NOVEL HYDROCOLLOIDS : PREPARATION & APPLICATIONS – A REVIEW

Meenu Kapoor, Dhriti Khandal, Geetha Seshadri, Saroj Aggarwal &
Rakesh Kumar Khandal[*]

Gautum Budh Technical University, I.E.T. Campus, Sitapur Road, Lucknow – 226 021 Uttar Pradesh, India
*: Corresponding Author E-mail: dr.r.k.khandal@gmail.com

ABSTRACT

Hydrocolloids, as the name suggests are the hydrophillic materials with the structural attributes that are responsible for formation of colloidal solutions. Generally, hydrocolloids are naturally occurring biopolymers. It does not mean that one cannot design hydrocolloids by synthetic route. All types of hydrocolloids are known from both renewable as well as non renewable resources. For various applications, preference is being given to the renewable hydrocolloids due to one reason or the other. Since the aim is to replace the existing conventional materials by the renewable ones for various applications, one needs to modify the available hydrocolloids to render certain unique features for the purpose. It is therefore necessary to create novel hydrocolloids based on the existing ones. Two of the industrially important natural hydrocolloids are starch and guar gum. In order to enhance their applicability in the industries, their derivatization is carried out to get novel derivatives with desired properties. The basic characteristics, various derivatives and the applications of these two hydrocolloids have been discussed in detail in the present paper.

1. INTRODUCTION

A colloidal system consists of two separate phases, or in other words, it is a mixture where one phase is dispersed (Dispersed Phase) in another phase (Dispersion Medium). It may be a combination of solid – liquid, liquid – gas or gas – liquid phases. Hydrocolloid is defined as a colloidal system wherein the colloidal particles are dispersed in aqueous phase. In other words, we can say that hydrocolloids are environment friendly colloidal systems. In a hydrocolloidal system, colloidal particles are spread throughout the aqueous phase and depending on the quantity of the hydrocolloid as also on the degree of hydration of hydrocolloid, the system can take up the form of either a gel or a sol. They may also alternate between these two states, i.e., gel and sol state, with the addition or elimination of heat.

Another way to define hydrocolloids is that they are hydrophillic polymers of vegetable, animal, microbial or synthetic origin and they generally contain many hydroxyl groups and may be polyelectrolytic in nature [Phillips G.O. et al., 2000]. They may have the chemistry of a polysaccharide or a protein if they are derived from natural source. On the basis of their origin, the commercially important naturally occurring hydrocolloids can be divided into various categories as given in Table – 1.1. Now-a-days hydrocolloids are being widely used in a variety of industrial sectors due to their excellent rheological properties [Torres M.D. et al., 2012]. There are two rheological properties, which are of major importance in hydrocolloidal science : gel and flow properties. Hydrocolloids perform various functions in a formulation including (i) thickening and gelling aqueous solutions; (ii) stabilising foams, emulsions and dispersions; (iii) inhibiting ice and sugar crystal formation and (iv) controlled release of flavours, (v) flocculation, (vi) film formation, etc. The various hydrocolloids used in the food industry are given in Table – 1.2. Other than the food industry, the applications of hydrocolloids can be summarized as in Table – 1.3.

Table –1.1:   Commercially Important Naturally Occurring Hydrocolloids and Their Origin

Origin	Hydrocolloids
Botanical • Trees • Tree Gum Exudates • Plants • Seeds • Tubers	Cellulose Gum arabic, Gum karaya, Gum ghatti, Gum tragacanth Starch, Pectin, Cellulose Guar gum, Locust bean gum, Tara gum, Tamarind gum Konjac mannan
Algal • Red Seaweeds • Brown Seaweeds	 Agar, Carrageenan Alginate
Microbial	Xanthan gum, Curdlan, Dextran, Gellan gum, Cellulose
Animal	Gelatin, Caseinate, Whey protein, Chitosan

Hydrocolloids can dramatically alter the viscosity of many times their own weight of water due to their interactions with the water molecules through hydrogen - bonding. A clear understanding of the rheological behaviour of the hydrocolloids has emerged over the last twenty years, which has lead in turn to the exploitation of guar gum in various industries. The viscosity of a polymer solution shows a marked increase at a critical polymer concentration, commonly referred to as c^* (Figure –1.1). This corresponds to the transition from the "dilute region", where the polymer molecules are free to move independently in solution without interpenetration, to the "semi-dilute region" where molecular crowding occurs which gives rise to the overlapping of polymer coils and thus interpenetration occurs.

The structural characteristics of hydrocolloids and their interaction with water affects the rheology of hydrocolloids in water leading to gelling, thickening etc.

*   Hydrocolloids form gels when the intra or inter – molecular hydrogen bonding is favoured over hydrogen bonding to water.
*   Polysaccharide hydrocolloids stabilize emulsions primarily by increasing the viscosity of the system. They also act as emulsifiers, wherein the emulsification ability is reported to be mainly due to accompanying protein moieties.
*   The hydrodynamic size of polymer molecules in solution is significantly influenced by its molecular structure. Linear and stiff molecules have a much larger hydrodynamic size than highly branched flexible polymers of same molecular mass and thus they give rise to higher viscosity values.
*   The charged polymers or the polyelectrolytes exhibit very high viscosity as compared to the non – ionic polymers of similar molecular mass.

So, on the whole we can say that the rheological properties of hydrocolloids form the basis for their wide applications in the industries and also that the unique rheological behavior of the hydrocolloids can be attributed to the presence of a large number of hydroxyl groups in their structure, which leads to their H-bonding interactions in the aqueous systems. This paper highlights the following aspects of the hydrocolloids:

*   Types of hydrocolloids
*   Structural chemistry
*   Essential characteristics
*   Isolation / extraction of hydrocolloids from the natural sources
*   Types of modification
*   Applications
*   Conclusions

Table – 1.2 : Industrial Applications of Hydrocolloids

S.No.	Sector	Application
1.	Oil Drilling	Drilling fluid
2.	Transport in pipelines	Drag Reducer
3.	Paper Treatment	Improves writing & printing properties
4.	Agriculture	Erosion Control
5.	Cosmetics & Textile Printing	Emulsifier, thickening & stabilising agent
6.	Beverages	Thickening & suspending agent
7	Ice Creams	Texture & Anti-freezing
8.	Pharmaceuticals	Stabiliser, thickener, binding agent

Table – 1.3 : Major Applications of various Hydrocolloids

| Hydrocolloid	Principal Function
Agar	Gelling agent
Alginate	Gelling agent
Arabic	Emulsifier
Carrageenan	Gelling agent
Processed euchema seaweed	Gelling agent
Carboxymethyl cellulose	Thickener
Hydroxypropyl cellulose	Thickener & emulsifier
Methyl cellulose	Thickener, emulsifier & gelling agent
Microcrystalline cellulose	Thickener & gelling agent
Gelatin	Gelling agent
Guar gum	Thickener
Karaya	Thickener
Locust bean gum	Thickener
Pectin	Gelling agent
Pectin (low methoxy)	Gelling agent
Propylene glycol alginate	Emulsifier & foam stabiliser
Starch	Thickener & gelling agent
Starch (modified)	Thickener & gelling agent
Tragacanth	Thickener
Xanthan gum	Thickener
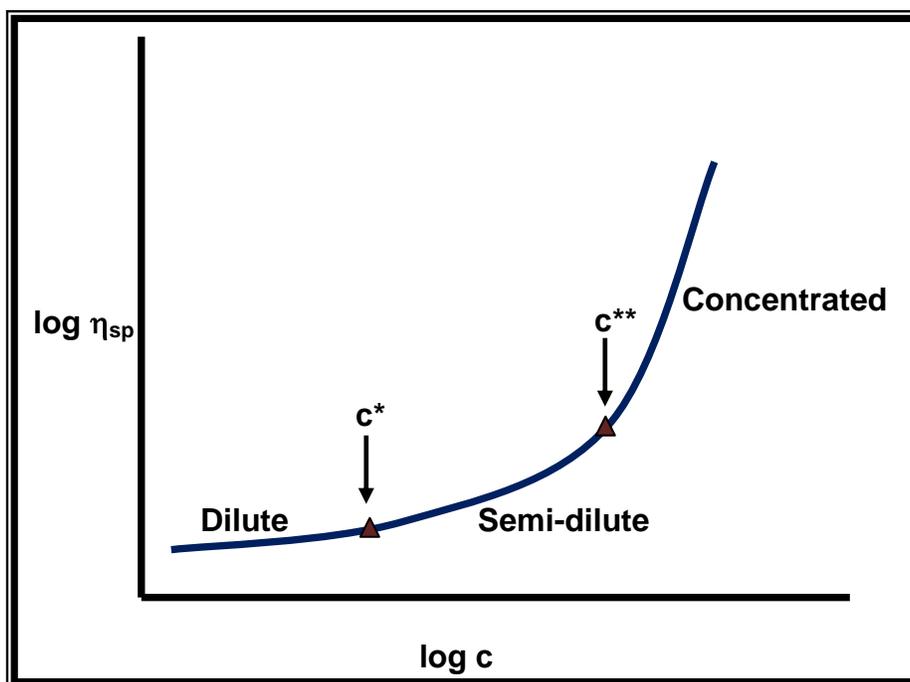
Figure – 1.1 : Viscosity of polymer solution increases with concentration of polymer in solution. The slope of the curve log c vs log η_{sp} changes on increasing the polymer concentration of solution. Dilute region : no interaction between polymer chains; Semi-dilute : weak interactions between polymer chains; Concentrated : interpenetration of polymer chains. The interpenetration begins at c**.

2.   TYPES OF HYDROCOLLOIDS

Hydrocolloids are the hydrophilic polymers and when added to water, they disperse evenly as microscopic particles. At sufficiently high concentrations, the polymers become entangled with each other forming loose networks that change the flow properties of the solution [Cassiday L., 2012]. Depending on their origin, hydrocolloids may be classified as natural, semi – synthetic and synthetic. The naturally occurring hydrocolloids have already been described in the previous section. The semi – synthetic hydrocolloids are the ones that are synthesized by modification of naturally occurring hydrocolloids. Methyl cellulose, carboxymethyl guar / cellulose are the examples of the semi – synthetic hydrocolloids. Synthetic hydrocolloids are the ones that are completely synthesized in the industries starting with petroleum derived base materials. The acrylate copolymers are an example of synthetic hydrocolloids [Cassidy L., 2012].

The naturally occurring plant hydrocolloids have the advantage of being inexpensive, easy to handle and non toxic but at the same time, they have the disadvantages of being required in large quantity to be effective as emulsifiers and are susceptible to microbial growth. The vegetable derived hydrocolloids are mainly used as oil in water emulsifiers. The animal derived hydrocolloids generally form water in oil emulsions. They are quite likely to cause allergies and are susceptible to microbial growth and rancidity. The semi synthetic hydrocolloids are stronger emulsifiers, are non-toxic and less likely to undergo microbial growth. The synthetic hydrocolloids are the strongest emulsifiers, are non toxic and they do not support microbial growth but their cost may be prohibitive. The synthetic hydrocolloids are mainly limited to use as oil in water emulsifiers.

The naturally occurring hydrocolloids may be proteins or carbohydrates as these are the two macromolecules naturally available. These two macromolecules are the major food for the human beings and are consumed every day. The human beings mainly derive their food from the plants as various parts of a plant are edible : seeds, stem, root, leaves, flowers, fruits, etc. The classification of hydrocolloids into proteins and carbohydrates is the classification based on their chemistry but actually hydrocolloids are classified on the basis of their origin as presented in Table – 1.1. Nowadays the hydrocolloids have become commercially important as they find application in most of the industry sectors. Their wide acceptance in various industries is a result of their unique structural chemistry giving rise to desired rheology.

2.1 STRUCTURAL CHEMISTRY

As described in the previous section, hydrocolloids are macromolecules and are either proteins or polysaccharides. In order to understand the structural chemistry of hydrocolloids, it is first necessary to discuss about the repeating units found in these macromolecules and to understand the chemical composition, functional groups present, chemical structure and the chemistry of formation of hydrocolloids. The repeating units of polysaccharides are monosaccharides and that of proteins are amino acids.

2.1.1 Polysaccharides:

Polysaccharides are actually nothing but carbohydrates and carbohydrates, as the name suggests, are the hydrates of carbon because their composition can be expressed by the formula $C_x(H2O)_y$. Polysaccharides comprise of the simplest carbohydrate units, i.e. the monosaccharides which are linked together to from long chains. So, we can say that the polysaccharides are the polymers of monosaccharides. In order to understand the chemistry of polysaccharides, it is important first to understand the chemistry of monosaccharide.

2.1.2 Monosaccharides:

Monosaccharides are the simplest carbohydrates. As described earlier, carbohydrates have the general formula $C_x(H2O)_y$, so that means only carbon, hydrogen and oxygen are present in them. Monosaccharides are classified into various types, depending on: (i) the number of carbon atoms present, (ii) whether an aldehyde or a ketone group is present and (iii) orientation of the various groups around the carbon atoms in a monosaccharide or its stereochemistry.

