seeds of *Cyanaoposis tetragonolobus* (leguminous) (Behari et al., 2001) plant. It is native to the Indian subcontinent and used as a green vegetable. *Guar gum*, also called guaran, is a galactomannan. It is primarily the ground endosperm of *Guar* beans (Fig. 1.17). India accounts for 80% of the total *Guar* are produced in the world. *Guar* has been important source of nutrition for humans as well as animals. It is mainly used as a natural thickener, emulsifier, stabilizer, bonding agent, hydrocolloid, gelling agent, soil stabilizer, natural fibre, flocculants and fracturing agent (Toti and Aminabhavi, 2004). *Guar gum* is commonly used as a thickening agent in food industries. It is white to yellowish white, nearly odourless powder with bland taste. It is practically insoluble in organic solvents. In cold or hot water, *Guar gum* disperses and swells almost immediately to form a highly viscous thixotropic sol (Shaikh and Kumar, 2011). It is an inherently biocompatible, biodegradable and non-toxic biopolymer.

![Fig. 1.17: Guar Beans](image-url)
Chemically, *Guar gum* is a polysaccharide composed of the sugar galactose and mannose. The backbone is a linear chain of β-1,4-linked mannose residues to which galactose residues are 1,6-linked at every second mannose, forming short side-branches. The ratio of mannose to galactose units ranges from 1.6:1.0 to 1.8:1.0, depending upon geographical conditions (Sullad *et al.*, 2010). Many research studies have been carried out on the synthesis and applications of hydrogels based on different backbones via chemical routes (Caykara *et al.*, 2006; Li *et al.*, 2006; Kaith *et al.*, 2012; Saraydin *et al.*, 2002). Because the unmodified *Guar gum* contains a large number of hydroxyl groups and greater branching; it has high water binding capacity and is able to form highly viscous solutions even at 1% concentration. *Guar gum* is soluble in cold water, hydrating quickly to produce viscous pseudo plastic solutions that although shear-thinning generally have greater low-shear viscosity than other hydrocolloids (Cheetham and Mashimba, 1990; Brosio *et al.*, 1994). This gelling property retards release of the drug from the dosage form, and it is susceptible to degradation in the colonic environment (Bhalla and shah, 1991; Jain *et al.*, 1992; Rama Prasad *et al.*, 1998).

Synthetic hydrogels usually have well defined structures that can be modified to yield tailor made biodegradability and functionality (Lin and Metters, 2006). Natural polysaccharide based hydrogels may not provide sufficient mechanical strength, may contain pathogens or evoke immune/inflammatory response and may pose difficulty in processing but they offer several advantages such as inherent biocompatibility, biodegradability and biologically recognizable moieties that support cellular activities, and such properties cannot be met with synthetic hydrogels (Sadeghi, 2011). Lokhande *et al.* (1993) and Biswal *et al.* (2007) prepared guar gum-g-copolymer by using γ-radiations as the initiation approach. It was found that ideal graft efficiency was obtained, and the graft efficiency is dependent on the dose of radiations. Behari *et al.* (1999) have investigated the kinetics and characterization studies of PAM (polyacrylamide) grafted *Guar gum*. Tiwari *et al.* (2009) modified *Guar gum* with MA to obtain guar gum-methacrylate (Ggum-MA) macromonomers and then polymerize them to form a hydrogel material.

Although advantageous, this viscosity is very difficult to control and that is why *Guar gum* is rarely used in its natural form. Moreover, *Guar gum* suffers drawbacks such as uncontrollable rate of hydration, instability of its solutions for longer time and its
susceptibility to microbial contamination. In order to minimize these drawbacks, to add new properties without any major changes to its natural characteristics and to expand the market for guar gum based products, Guar gum must be chemically modified. Chemical modification may be done by grafting. Grafting is generally considered to result from propagation of radical sites generated on polymeric substrates and therefore minimizes the formation of homopolymer.

1.10 Problem Statement

It is evident from the literature survey that lot of studies have been concentrated on the synthesis, characterization and swelling behavior of hydrogels based on Guar gum with different vinyl monomers in hot air oven but less reports are available in the synthesis of cross-linked hydrogels based on Guar gum and vinyl monomers under the influence of microwave radiations and under vacuum. Secondly, it is clear from literature that there is no report available on the synthesis and characterization of Guar gum based conducting hydrogels under different reaction conditions. Whereas lot of results have been reported on the use of synthetic and natural polysaccharides for the synthesis of conducting hydrogels.

From the literature it has been found that the studies on the biodegradation and removal of dye from wastewater are not reported for conducting hydrogels. Therefore an initiative was taken towards the synthesis of conducting hydrogels based on Guar gum through grafting with different vinyl monomers. Further conducting hydrogels based on Guar gum, vinyl monomers and PANI was used in soil water retention and water purification applications. Nowadays, challenges are being posed to solve the issues related to environment problems. Synthesized semi-IPNs and IPNs have proved to be key solution to these great challenges.

1.11 Objectives:

The aim of present investigation is to synthesize cross-linked hydrogels based on Guar gum, vinyl monomers and aniline under different reaction conditions. The main objectives of the present work are:
• To synthesize the semi-interpenetrating networks (semi-IPNs) of Guar gum (Ggum) with itaconic acid and acrylic acid using ammonium persulphate (APS) as initiator and hexamine as cross-linker under different reaction conditions such as in air, under the influence of microwave radiations and under vacuum.

• Characterization of semi-interpenetrating networks like Ggum-cl-poly(AA) and Ggum-cl-poly(IA) cross linked hydrogels using some modern techniques such as Fourier transform infra red spectroscopy (FTIR), Thermogravimetric analysis (TGA) and Scanning electron microscopy (SEM) in order to know their cross-linking, thermal behavior and morphology.

• To synthesize the Interpenetrating networks (IPNs) of Ggum-cl-poly(IA) and Ggum-cl-poly(AA) with polyaniline under neutral and acidic (0.5N HCl) conditions.

• Characterization of different IPNs using some modern techniques like Fourier transform infra red spectroscopy (FTIR), Thermogravimetric analysis (TGA) and Scanning electron microscopy (SEM) in order to know their cross-linking, thermal behavior and morphology.

• Doping of IPNs with different concentrations of HCl.

• To study the conductivity of different doped conducting interpenetrating networks using two probe system.

• To study the moisture retention property of different semi-IPNs and IPNs with different types of soils.

• To study the application of different semi-IPNs and IPNs as effective removal of methylene blue dye from waste-water.

• To carry out the biodegradation studies of different semi-IPNs and IPNs using soil burial and composting methods.