Thus, on the basis of the number of carbon atoms present, a monosaccharide may be a triose (3 carbon atoms), tetrose (4carbon atoms), pentose (5 carbon atoms) and hexose (6 carbon atoms). If a monosaccharide has an aldehyde group, it is classified as an aldose and if it has a ketone group, it is classified as a ketose. Depending on the stereochemistry of a monosaccharide, it is designated as + or -, D or L and R or S. The important thing to note here is that monosaccharides can be depicted in the form of Fisher projection formula (Figure – 1.2) but actually this open chain structure exists in equilibrium with two cylic forms (Figure – 1.3)
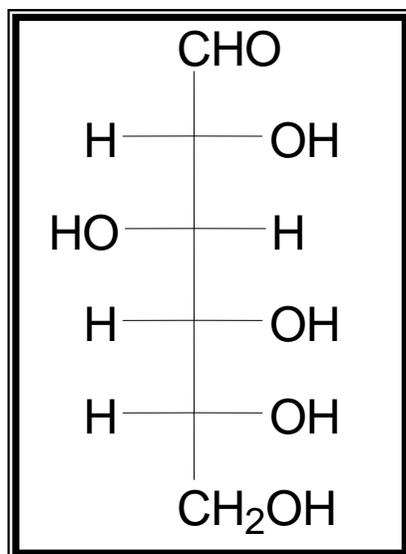
Figure 1.2 : Fisher Projection Formula of D- (+) – glucose

The aldehyde & ketone, as we know, form hemiacetals & hemiketals by reacting with hydroxyl groups. This reaction of aldehydes & ketones leads to the formation of cyclic structure in the case of monosaccharides. Since in the case of hemiacetal formation, the addition is taking place across a double bond, it can be from either above or below and thus two different diasastereomers (also called anomers) are fromed : α if –OH is trans to –CH$_2$OH and –β if –OH is cis to the –CH$_2$OH groups.
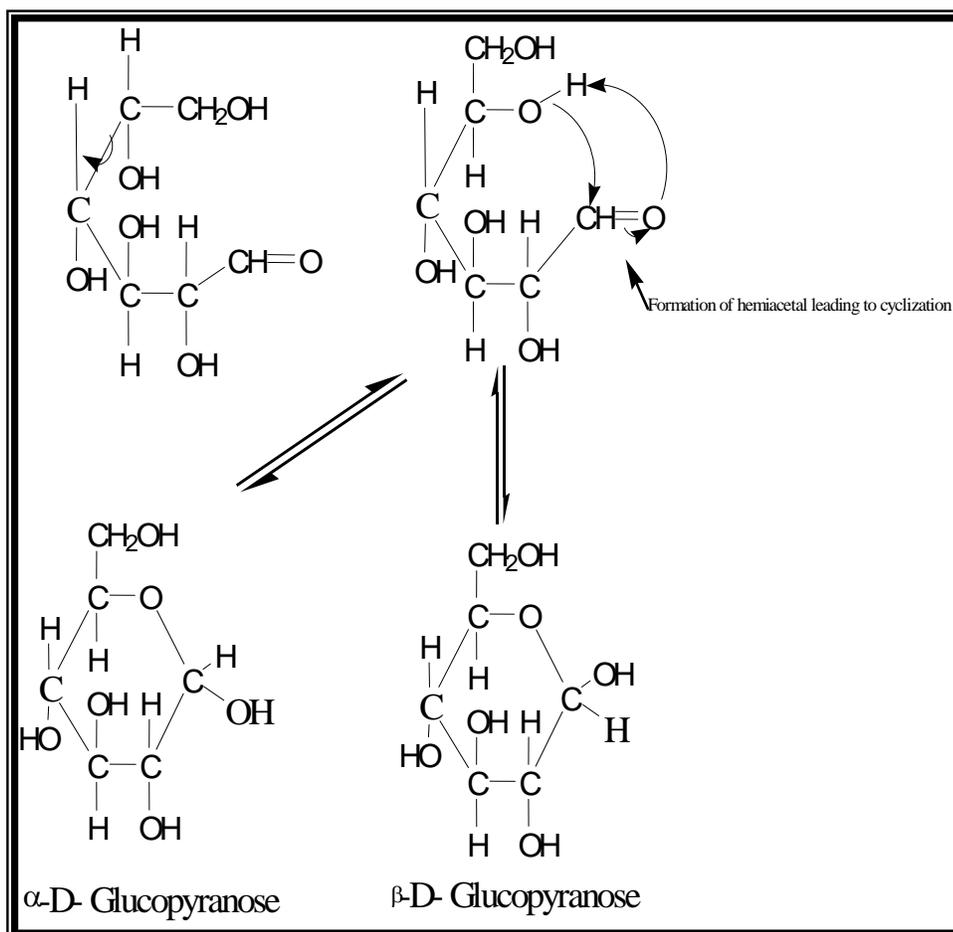

Figure – 1.3 : Mechanism of the formation of cyclic structure in case of glucose

2.1.3 Structure of Polysaccharide:
Polysaccharides can be either homopolysaccharides, which comprise of one type of monosaccharides units and heteropolysaccharides, which comprise of two or more types of monosaccharide units.
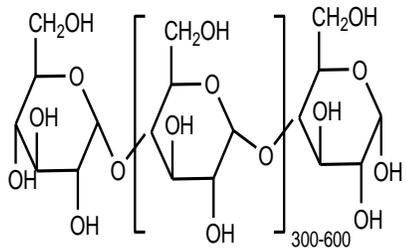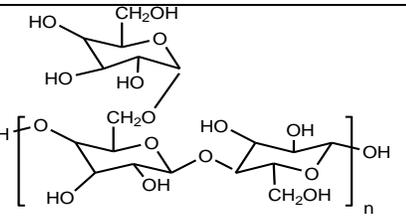
The monosaccharide units comprise of hydroxyl groups at 1,2,3,4 & 6 carbon atoms out of which hydroxyl groups at 1, 2, 3 & 4 positions are part of the cyclic ring structure. The monosaccharide units get joined together by α or β glucosidic linkages formed when hydroxyl groups from the different monosaccharide units join together by loss of a water molecule, i.e. they undergo condensation reaction leading to polymer formation.
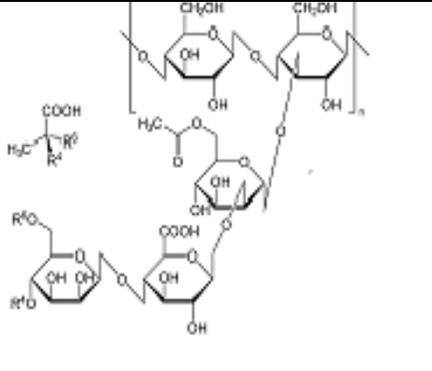
In this way, several monosacchrides get joined together to form the polysaccharides. Now, it is very interesting to note here that the type of polymerization taking place here is condensation polymerization. Since, there are various types of monosaccharides and they can join together by different types of linkages and they can join in homo or hetero ways, there are a vast number of polysaccharides (Table – 1.4) known. In the present chapter, two commercially important polysaccharides : starch and guar gum have been described in detail in the subsequent sections.

2.1.4 Proteins:
Proteins perform diverse functions in living systems and thus come in various shapes and sizes. They generally have very high molecular weights. If we look at the chemistry aspect, then we can call protein as polyamides as they have amide linkages in their structure. The monomer units of these polyamides are the amino acids. To understand the structure of proteins, let us look at the basic structure of these amino acids first.

Table –1.4 : Examples of a few Polysaccharides : homo as well as hetero

Polysaccharide	Monosaccharides Present	Type	Structure of repeat unit
Starch	Glucose	Homo	STARCH
Guar gum	Galactose, Mannose	Hetero	GUAR

Xanthan gum	Glucose, Mannose, Glucuronate	Hetero	
Cellulose	Glucose	Homo	
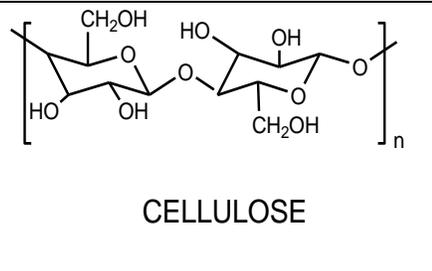
2.1.5 Amino acids:

These are organic compounds having an amine group '-NH$_2$' and a carboxylic group '-COOH' in their structures. So, a general depiction of an amino acid will be as given in Figure –1.4.
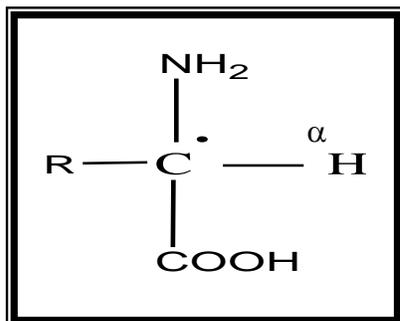
Figure –1.4 : Structure of an amino acid : An amino acid comprises of an amine (-NH$_2$),a carboxylic(-COOH) and an alkyl groups (-R) on a carbon atom. R can be an alkyl, aryl or a heterocyclic group

Now , one thing evident from Figure – 1.4 is that amino acids are chiral molecules since the α carbon atom has all four different groups attached to it except in the case of amino acid called glycine, where R = H. The amino acids have a structural feature in common except glycine that almost all naturally occurring amino acids have the L- configuration at the α carbon, which means that they have same relative configuration as L- glyceraldehydes. Thus, we can depict an L -α- amino acid as shown in Figure – 1.5.

There are 22 different α-amino acids that are present in the proteins. Depending on the nature of R group, an amino acid can be neutral, basic or acidic in nature.

Figure – 1.5 :Structure depicting the L -α- amino acid

These amino acids combine together and lead to the formation of an amide linkage between two amino acids with the loss of a water molecule. Here, also it showed be noted that the formation of a natural polymer is by 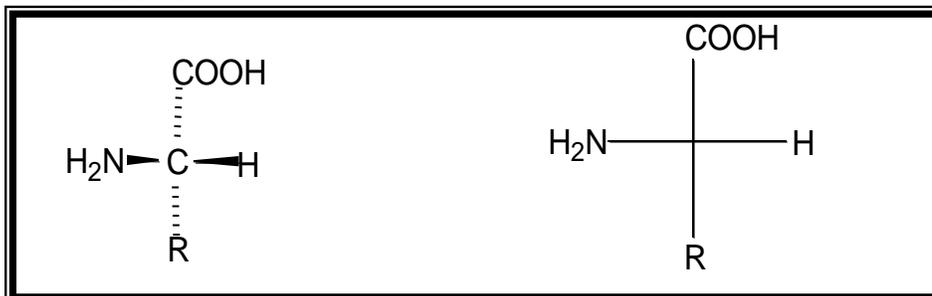condensation of water from the monomeric units leading to the formation of an amide linkage and loss of a water molecule at the same time (Figure – 1.6).

The linkage formed between two amino acids is an amide linkage and is also called peptide bond. Thus, by formation of 2, 3 or more peptide bonds, dipeptides, tripeptides, oligopeptides and polypeptides are formed. Proteins are nothing but polypeptides, having free $-NH3^+$ group at one end and $-COO^-$ group at the other end.

3. MODIFICATION

The basic idea behind modification of hydrocolloids to yield novel hydrocolloids is to enhance their attributes and make them more suitable for application in various industries. When a hydrocolloid is modified, what actually happens is that its properties get modified, i.e., properties are adapted for making the hydrocolloid suitable for a certain application.
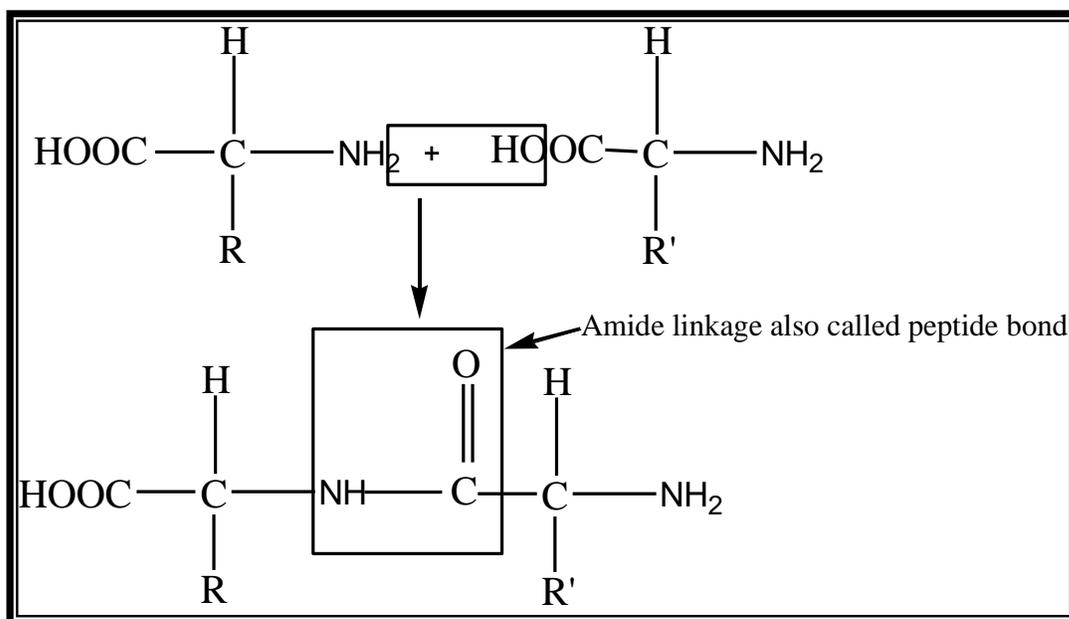
Figure – 1.6 : Formation of Dipeptide by amide linkage between two amino acids with the loss of a water molecule. R, R^I = alkyl, aryl or heterocyclic groups.

There are several aspects that have to be kept in mind before carrying out any modification in a hydrocolloid:
- Effect of modification on the H-bonding in the hydrocolloid
- Identification and availability of sites where modification is to be carried out

The modification of hydrocolloids can be carried out by physical or chemical methods.

3.1 Physical Modification:

The physical modification is carried out by subjecting a hydrocolloid to dissolution or cooking or some thermal treatment may be given. As a result of physical modification, changes take place in the hydrogen bonding existing in the hydrocolloids, thereby bringing a change in solvent – solute interactions or the solubility. The physical modification is carried out mainly in case of starch and has been discussed in detail in section 1.4.

3.2 Chemical Modification:

The chemical modification of hydrocolloids involves their treatment with various chemical substances such as alkali, ester etc by way of which final groups are added to the hydrocolloids thus modifying the chemical structure leading to changes in the chemical structure of the hydrocolloids. The major techniques used for chemical modification are : (a) grafting, (b) oxidation, (c) depolymerisation (d) substitution and (e) crosslinking (Figure – 1.7).

3.2.1 Grafting:

This technique involves the covalent attachment of a chemical moiety to the backbone of a polymer. The products obtained as a result of grafting are also called as graft copolymers as they are nothing but branched macromolecules comprising of various branches, which are different from the backbone of the macromolecule. These grafted molecules have a variety of industrial applications as a result of their wide range of properties. The grafting can be carried out by either the conventional routes or by unconventional methods : (a) Chemical methods, (b) Enzymatic methods and (c) Radiation processing
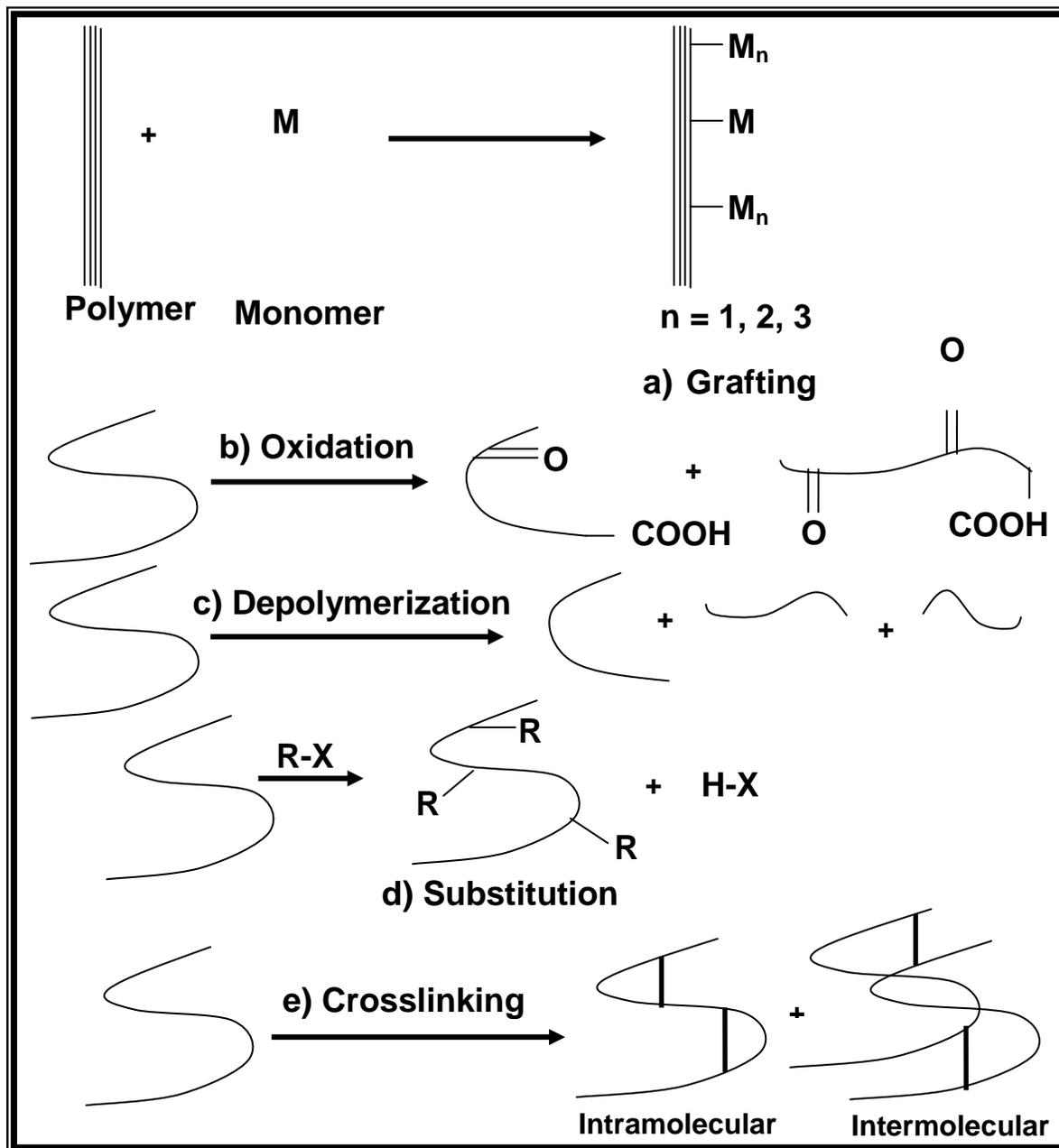

Figure – 1.7 : Major techniques used for modification of polymers : (a) Grafting; (b) Oxidation; (c) Depolymerisation; (d) Substitution; (e) Crosslinking

The conventional chemical route for grafting of polymers is mainly by the use of redox initiator systems. In this method, various types of redox reagents may be used and the basic chemistry involved here is that free radicals

generated from redox initiator systems help in creating free radical sites on the polymer. The monomers in the vicinity of these polymers react with free radical available on the polymer chain thereby causing the chain initiation. The important features of these redox initiator systems are :

- Simple methodology
- Reaction at ambient temperature conditions
- Reaction feasible in aqueous systems
- Extent of grafting can be controlled by varying the reaction parameters including recipe and conditions

The Fenton's reagent or the Fe^{2+}/H_2O_2 system (Figure – 2.8) is one such redox initiator system, which is used for grafting reactions [Barros JAG et al., 2006]. Another redox system used for grafting is Fe^{2+} / persulphate. Misra et. al [Misra B.N. et al., 1984] have established that during the grafting of vinyl monomers onto wool / cellulose, $OH^•$ generated from Fe^{2+}/ persulphate redox system is more reactive than the SO_4^{-} generated from the same system. In order to generate free radical sites on the polymer backbone, another very effective method is by direct oxidation of the polymeric backbone by using certain transition metal ions, like $Ce^{4+,}$ Cr^{6+}, V^{5+} & Co^{3+} [Kurkuri M.D., et al., 2006; Bhattacharya S.N. et al., 1984; Athawale a.D. et al., 1999].

$$H_2O_2 + Fe^{2+} \longrightarrow OH^• + OH^• + Fe^{3+}$$

$$OH^• + \underset{\text{Polymer}}{P\text{-}H} \longrightarrow P^• + H_2O$$

$$P^• + M \longrightarrow P\text{-}M^• \qquad \text{Chain Initiation}$$

Figure –1.8 : Mechanism of Chain Initiation in grafting of monomer on polymer using Fenton's Reagent

Living Radical Formation is another technique for grafting in which, the chain termination is not carried out by either increasing the rate of initiation with respect to chain propagation or by eliminating chain termination and transfer reactions. The major advantage of using this route is that the product formed is either mono disperse or it has very narrow dispersity. The living radical formation may be carried out by following methods : (a) atom transfer, (b) nitroxide mediated, (c) degenerative transfer, etc.

(a) Atom transfer : In case of living radical formation through atom transfer, the molecule containing halogen at the α - position undergoes pseudohalogen hemolytic transfer to yield the propagating radical. The halogen is taken up by a transition metal complex [Wang J.S. et al., 1995] and in general the reaction can be depicted as shown in Figure – 1.9.

$$\underset{\text{Polymer Chain}}{\Big|} - X \quad + \quad M^n / L \quad \underset{k_d}{\overset{k_{act}}{\rightleftarrows}} \quad \Big|^* \quad + \quad X - M^{(n+1)+} / L$$

Figure 1.9 : Mechanism of Free Radical Generation in Atom Transfer Technique; where M^n is the transition metal. L is the complexing ligand and X is either Br or Cl

Polymers prepared by other processes can be functionalized at the terminus or along the backbone and incorporated into an ATRP as a macro initiator or a macro monomer or both to improve the incorporation of macro monomer onto the polymer leading to well – defined block and graft copolymers [Janata M. et al., 2001; Deng G. et al., 2005; Hong S.C. et al., 2001; Shinoda H. et al., 2001; Hong S.C. et al., 2002; Matyjaszewski K. et al., 1998].

(b) Nitroxide mediated : Another method for carrying out grafting by living radical mechanism is by using free – radical nitroxides, such as TEMPO. The preparation of dendritic polymers can be carried out by this method [Miwa Y. et al., 2001; Hawker C.J. et al., 1997; Hawker C.J. et al., 2001; Grubbs R.B. et al., 1997, Percec V. et al., 2000; Tsoukatos T. et al., 2000].

(c) Degenerative transfer : In case of degenerative transfer method, reactions take place through the chain transfer reagents. In this method, the polymer is attacked by the propagating radical to form the active and the dormant species [Goto A. et al., 2004; Schellekens M.A.J. et al., 2000].

(ii)　Enzymatic Route :

In this type of grafting, the reaction is a mix of enzymatic and non – enzymatic paths. Initially, the generation of free radical species takes place by using enzymes, such as oxido-reductase enzymes [Kumar G. et al., 1999; Chao A.C. et al., 2004; Sampaio S. et al., 2005; Jayakumar R. et al., 2005] and then the reaction proceeds non – enzymatically. The use of oxidative enzymes in the grafting reactions has been studied exhaustively in the case of natural polymers rather than the synthetic ones [Zhao J.C. et al., 2004; Zhao J. et al., 2005].

(iii)　Radiation Route for Grafting :

In this route, radiation energy is used to generate reactive species such as free radicals or the ions on a substrate and reaction proceeds by covalent bonding of these reactive species with the monomers added. The use of radiation energy for carrying out grafting was initially carried out when it became known that radiation interacts with matter or specifically with organic or inorganic molecules to produce free radicals or ions. The following types of radiation have been used : (a) Gamma rays, (b) Electron beam, (c) Photoirradiation, (d) Microwave & Infrared radiation.

(a)　Gamma rays & electron beam : Radiation is a term which covers the electromagnetic and particulate radiation from gamma rays with wavelength of picometers to radiowaves with wavelength of hundreds of meters. High energy radiation can be understood to mean the radiation which can cause ionization in chemical compounds, which requires 10eV corresponding to 1000 kJ per mole and a wavelength of 100 nm. The characteristics of radiation which are mainly used to irradiate polymers / monomers are given in Table – 1.5.

(b)

Table –1.5 : Characteristics of various types of radiation alongwith their source and energy

Radiation	Source	Energy
Electron Beam	E-Beam accelerators	20 kV – 10 MV
Gamma Rays	Radioactive Material (^{60}Co, ^{137}Cs)	1 MV
X – Rays	Generator Synchrotron	50 – 200 kV

The high energy radiation mainly used are gamma (γ) radiation and the electron beam radiation. Grafting by using high energy radiation route can proceed mainly via three methods:

i.　Pre-irradiation technique :

In this technique used for grafting, first the polymer is exposed to radiation usually under vaccum or in inert conditions so that stable free radicals get generated on the polymeric backbone, which are subsequently reacted with the monomer, at elevated temperature [Hegazy E.A. et al., 1982; Momose T. et al., 1991; Dworjanyn P.A. et al., 1992; Gupta B. et al., 1994; Bhattacharya A., 2000]. The major advantage of this technique is that the homopolymer formation gets prevented since the monomer is not being exposed to radiation. But at the same time this process has the disadvantage that if the polymer is sensitive to degradation, then chain sissioning takes place in the polymer, which may cause the formation of block copolymer rather than a grafted one. Another aspect worth mentioning is that the grafting reaction here depends on the ability of the polymer to trap the radicals or ions formed and on the ability of the polymer to trap the radicals or the ions formed. If the free radicals or ions are not available, then grafting will not proceed when the monomer is added. Keeping the above in view, this is not a preferred method for carrying out grafting. The mechanism can be depicted as shown in Figure – 1.10.

ii.　Peroxidation Technique :

In this technique, the polymer is exposed to radiation under air or oxygen pressure, which leads to the formation of hydroperoxides or diperoxides depending on the nature of the polymer and the irradiation conditions employed [Ishigaki I. et al., 1982; Bozzi A. et al., 1988; Takacs E. et al., 2005].

These peroxy or diperoxy products are stable once formed and are treated with monomers at the temperatures at which these peroxides undergo decomposition into radical species, thereby initiating grafting [Figure – 1.11].

This is also a pre-irradiation method of grafting and has similar advantages and disadvantages as the pre-irradiation technique. But, since the storage time of intermediate peroxy trunk polymers is long, it is an obvious advantage.
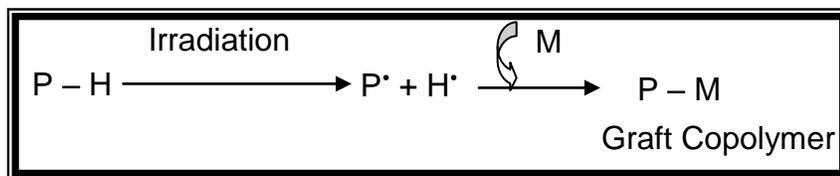
$$P - H \xrightarrow{\text{Irradiation}} P^\bullet + H^\bullet \xrightarrow{\text{M}} P - M$$
Graft Copolymer

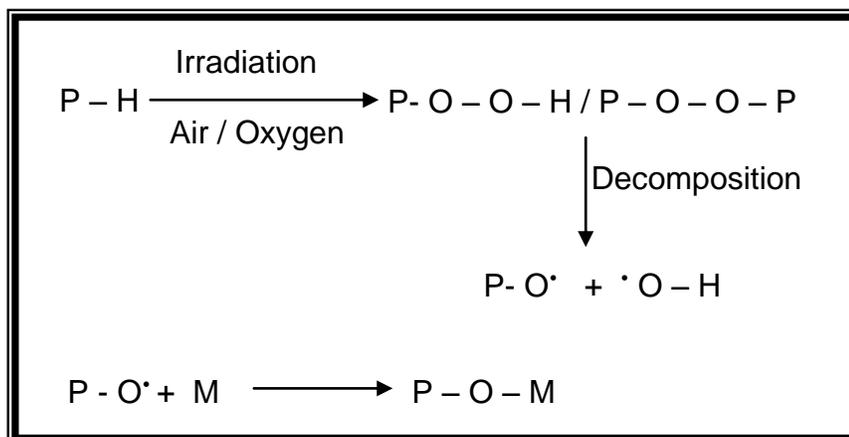**Figure – 1.10 : Mechanism of Grafting by preirradiation Technique; where P – H is the polymer and M is the monomer**

$$P - H \xrightarrow[\text{Air / Oxygen}]{\text{Irradiation}} P\text{-} O - O - H / P - O - O - P$$

$$\downarrow \text{Decomposition}$$

$$P\text{-} O^\bullet + {}^\bullet O - H$$

$$P - O^\bullet + M \longrightarrow P - O - M$$

Figure 1.11 : Mechanism of Grafting by Peroxidation Technique; where P is the polymer, M is the monomer, P-O-O-H is the peroxide initiator and P-O-O-P is the diperoxide

iii.   Simultaneous Method:

In this method, the substrate and the monomer are irradiated simultaneously and here the monomer may be either in liquid (solution/pure) or in gaseous form [Misra B.N. et al., 1985; Bhattacharya S.N. et al., 1986; Bhattacharya S.N. et al., 1983; Nho Y.C. et al., 1992; Basu S., et al., 1994; Liu Q. Et al., 2007]. In this case, the irradiation is carried out in either inert conditions or under vacuum [Figure – 2.12].

On exposure to radiation, active sites are generated on both the monomer as well as the substrate simultaneously, since both are exposed to radiation simultaneously. In this method, the radiation dose required to achieve grafting is lesser than that required in the previous two irradiation techniques.

This is because in this method, the radicals or active species as soon as they are formed, react with other molecules and do not need to be stable or stored for any period of time. The active species here can be either the free radicals or ionic species; cationic or anionic.
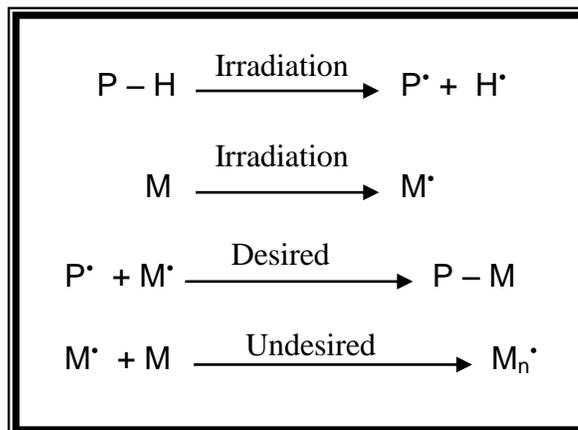
$$P - H \xrightarrow{\text{Irradiation}} P^\bullet + H^\bullet$$

$$M \xrightarrow{\text{Irradiation}} M^\bullet$$

$$P^\bullet + M^\bullet \xrightarrow{\text{Desired}} P - M$$

$$M^\bullet + M \xrightarrow{\text{Undesired}} M_n{}^\bullet$$

Figure 1.12 : Simultaneous Method for Radiation Grafting : Free Radical Route ; where P-H is the polymer, M is the monomer M_n is the homopolymers and P-M is the grafted polymer

This is a preferred method for carrying out grafting but the obvious disadvantage here is the formation of homopolymers.

(iv) Use of Photoradiation Energy:

The interaction of photoradiation energy with a substrate leads to the generation of free radical species causing the initiation of the grafting reaction. Actually, photoinitiation of a reaction takes place either by the generation of free radicals on the substrate itself by its direct irradiation or takes place by the generation of free radical species on a reactive molecule which then interacts with a substrate to create free radicals on it [Taniguchi M. et al., 2003; Yamagishi H. et al., 1995; Irwan G.S. et al., 2002; Kubota H. et al., 1997; Peng T. et al., 2001; He D. et al., 2001; Rohr T. et al., 2003] . The major requirement in the photoinitiated reactions is the presence of a photoactive group or species which absorbs photoradiation energy to generate reactive free radical species. A source of this energy can be the UV radiation from UV lamps. This technique is not feasible for adoption at the industrial scale.

(v) Use of Microwave and Infrared:

The microwave and infrared radiation have also been used for carrying out grafting. These radiations mainly produce heat and thus temperature sensitive initiators are used while carrying out grafting reactions using microwave & infrared radiation. These initiators disintegrate into reactive species at a certain temperature and initiate the reaction. Thus, we can say that these radiations are actually used to raise the temperature or provide thermal energy to the reaction. The use of microwave & infrared is feasible only at laboratory scale for providing thermal energy and thus are not in use.

3.2.2 Crosslinking :

Crosslinking is yet another method by which the polymer and the monomers get associated with one another through the formation of a chemical bond. As the name suggests, in case of cross linking, one molecule forms linkages with two molecules leading to the formation of a network like structure. The essential requirement for crosslinking to take place is the presence of di or multi functionality in the molecules taking part in crosslinking.

Crosslinked structure or polymer may get formed either by reaction of multifunctional molecules or it may result due to an introduction of a crosslinker molecule into a polymer which leads to linkage formation between the several chains of the polymer through the crosslinker.

Various initiator systems are used for carrying out crosslinking reactions and the mechanism remains the same as for grafting, except that a crosslinker is required in the reaction [Thomas T.L. et al., 2002; Yener K.M. et al., 2003; Naghash H.J. et al., 2002; Chen Q. Et al., 2001; Huang J.X. et al., 2003; Sanda F. et al., 1994; Kampouris E.M. et al., 1987; Bremmer T. Et al., 1993; Wang A.R. et al., 2002; Wang A.R. et al., 2005; Yu Q. Et al., 2006; Huang W. Et al., 2001]. The crosslinking of polymers is a common and a useful tool for their modification to achieve desired properties.

3.2.3 Oxidation:

This technique is a type of chain cleavage reaction of polysaccharides, wherein carbonyl (C=O) or the carboxylic acid (-COOH) groups are introduced on the polysaccharide. The oxidizing agents, such as hydrogen peroxide, peracetic acid, permanganate, persulfate etc may be used for oxidizing polysaccharides but the main reagent used for the purpose of oxidation of polysaccharides is the hypochlorite. The halogens such as chlorine & bromine and hypochlorite & hypobromite produced by their reaction with water oxidize polysaccharides, particularly starch, in various ways [Newton J.M. et al., 1950; Degering e.F. et al., 1953].

While carrying out the oxidation, two modifications actually take place : one is the introduction of carbonyl and carboxylic acid groups by addition of oxygen and the other being the partial depolymerisation of the polysaccharide chain. The oxidised polysaccharides exhibit lower viscosities than the parent polysaccharides due to the depolymerisation. In the case of polysaccharides such as starch, oxidation reduces the gel strength. This is because of the fact that introduction of bulky groups such as carbonyl and carboxylic groups gives rise to steric hindrance amongst the shorter starch chains. The chains are not able to associate as they are not able to come close together [Whistler R.L. et al., 1984; Wurzburg O.B., 1986].

Oxidation of hydrocolloids is a well known and established technique for their modification especially in case of starch.

3.2.4 Depolymerisation :

The joining together of repeating units or the monomers to form long chain molecules is called polymerisation and the process of depolymerisation is actually the reverse of polymerisation. In case of hydrocolloids, depolymerisation is carried out to modify their solution and rheological properties. It is usually carried out either by enzymatic or chemical processes. The type of enzymes to be used depends on the type of sugars and linkages present in a

particular polysaccharide. In the case of chemical process, peroxides, persulfates etc. are generally used for depolymerization.

In several industrial applications, low molecular weight materials are required and in these cases depolymerisation methodology is adopted for modification of hydrocolloids to get desired molecular weight materials.

3.2.5 Substitution:

In order to carry out substitution on the hydrocolloids, first the reactive sites have to be identified. The substitution is carried out mainly in the case of polysaccharides and here the reactive sites are the large number of hydroxyl groups present on the polysaccharide backbone. By the functionalization of these hydroxyl groups, a wide variety of derivatives of parent polysaccharides are synthesised. The different functional groups impart different characteristics to polysaccharides and thus the properties of these polysaccharides can be tailor made to suit the various industrial applications by carrying out derivatisation with a suitable reagent to a certain desirable extent.

These derivatising agents may be anionic, cationic, neutral, zwitterionic or hydrophobic in nature. (Table – 1.6). The different functional groups impart different characteristics to the hydrocolloid thus making it suitable for use in various industrial applications.

Table - 1.6 : List of Reagents used for Imparting various Functionalities to Hydrocolloids

Type of Functionality	Derivatives / Group	Reaction
Anionic	Sodium carboxyalkyl	Etherification
	Sodium alkyl sulphonate	Etherification
	Sodium phosphonomethyl	Etherification
	Polyacrylate	Grafting
Cationic	Tetraalkyl ammonium hallide	Etherification
Neutral	Hydroxyalkyl	Etherification
	Alkyl	Etherification
	Aminoethyl	Etherification
	Cyanoethyl	Etherification
	Benzyl	Etherification
Zwitterionic	1-vinyl-3-(3-sulphopropyl) imidazolium salt	Grafting
Hydrophobic	Polyalkoxyalkyleneamines	Etherification

The derivatising reaction involves treatment of the hydrocolloid with a derivatising agent in the presence of an alkali. The extent of modification or derivatisation may be determined by measuring the degree of substitution or the molar substitution either by chemical method or by an instrumental technique. The term 'degree of substitution (D.S.)' (Figure –12.13) is defined as the average substitution of functional groups per anhydro sugar unit. One unit in a polysaccharide hydrocolloid is called as the anhydro sugar unit and on an average one such unit has three hydroxyl groups, i.e., three sites are available for substitution of a functional group. If all three sites get substituted, then the degree of substitution is 3.0, which is the maximum that can be achieved. The required D.S. value can be achieved by optimising the reaction recipe. The term 'molar substitution' is defined as the average number of moles of functional groups substituted per anhydro sugar unit. Molar substitution (M.S.) is used to describe the substitution level in the case of reagents, which tend to form long chains by reacting amongst themselves. One such example is that of hydroxyethyl derivatives, where the functional reagent used is ethylene oxide. When one molecule of ethylene oxide reacts with the hydroxyl group of the polysaccharide, etherification of the hydroxyl group takes place and there is the formation of $-OCH_2CH_2OH$ group. When the next molecule of ethylene oxide reacts, it can etherify the hydroxyl group of OCH_2CH_2OH group. At the end of the reaction, the degree of substitution maybe less as compared to the total number of moles of ethylene oxide that react with the polysaccharide. Thus, molar substitution is measured in these cases.

From the above discussion, it is evident that the method described here is based on chemical processing of the hydrocolloids to achieve desired functionalization, which is not environment friendly. If we look at the process steps for carrying out functionlisation of hydrocolloids, then it can be summed up that hydration, chemical reaction, purification and dehydration are the basic steps as shown in Figure – 1.14. This makes the process highly cumbersome, energy & time intensive. In the author's opinion there is a need for the development and adoption of a novel technology which overcomes the disadvantages of the current technology. The radiation processing technology is one such technology which offers an environment friendly and time & energy efficient method for the functionalisation of the materials. Now, having discussed the basic structure of carbohydrates and the types of modifications carried out, various aspects of two of the commercially important carbohydrates / polysaccharides are described in detail in the subsequent sections.

4. STARCH

Starch is a very important food ingredient and it possesses several attributes, which make it suitable for innumerable industrial applications [Tharanathan, R.N., 1995]. It exhibits a wide range of functional properties and is a most commonly used hydrocolloid. It is either used as extracted from the plant and is called as native starch or it is used after one or more modifications and is called as modified starch.

4.1 Background :

Starch is a anhydroglucose polysaccharide, which means that repeating monosaccharide units in starch are glucose. These glucose units are arranged both linearly (amylase) and in branched manner (amylopectin) as shown in Figure – 1.15. In case of linear amylase structure, glucose units are joined together by α-1,4 glucosidic bonds and in case of branched amylopectin structure, the branching occurs by α-1,6 linkage.

4.2 Extraction :
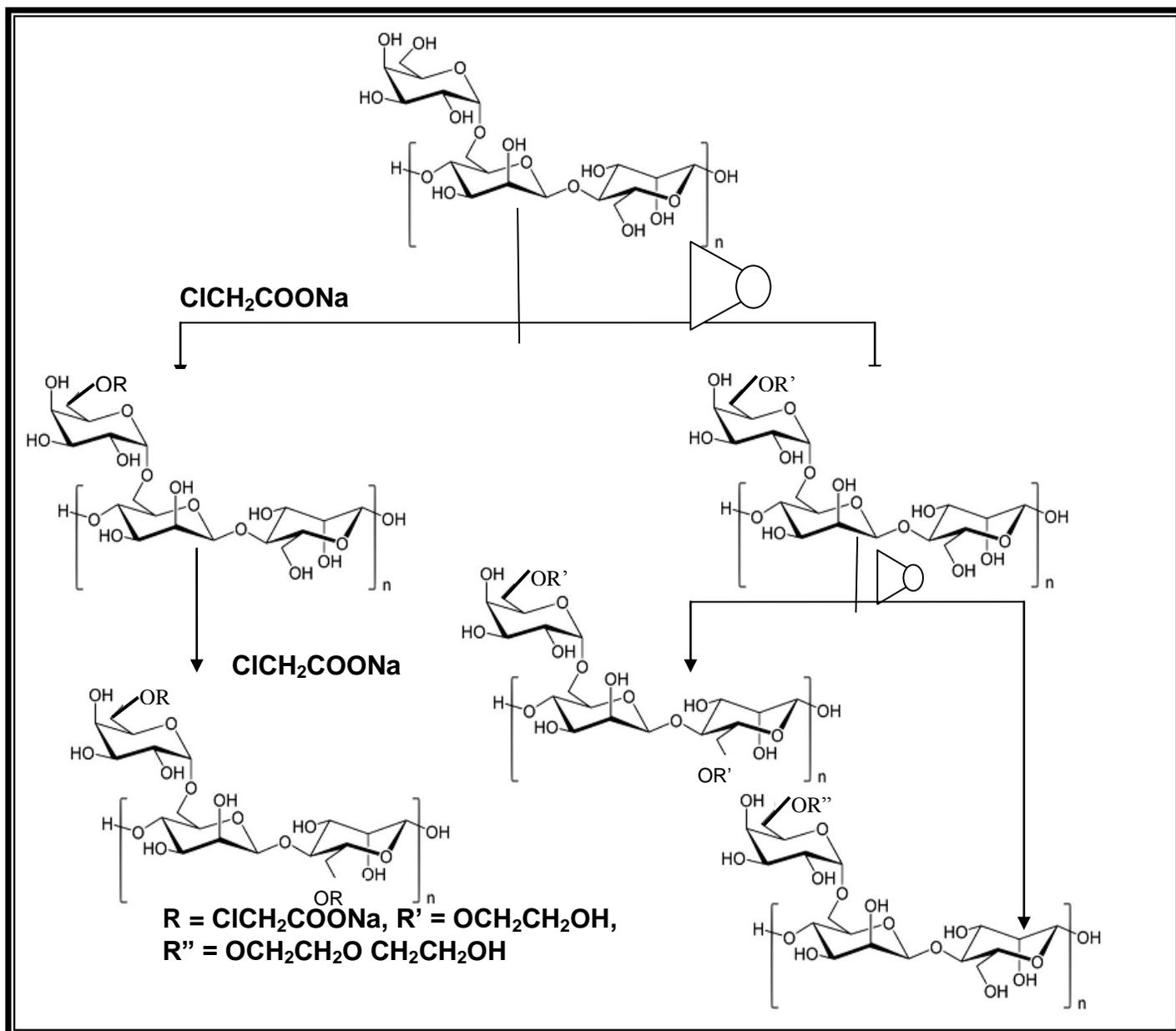
Figure – 1.13 : Substitution on polysaccharide Polygalactomannan using ethylene oxide and sodium salt of mopnochloroacetic acid. (i) Degree of substitution defined by no. of OH groups substituted and (ii) Molar substitution defined by moles of reagent that gets attached to sugar units.

like wet milling, etc., in which it is separated from fibre, oil and tightly bound protein. The objective of the extraction process is to recover the insoluble starch as undamaged and intact granules.

Starch is present in the form of insoluble, compact and microscopic semi – crystalline granules of size 1 – 100 μm. The crystallinity is induced due to the orientation of various chains in an ordered manner due to hydrogen bonding between the hydroxyl groups present in the structure. This ordered arrangement gives rise to crystalline regions in the starch granules. Thus, the starch granules consist of both crystalline and amorphous regions. The amorphous regions mainly contain the amylase and also a considerable amount of amylopectin. The crystalline regions consists primarily of the amylopectin [Sajilata,M.G., et al, 2006]. The microscopic appearance of each granule of starch is diagnostic of its source and so it can be used as a tool for identification.

```
┌─────────────────────────────────┐
│  Polysaccharide powder/ split   │
└─────────────────────────────────┘
                ▼
┌─────────────────────────────────┐
│         Slurry/ soaking         │
└─────────────────────────────────┘
                ▼
┌─────────────────────────────────┐
│        Derivatizing agents      │
└─────────────────────────────────┘
                ▼
┌─────────────────────────────────┐
│           Temperature           │
└─────────────────────────────────┘
                ▼
┌─────────────────────────────────┐
│            Washing              │
└─────────────────────────────────┘
                ▼
┌─────────────────────────────────┐
│            Drying               │
└─────────────────────────────────┘
                ▼
┌─────────────────────────────────┐
│           Grinding              │
└─────────────────────────────────┘
                ▼
┌─────────────────────────────────┐
│            Sieving              │
└─────────────────────────────────┘
                ▼
┌─────────────────────────────────┐
│            Product              │
└─────────────────────────────────┘
```
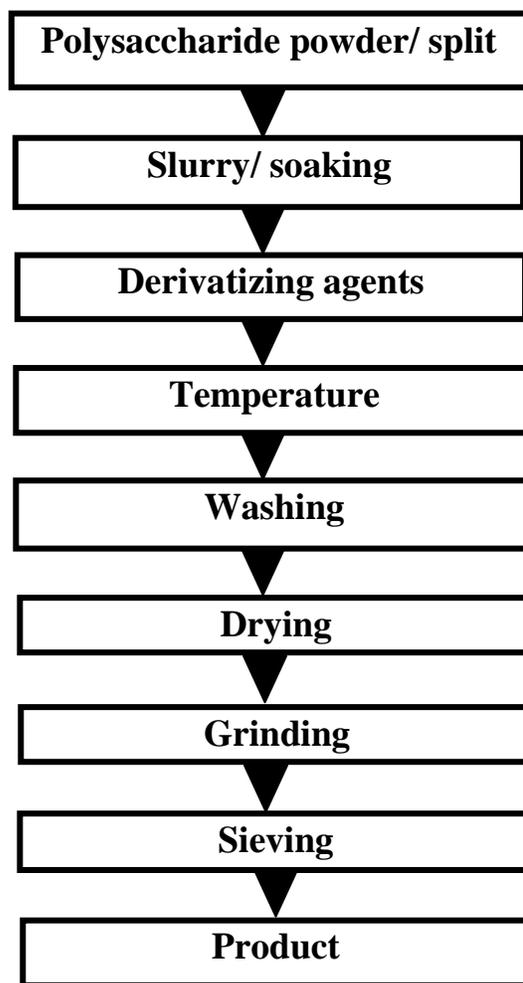
Figure 1.14: Processing steps involved in Derivatisation of Hydrocolloids by Chemical Synthesis Route

4.3 Characteristic Features:

The most important feature of starch which governs its properties lies in the structure of starch, which comprises of a large number of hydroxyl groups. These hydroxyl groups act as the driving force for introducing crystallinity or ordered arrangement of starch chains due to hydrogen bonding. The aqueous chemistry of starch is also governed by the hydrogen bonding, but here the hydrogen bonding is between hydroxyl groups of glucose units and water. But, the important point to be noted here is that the hydrogen bonding interactions within starch itself are very strong and in order to replace this interaction with starch – water interactions, modification of starch is needed.

Starch and other hydrocolloids find vast usage in food processing industry due to their ability to provide desired texture, control moisture and water mobility, improve overall quality & stability of the products and facilitate processing. The use of starch alone is sometimes hampered due to their tendency to syneresis,
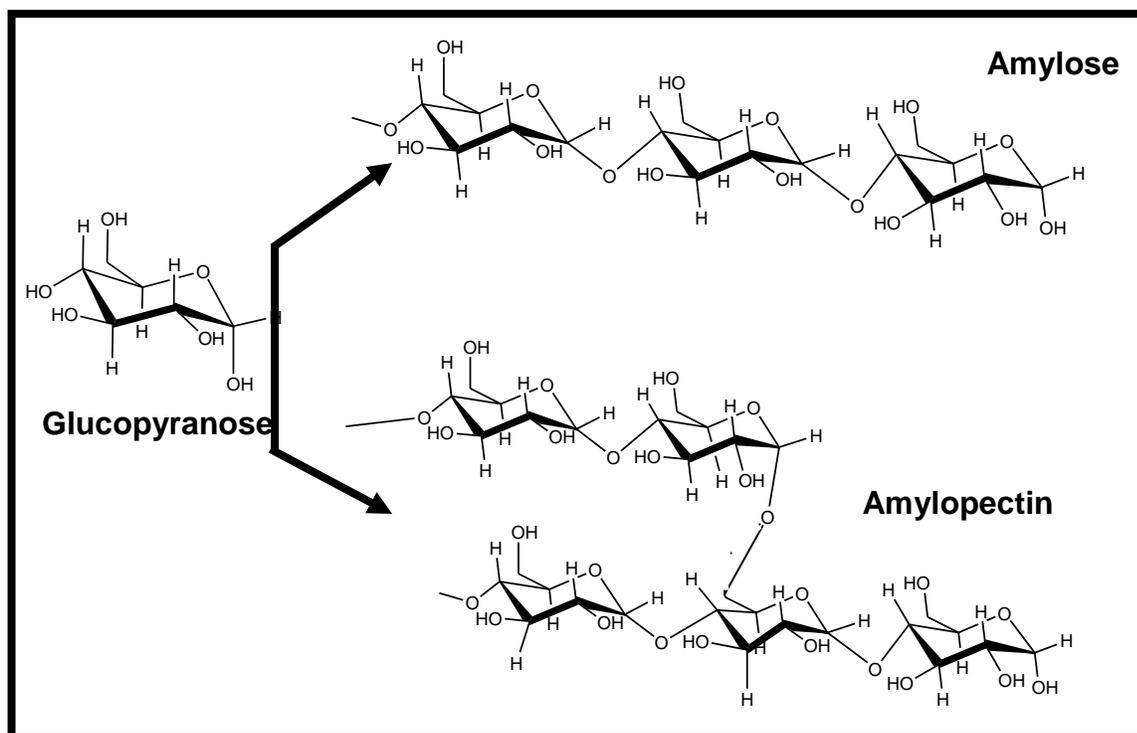
Figure 1.15 : Structure of Starch showing amylase and amylopectin

retrogradation and breakdown when subjected to cooking, shear stress and cooling, which leads to increased hardness and undesirable gels [Barcenas et al., 2005; Ribotta et al., 2010]. Numerous studies have been carried out to study the effect of addition of various hydrocolloids on wheat starch, which have revealed that the effect is greatly dependent on the hydrocolloid structure and concentration [Alloncle et al., 1989; Christianson et al., 1981; Rojas et al., 1999]. The interaction also depends on the starch origin because of the difference in granule size and microstructure [Techawipharat et al., 2008].

Rice starch also finds usage in many food applications for its desirable rheological properties [Rosell & Gomez, 2006]. But, sometimes use of other hydrocolloids in combination with starch becomes necessary to control or modify the gel or dough properties [Gujral et al., 2003; Marco et al., 2008]. A few fundamental studies have been conducted on the effect of different hydrocolloids on the pasting and rheological properties of rice starch, maize starch, tuber starch, wheat starch [Liu et al., 2003; Kim et al., 2006; Techawipharat et al., 2008; Rosell C.H. et al., 2011, Aguirre-Cruz A., et al., 2005; Huang C.C. et al., 2009, Pongsawatmanit R. et al., 2006, Viturawong Y. et al., 2008]. In the studies it has been revealed that starch – hydrocolloid blends exhibited a phase – separated microstructure in which amylase and amylopectin rich domains were dispersed in a hydrocolloid – rich continuous phase [Alloncle et al., 1991; Techawipharat et al., 2008]. In the absence of hydrocolloids, starch formed micellar networks through association of segments of amylase or amylopectin molecules, which control the swelling process during heating.

4.4 Modification:

In order to meet the growing demands of the modern industry, starch is modified by various methods to achieve desired properties. Basically, starch modification is carried out to overcome its various shortcomings leading to enhancement in the versatility of starch properties and applicability [Be Miller, J.N., 1997]. Depending on the application, these shortcomings may include the lack of free-flowing properties or water repellency, insolubility or failure to swell and develop viscosity in cold water, excess or uncontrolled viscosity after cooking, cohesive or rubbery texture of cooked starch, sensitivity towards cooking, etc. The unprocessed native starches are structurally weak and functionally restricted and cannot be used as such in the industries. Thus, processing of starch is necessary and can be carried out physically, chemically or biochemically.

4.4.1 Physical Modification :
Under this type of modification, starch is modified by giving it certain physical treatments. The physical modification of starch is mainly applied to change the granular structure of starch to convert the native starch into cold water soluble starch. The hydrothermal treatments, such as extrusion, cooking, sonication and pressure treatments are the physical modification methods used in modification of starch. Starch exhibits phenomena like gelatinization, pasting and retrogradation when it is cooked due to the structural transformations taking place in the starch granules.

When starch – water mixture is heated (Figure – 1.16), initially no rise in viscosity is observed because the hydration of starch granules takes place. The crystallinity is lost in this process as starch chains allow water molecules to come in between. When crystallinity is lost, gelatinization sets in, where if starch – water mixture is allowed to cool, then the starch granules get deswelled and return to their original stage. Once this stage is crossed and the granules reach the critical pasting temperature, rapid onset of viscosity is observed in the solution. The structural changes in the granule at this stage are irreversible.

On continuing the heating, viscosity increases and reaches a peak value, called the peak viscosity and then the viscosity starts decreasing as at this stage the granules rupture. On cooling, retrogradation and gel formation set in due to reassociation of amylase polymer. Different types of starches, i.e., starches obtained from different sources exhibit different pasting temperatures and peak viscosities as these properties are governed by the ratio of amylase to amylopectin, amount of lipids and other functional groups present in the starch granule.

Another type of physical modification is the pregelatinisation. This is a type of physical modification of starch where starch is precooked to achieve cold thickening starches. In this process, the starch is cooked and dried simultaneously by drum drying, extrusion or spray drying. The major methods used in the preparation of cold water soluble starches involve instantaneous cooking – drying of starch suspensions on heated rolls, continuous cooking – puffing – extruding and spray drying [Jarowrenko, 1986].

Pitchon et al have described a method involving injection and nozzle spray drying for the preparation of granular cold water – soluble starches. The high pressure treatment of starch is considered to be a minimal processing technique [Stute et al, 1996].

Annealing of starch is another hydrothermal modification, where the starch granule is heated in excess water at a temperature above T_g. In this treatment, significant changes take place in some of the properties of starch [Hoover, R. et al, 1994].

The physical modification of starch is well established and is carried out industrially to enhance the applications of starch.

4.4.2 Chemical Modification :
Several chemical modifications of starch are carried out to impart various new functionalities to it and for improving some specific properties to suit industrial processes [Tijsen et al., 2001a, 2001b]. The chemical modification are brought about by chemistries such as etherification, esterification, crosslinking, oxidation, cationization and grafting of starch. The property profile of the modified starch depends largely on its source, reaction conditions adopted, type and extent of substitution [Singh, J. et al, 2007]. The modification of starch alters its gelatinization, pasting and retrogradation behavior [Chor, S.G. et al, 2003, Kim H.R., 1993, Perera, C. et al, Liu, H. et al, 1999 and Seow, C.C. et al, 1993] leading to novel applications.

 Carboxymethylated starch [Tijsen et al., 1999] is synthesised by reacting starch with monochloroacetic acid after activating starch polymer by caustic treatment. The degree of substitution determines the properties of carboxymethylated products [Heinze T., 2005]. The addition of bulky groups like carboxymethyl reduce the tendency of starch to recrystallize and makes the starch less prone to damage by heat and bacteria. Liu J. et al have attempted the synthesis of carboxymethyl starch using microwave energy. It was observed that the reaction rate increases under microwave as compared to conventional processes.

Acetylation of starch is carried out by treating starch with acid. This is an esterification reaction where starch loses a hydroxyl group and the acid loses a proton leading to the formation of an ester linkage between the starch and the acid. The acetylation of cassava starch has been reported to impart increased swelling power [Rutenberg, M.W. etal, 1984] and enhanced water solubility [Aziz A., etal, 2004] to the starch granules.

Shorgen, 2003 has described a very efficient method for the synthesis of starch acetates, which involves heating dry starch with acetic acid and anhydride at 180^oC for 2 – 10 minutes. The methodology does not involve the addition of any catalyst or solvent. At the reaction temperature, starch melts in acetic acid [Shorgen, R.L., 2000] and thus the reaction takes place homogeneously. In another publication by Shorgen, 2008, a scandium triflate catalysed acetylation of starch at low to moderate temperature has been reported. The acetylated starches are particularly stable against heat and acids and are reported to form flexible, water soluble films.

Hydrophilic groups, such as hydroxyl groups improve the solubility of starch. These groups disrupt the inter and intra – molecular hydrogen bonds in starch chains, thereby weakening the granular structure of starch leading to an increase in motional freedom of starch chains in amorphous region [Chor, S.G. etal, 2003, Seow, C.C., et al, 1993 and Wootton, M. et al, 1983]. The functional properties of starch pastes such as its shelf life, freeze thaw stability, cold water swelling, etc also get improved on hydroxypropylation [Wootton & Chaudhry, 1981].

The modification of starch by **succinylation** is known to modify its physicochemical properties, thereby widening its applications in food and non – food industries. Succinylation of starch leads to reduction in its gelatinization temperature and retrogradation, improves the freeze – thaw stability as well as the stability in acidic and salt containing medium [Trubiano, P.C., 1997, Trubiano, P.C., 1987, Tukomane, T. et al, 2008]. The incorporation of bulky octadecenyl succinic anhydride grouping to hydrophilic starch molecules imparts surface active properties to starch and modifies its rheological properties [Trubiano, P.C., 1997; Park S. et al., 2004].

Another type of chemical modification of starch is by **phosphorylation** and the product of this reaction is either a monostarch phosphate or a distarch phosphate, which is actually a crosslinked derivative. The presence of a phosphate group in starch increases the hydration capacity of starch pastes after gelatinization and results in the correlation of starch phosphate content to starch peak viscosity, prevents crystallization and gel – forming capacity [Nutan, M.T.H., et al, 2005]. Traditionally, starch phosphorylation is carried out by the reaction of starch dispersion in water with reagents like mono or di sodium orthophosphates, sodium hexametaphosphate, sodium tripolyphosphate, sodium trimetaphosphate or phosphorous oxychloride. The alternative methods such as extrusion cooking, microwave irradiation and vaccum heating have also been reported [Jyothi A.N., et al, 2008, Sitochy, M.Z., et al, 2001].

Graft copolymerization has proved to be an effective method for the combination of natural and synthetic polymers to achieve novel properties. In case of graft copolymerization, the guest monomer imparts certain desired novel properties to the host polymer resulting into vast applications of the copolymer [Fares, et al, 2003]. The grafting procedure basically involves creating a free radical site on starch backbone and then allowing it to react with an unsaturated compound such as vinyl or acrylic monomers. Both chemical initiation and irradiation processing have been employed to graft polymerize various monomers onto starch [Fanta et al., 1977].

Li et al have devised a new approach for graft copolymerization of allyl starch with carboxyl containing vinyl monomers using fenton's initiator for enhancing grafting efficiency. The effect of allyl etherification of starch on the copolymerization has been studied. The grafting efficiency and grafting ratio are the two essential parameters and they directly determine the performance of copolymers [Zhang et al, 2005]. The investigators have tried to enhance the grafting efficiency through exploring suitable initiators [Willett J.L. et. al, 2006], pre – gelatinizing starch before copolymerization [Nguyen C.C. et al., 1991] and by choosing a suitable medium for the copolymerization [Chen L. et al., 2005, Xu Q. et al., 2008 and You Y.C., 2000].

Previously, many researchers have explored suitable conditions for the copolymerization of natural starch with vinyl monomers [Zhang B., 2008 and Hebeish A., 1998]. Various initiator systems have been used for the graft polymerization of vinyl monomers onto starch, such as Ce^{4+} system, persulphate, Fe^{2+}/H_2O_2, manganic pyrophosphate, etc [Mino G. et al, 1958, Duke F.R. et al, 1949, Fanta G.F. at al, 1969, Fanta G.F., 1983, Gugliemelli l.A. 1977, Vazquez B. et al., 1992, Athawale V.D. 1997, Hebeish A., 1988, Abo-Shosha M.H. et al., 1992, Cao B. et al, 1992, Wu G. et al 1991, Wu G. et al 1994, Wang X. et al., 1997, Brockway C. E. 1964, Vazquez B. et al 1989, Khalil M. I. et al 1990, Mehrotra R. 1977]. Rui-He Y. et al have studied the grafting of poly(1,4-dioxan-2-one) onto starch via 2,4-toluene diisocyanate.

In addition to using the above mentioned chemical method, irradiation using Co^{60} and electron beam source can also be carried out to generate free radicals on the starch backbone [Fanta G.F. et al., 1987]. Fanta G. et al have studied the use of a mixture of acrylamide and 2-acrylamido – 2- methyl propanesulfonic acid for grafting on starch by gamma irradiation. It was found that the conversion of monomers to graft copolymer was nearly quantitative when pregelatinized wheat starch was irradiated alongwith the monomer.

The grafting of acrylic acid on starch has also been studied by reacting together pre – irradiated starch with aqueous solution of acrylic acid [Reyes Z. et al, 1966]. The rate of grafting was found to increase initially with time and then decreased when the grafting percentage reached a maximum. At a given radiation dose, the rate of grafting was found to be proportional to the first power of concentration of irradiated starch and to the 1.5 power of the initial concentration of acrylic acid. The crosslinking of starch has also been attempted for imparting desired properties [Woo & Seib, 2002]. **Crosslinked** starches offer acid, heat and shear stability better than their parental native starches [Mason, 2009]. The crosslinking agents generally used for starch in case of food applications include crosslinking agents generally used for starch in case of food applications include phosphorous oxychloride (POCl$_3$), sodium trimetaphosphate (STMP) and mixes of adipic acid anhydride and acetic acid anhydride [Thomas & Atwell, 1999]. The crosslinking is done to a very low extent (D.S. = 0.0005 – 0.002) resulting in only one crosslink per 500 – 2000 glucose residues.

The above mentioned derivatives of starch are being produced on commercial scale and they find usage in various industries.

4.4.3 Starch Formulations:
Apart from carrying out the modification of starch for changing its behavior and enhancing its applications, another method for modification of properties of starch is by the preparation of synergistic formulations of starch. Blends of native starches and other polysaccharide hydrocolloids have been used in the modern food industry to modify and control the texture, improve moisture retention and control water mobility & eating quality of food products.
 Several scientists have studied the interaction of starch with various gums [Chaisawang M. et al., 2006; Kim C. et al., 2006; Achayuthakan P. et al., 2008; Ptaszek P. et al., 2007]. It has also been reported that guar and xanthan gums affect the pasting and rheological properties of cationic [Chaisawang et al., 2005], native & anionic tapioca starch [Chaisawang et al., 2006].The effect on pasting and rheological properties of waxy corn starch has also been studied in presence of guar and xanthan gums.
Funami T. et al have studied the effect of addition of non – ionic polysaccharides, such as guar gum, tara gum, locust bean gum and konjac glucomannan on gelatinization and retrogradation behavior of wheat starch. It was concluded from the study that galactomannans interact with amylopectin upon heating, leading to increase in the paste viscosity of the system. The fewer are the galactose side chains, the greater is the increase in viscosity of the system. A similar study has been carried out on gelatinization behavior of corn starch [Funami T. et al, 2005] and on viscoelastic behavior of tapioca starch [Fuongfuchat A. et al, 2012].
The effects of salts on the pasting, thermal and rheological properties of rice starch in presence of non-ionic or ionic hydrocolloids has been studied by Samutsri W. et al.
The effect of various gums such as xanthan, guar, pectin, κ-carrageenan, arabic, gellan, locust bean and sodium alginate, on the flow behavior and yield stress of sweet potato starch has been evaluated by Choi et al., 2009. Most of the gums showed a synergistic effect on the elastic properties of starch – gum mixtures and the effect is dependent on the type of concentration of gum added.
 Baranowska H.M. et al., 2008 & 2011 have carried out a study on the formation and structure of starch – hydrocolloid binary gels based on the relaxation times of the water molecules. In their study, various types of starches and gums have been included.
The gelatinization and retrogradation behaviour of corn starch has been studied in the presence of fenugreek gum [Funami T., et al., 2008-1, 2]. It was revealed from the study that addition of fenugreek gum inhibited the structural hardening of the composite system.
Rheological properties of rice starch-galactomannan mixtures at different concentrations of guar gum and locust bean gum were investigated in steady and dynamic shear [Yoo D. et al., 2005]. Rice starch – galactomannan mixtures showed high shear-thining flow behaviour.
All these studies have provided sufficient data for understanding the interaction of starch with other materials present in a formulation and has helped in optimization of the formulations to get desired properties and for use in various industries.

4.4.4 Biochemical Modification :
Under this type of modification, biologically active molecules, such as enzymes are used to bring changes in starch. The enzymatic modification of starch still needs to be explored and studied. The enzymatic modification can provide an alternative route for the chemical modification of starch. The enzymes mainly used for biochemical modification include pullulanse and isoamylase. These enzymes hydrolyse different linkages in the starch macromolecule.
Isoamylase is known to totally hydrolyse α-1,6 glycoside bonds in amylopectin, glycogen and some branched maltodextrins and oligosaccharides, but is characterized by low activity in comparison to pullulan [Norman, 1981].
Kim & Robyt have demonstrated in their study that starch granules can be modified in situ by using a reaction system where glucoamylase reacts inside starch granules to give conversion of about 10 – 50% D-glucose inside the granule.

Although enzymatic processes have been studied in detail by several scientists but due to the high cost of the enzymes and sometimes slow reaction kinetics, these processes have not been widely accepted at the industrial scale.

4.4.5 Applications of Starch :
 Starch is one of the most widely used hydrocolloid in the industry. It finds application in almost every industry sector. Starch derivatives being easy to prepare, non toxic and renewable, play an important role in industries such as food, pharmaceuticals, textile and paper [Bhattacharyya et al., 1995b; Khalil et al., 2006].

Starch graft copolymers are widely used in water treatment [Gamze G. et al., 2007], paper – making [Lu S.J. et al., 2004], printing [Ghosh R.N. et al., 2004], finishing & sizing [Hebeish A. et al., 2008, Zhang X.D. et al., 2003, Mostafa K.M. et al., 1997]. It has been demonstrated that copolymerization is an effective method for improving the end-use ability of starch [Kalia S. et al., 2008, Jia Z. et al., 2006].

Carboxymethylated starch (CMS) has attracted a lot of attention in both research & industry [lawal et al., 2007] due to its unique properties : low gelatinization temperature, excellent flexibility, improved paste storage stability & clarity [Qiu & He, 1999]. CMS with D.S. ≤ 0.4 can be used as stabilizer, thickening agent and water retaining agent to improve the quality of food [Bjorck et al., 1988; lawal etal., 2007; Stojanovic et al., 2000; Ostergard et al., 1988]. CMS has vast usage in the area of drug delivery. It is known to absorb about 23 times its weight of water and this characteristic is responsible for high rate of disintegration and drug release from carboxymethylated starch based tablets. Saboktakin et al have described the synthesis and in vitro evaluation of carboxymethyl starch – chitosan nanoparticles as drug delivery system to the colon and have shown it to be a promising system for drug delivery to colon.

Several researchers have explored the use of carboxymethyl starch as an excipient for controlled drug release [Koninck P.D., 2010, Lemieux et al., 2009, Massicotte et al., 2008]. A study carried out by Pu has suggested that an oral colon targeting controlled release system based on resistant starch acetate as a film – coating material has an excellent colon – targeting release performance and also possesses universality for a wide range of bioactive compounds.

Starch acetate has been used in several pharmaceutical formulations [Chen et al., 2007, Nutan et al, 2005, Tuovian 2003, Tuovien et al, 2004 & Tuovinen et al, 2004b].

Onfre & Wang have shown that hydroxypropylation of starch improved the sustained release ability of amylase containing starch matrices and conferred additional resistance to the hydrolytic action of pancreatin under simulated gastrointestinal conditions.

Apart from using starch for various industrial applications, another upcoming area is the synthesis of monomers (lactic acid) for making biodegradable polymers and for generation of energy. Starch is an abundant renewable resource suitable for bio-hydrogen generation. Orozco R.L. et al. have carried out a study on the hydrothermal hydrolysis of starch with carbon dioxide to produce hydrogen as the end product. The potential utilization of starch hydrolysates from hot compressed water treatment for upscale fermentations has been shown to be promising. Along similar lines, glucose production from starch under hydrothermal conditions has also been attempted [Nagamori M. et al., 2004]. Thus, starch and its derivatives find usage in various industrial applications.

5.　GALACTOMANNANS

Galactomannans are the hetero polysaccharides comprising of galactose and mannose sugar units. They are of several types depending on the ratio of mannose to galactose units present and this ratio varies from 1:1 to 5:1 (Figure – 1.16).

5.1 Background : The galactomannans comprise of a linear backbone of 1→4 linked β-D-mannan chains with galactose branches linked to mannose units by 1→6 –α-glycosidic bonds (Figure – 2.17). The structural composition of galactomannans has been studied by several techniques [Painter T.J. et al., 1979; Grasdalan H. Et al., 1980]. Das et al presented a method that enables rapid determination of the structure of galactomannans using specific enzymatic degradation. Galactomannans are degraded by enzyme that specifically catalyses the hydrolysis of β-1,4-mannosidic linkages : β-mannanase, although its ability to degrade galactomannans depends
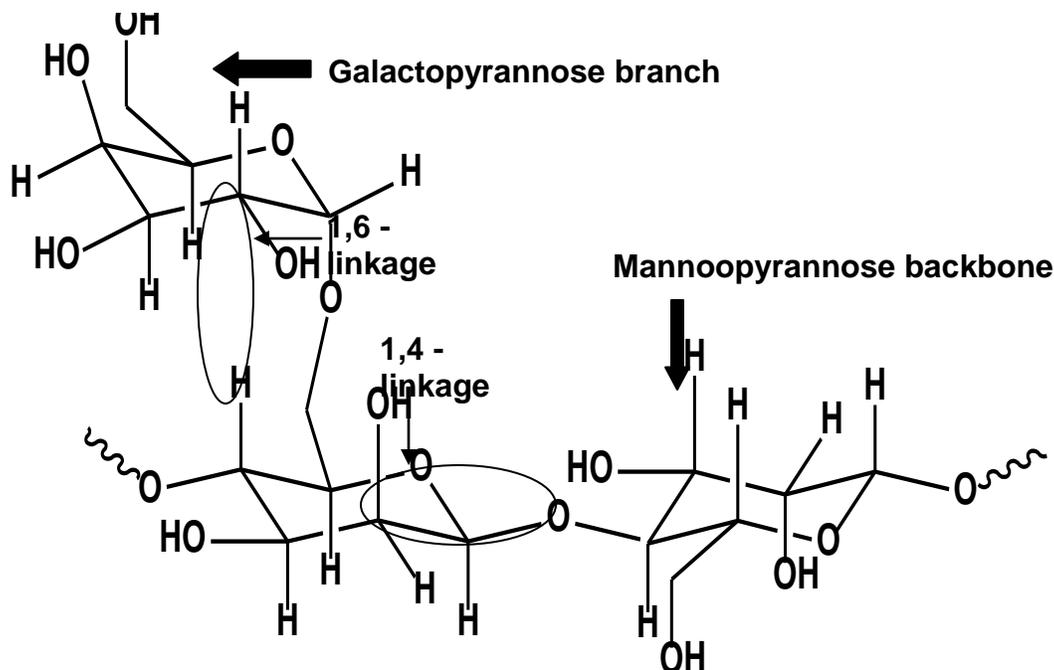
- M – M – M – M – M – M – M – M – M – M – M – M – M – M – M – M –
      | | |
     G   G   G

M : G = 5 : 1, e.g., Cassia Gum

- M – M – M – M – M – M – M – M – M – M – M – M – M – M – M – M -
   | | | |
  G   G   G   G

M : G = 4 : 1, e.g., Locust Bean Gum

- M – M – M – M – M – M – M – M – M – M – M – M – M – M – M – M –
     | | | | |
    G   G   G   G   G

M : G = 3 : 1, e.g., Tara Gum

- M – M – M – M – M – M – M – M – M – M – M – M – M – M – M – M –
    | | | | | | |
   G   G   G   G   G   G   G

M : G = 2 : 1, e.g., Guar Gum

- – M – M – M – M – M – M – M – M – M – M – M – M – M – M –
    | | | | | | | | | | | | |
   G G G   G G   G   G   G G   G   G   G   G

M : G = 1 : 1, e.g., Fenugreek Gum

Figure 1.16 : Pictorial representation of the structures of various galactomannans depicting the number of mannose & galactose units. In the various structures shown, M stands for a mannose unit and G stands for a galactose unit

on degree of polymerization and M/G ratio of galactomannans [Cheng Y. et al., 2000]. The work carried out by Tapie N. et al. describes the validation of an easy, fast and efficient precolumn derivatization method for the quantification of oligosides, mannose and galactose obtained by degradation of galactomannans. In this work, acid hydrolysis and enzymatic degradation methods have been combined and the quantification of released residues has been studied by HPLC system. The thermal degradation pattern of guar gum has been studied by Bradley T.D. et al.

Figure 1.17 ∶ Structure of a Polygalactomannan unit showing linkages between mannose units and between mannose & galactose units

5.2 Extraction :

The galactomannans are actually the reserve carbohydrates of various albuminous or endospermic seeds. The seed comprises of hull, germ and the endosperm. The weight percentage of these three components depends on the type of galactomannan seed being considered. In the case of guar, hull is 20-22%, gum is 43 - 44% and endosperm 34-36% in weight whereas in the case of carob bean or locust bean kernels (seed), hull is 30-35% , gum is 20-25% and endosperm is 40-45% in weight. Out of various types of galactomannans available, the focus of this paper will be on guar gum.

5.3 Characteristic Features:

As mentioned earlier, in the case of starch, the entire property profile of the galactomannans is based on their structure and the inter & intramolecular hydrogen bonding interactions of the macromolecular chains of galactomannans. The galactose branches on the mannose backbone keep the chains apart from each other, thereby creating space for water to enter and form solvent – solute interactions leading to solubility. But in the case of galactomannans having high mannose to galactose ratio, water solubility decreases because the galactose branches are far apart and thus mannose units form hydrogen bonding linkages thereby not allowing solvent solute interactions. The solubility of galactomannans is governed entirely by the amount of galactose present; higher is the amount of galactose, greater is the water solubility.

The linkages formed between the mannose backbone of various chains due to low amount of galactose leads to the formation of small crystalline regions in the structure which alternate with the much bigger amorphous regions. These crystalline regions can be dissociated using hot water and thus some galactomannans are soluble only in hot water (Table – 1.7).

Guar, a Polygalactomannan polysaccharide, is one of the important commercial crops of India. India is the world's largest producer of guar and accounts for about 80% of the world market share [Kumar & Singh, 2002]

5.4 Guar Gum :
Guar gum is a polygalactomannan isolated from the seed of two leguminous herbs Cyamopsis tetragonolobus and psoraloids [Reid G.J.S., 1985]. It consists of a long linear β (1-4) mannose backbone (1000 – 1500 units) to which the α (1-6) galactopyranoside subunits are attached as single unit side chains [McCleary B.V. et al., 1981]. Castillo G.E. et al. have described the basic characteristics and applications of guar gum in detail in their publication.
In order to extract the endosperm from the seeds of guar, the whole seeds are fed into an attrition mill or any other mill having two grinding surfaces. In this mill, the seed gets split into two endosperm halves still covered with the hull and the germ. These endosperm halves are heated to soften the hull and are then put into another mill for the removal of hull and germ by hammering or abrading. The fines are sifted off to get the endosperm, also called as the splits. These splits are then ground to get the powder form. The hull and germ are called the meal and is used as cattle feed.

Table – 1.7 : Characteristic features of various Galactomannans

Guar gum is different from other galactomannans with respect to the ratio of mannose : galactose (2:1) [Neukon H.,

S. No.	Type	Mannose : Galactose Ratio	Inherent	Desired
1.	Cassia gum	5.0: 1.0	Insoluble in water	Solubility in cold water
2.	Locust bean gum	4.0: 1.0	Soluble in hot water	
3.	Tara Gum	3.0 : 1.0	Hydration on heating	
4.	Guar gum	2.0 : 1.0	Cold water	Thermal stability
5.	Fenugreek gum	1.0 : 1.0	Cold water	Tailor making of rheological properties

1993]. It is commonly used in the food industry as a thickening agent. The sugar composition of food gums can be determined using chromatographic techniques [Doner L.W., 2001].
In the area of pharmaceuticals, it has been studied as a vehicle for controlled release purposes [Baveja S.K. et al., 1991; Skinner G.W. et al., 1998] and also for colon targeting [Wong D. Et al., 1997; Rubinstein A. et al., 1995].

5.4.1 Characteristics:
Galactomannans provide a high degree of viscosity at low concentrations through entangled networks which restricts the movement of individual chains leading to trapping of water, modified texture and stabilizing product consistency to changes in temperature [Fox, 1992]. The dissolution and viscosity of galactomannans in aqueous solutions depends on time, concentration, pH, ionic strength and degree of mechanical dispersion used in preparation [Wang Q. et al., 2003; Doublier & Launay, 1976; Kok, Hill & Mitchell, 1996; Morris et al., 1981]. The viscosity is also influenced by the temperature of processing, as at elevated temperatures depolymerisation occurs leading to lowering down of viscosity. Although the use of antioxidants is common in food industry, they are used to prevent lipid oxidation and not to ensure reduction of polysaccharide degradation. Studies have been carried out to show that the protein component of the gums actually plays a role in preventing their degradation by scavenging the free radicals [Bradely & Mitchel, 1988]. The influence of pH and antioxidants on the depolymerisation of guar & locust bean gums have been evaluated at elevated temperatures [Kok M./S., 2010].

In case of any material, effect of ageing is a very important parameter for study. Barre L.L. et al, have shown that the solid state ageing in guar leads to scission of the molecular backbone.

Guar macromolecules have a tendency to aggregate together due to the formation of intermolecular hydrogen bonding. In case of the application of guar gum in hydraulic fracturing, the formation of aggregates is detrimental to oil recovery because it clogs the fractures, restricting the flow of oil [Cheng Y. et al., 2002]. Keeping this in view, crosslinking of guar chains is carried out using metal (chromium, aluminium, antimony, zirconium and boron) based additives leading to the formation of metal-hydroxyl complexes. Boron, in the form of $B(OH)_4$ reacts with the hydroxyl groups to link polymer chains together to form bis-diol complexes [Lapsin R. et al., 1995]. Yan Y.F. have studied the inter and intra-molecular interactions of guar gum in solution and have determined the critical concentration of guar gum required to enhance the viscosity. It was determined that if concentration of guar in solution is greater than 0.045g/dl, polymer chains will associate together leading to increase in viscosity.

Studies have been undertaken to characterize guar gum and other hydrocolloids by using both physical and chemical methods. Ng D. et al. have investigated a new technique based on refractive index for the measurement of the concentration of galactomannan solutions. The results of this investigation showed that DRI is a more accurate and reliable technique for determining the concentration of galactomannan solutions, having an average error of $\pm$ 0.5%. Akiyama T. et al have developed a method for the identification of thickening polysaccharides and the suitability of the method was evaluated for seven thickening polysaccharides – carob bean, guar, karaya, Arabic, ghatti, tragacanth and peach gum. The method comprised of mainly two steps : derivatization with diethyldithioacetal followed by analysis on GC. The amount of monosaccharides in the thickening polysaccharides were successfully estimated by this method. Jiang J.X. et al. have also worked on the structure determination of galactomannans by using techniques such as GC, ^{1}H NMR and ^{13}C NMR.

The dissolution kinetics and rheology being the most important properties of guar gum and other galactomannans [Whitcomb P.J. et al., 1980; Wienties R.H.W. et al., 2000; Wang Q. et al., 2002; Robinson G., et al. 1982; Daas P.J.H. et al., 2002; Zhu R.T. et al., 2009; Doyle J.P.. et al., 2009; Wang Q. et al., 2008; Morris G.A. et al., 2008; Vega Canter Y.I. et al., 2006], it becomes necessary to study them, especially over a period of time. The analysis of degradation rates over a prolonged time scale is an area of interest [Cheng & Prudhomme, 2000; Barre et al., 2007]. It has been determined through several studies on galactomannan degradation that hydrolysis is the main mechanism for degradation [Garti & Leser, 2001; Lai V. et al., 2000]. Chenlo F. et al. have evaluated the rheological properties of guar gum as a function of storage time under study and dynamic shear conditions using a controlled stress rheometer. The effect of several materials like synthetic sweeteners, salts, sucrose, solvent and pH conditions, temperature, concentration, etc have been studied on rheological and physical properties of dilute guar gum solutions [Samavati V. et al., 2008; Richardson P.H. et al., 1998; Elfak A.M. et al., 1977; Goycoolea F.M. et al., 1995; Wang Q. et al., 2000; Ben – Kerrour L. et al., 1980; Ma X. et al., 2007; Gittings M.R. et al., 2001; Kok M.S. et al., 1999; Spyropoulos F.et al., 2010]

The formulations used in various products in the industry comprise of several ingredients and it becomes necessary to study the combined effect of these ingredients on the rheology of the formulations. Keeping this in view, several scientists have evaluated the effect of various materials on the rheological profile of guar or vice versa. One such study has been reported by Galmarini et al wherein they have studied the effect of guar gum addition on the viscosity of trehalose and sucrose solutions. The addition of guar gum led to a synergistic effect on the viscosity for both the disaccharides, particularly for trehalose.

Galactomannans and their derivatives can synergistically interact with other biopolymers such as κ-carrageenan, xanthan, cellulose, tragacanth, starch, arabic gum and their derivatives resulting in improved product quality and reduced production cost [Dea et al., 1977; Pinheiro A.C. et al., 2011; Masato T. et al., 2006; Ahmed J. et al., 2005; Wang F. et al., 2002; Wu Y. et al., 2009; Chenlo F. et al., 2009; 2011; Khouryieh H.A. et al., 2007; Bresolin T.M.B. et al., 1997; Koop H.S. et al., 2009]. They also interact synergistically with their own derivatives. Wu M. has studied the flow properties of guar and carboxymethyl gum mixtures. The results indicate that network structure of solution changes due to addition of carboxymethyl guar due to changes in interaction between macromolecular chains.

The galactomannan gums have the capability of modifying the rheological and thermal properties of starch. Several studies have been carried out to evaluate the interactions between galactomannans and starch based products comprising of gums [Aguirre Cruz et al., 2005; Funami et al., 2005; Huang 2009; Pongsawatmanit et al., 2006; Viturawong et al., 2008; Choi H.M. et al., 2008; Sudhakar V. et al., 1996]. Kim W.W. et al., have carried out a study on rheological and thermal effects of galactomannan addition to acorn starch paste. The results suggest that presence of galactomannan in acorn starch paste modifies the rheological and thermal properties and these modifications depend on the type and concentration of gum.

The characteristic features of guar gum that make it highly useful as an industrial product can be summarized as follows :

➢ Cold water solubility due to a galactose content of about 33-40%.

➢ The viscosifying or the thickening property due to the interactions with the aqueous medium.

➢ Availability of hydroxyl groups, which can be derivatised leading to addition of desired functionality on guar (Figure – 1.18).
➢ Availability of cis - hydroxyl groups, which can take part in formation of cyclic complexes with multivalent reagents such as Borates and Zirconates leading to gel formation.

The unique rheological behaviour of guar and the options of modifying the rheology as per the need make it a highly useful industrial product. Guar gum is highly hydrophilic, which sometimes poses a problem in achieving complete hydration. Also, being of natural origin, guar solutions exhibit low thermal and shear stability. Keeping these disadvantages of guar in view, it becomes necessary to modify it to meet the present day industrial requirements.

5.4.2 Modification of Guar :
As described in Figure – 16, there are a large number of hydroxyl groups present on the guar macromolecules, which provide a reactive site in the structure of guar. Thus, one way to modify guar is by making use of the reactive –OH groups present and carrying out their functionalization by reacting with various reagents.
Apart from making use of the hydroxyl groups, another way to modify guar is by carrying out copolymerisation of guar by free radical mechanism. Both of these pathways for the modification of guar macromolecule have been explored thoroughly by the scientists worldover to come up with novel derivatives of guar for various industrial applications.
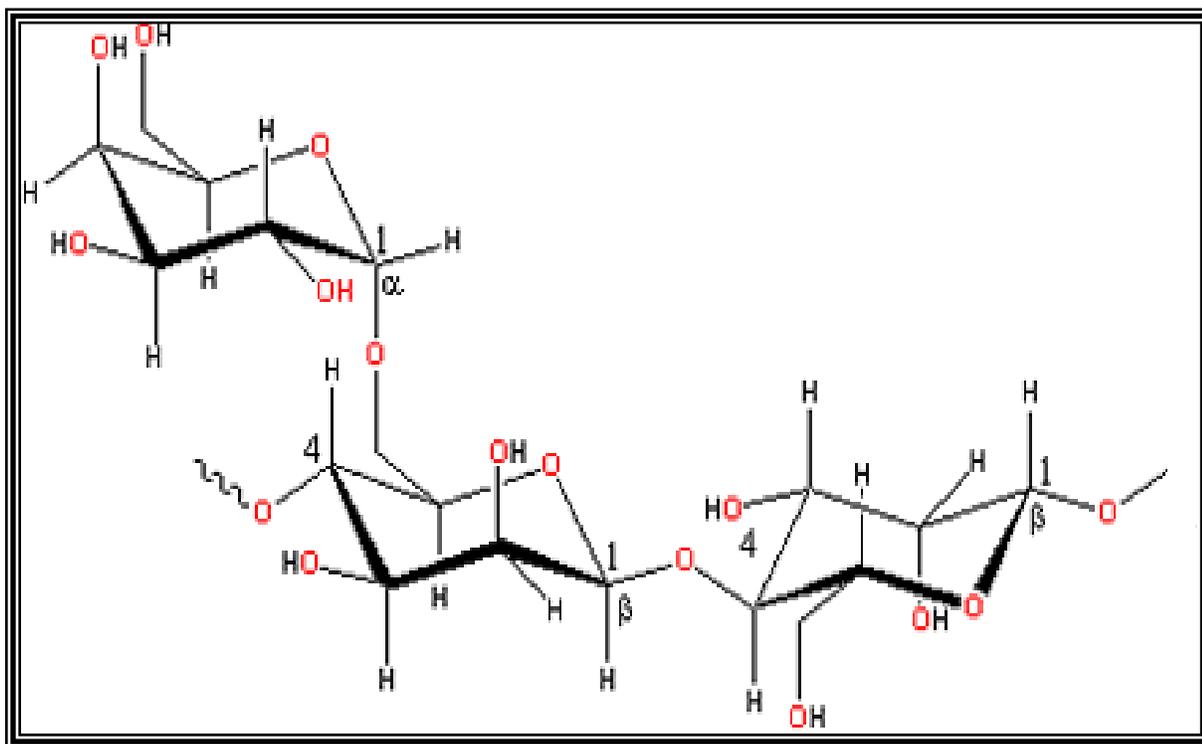
Figure – 2.18 : Repeat unit present in guar gum showing the hydroxyl groups

5.4.3 Using Hydroxyl group:
The chemistries that can be made use of for modification of guar at the hydroxyl groups are mainly etherification and esterification. The various types of reactions that can be carried out on guar are described in this section.

5.4.4 Hydroxylalkylation :
Under this category, mainly two types of derivatives are synthesized; hydroxypropyl and hydroxyethyl guar. Swamy N.N.G. et al have described the derivatisation of guar to various hydroxyalkyl derivatives and their characterization. These derivatives are synthesised by an irreversible nucleophilic substitution using propylene / ethylene oxide in the presence of an alkaline catalyst [Laposin et al.,1995; Wang C. et al., 2008]. The chemical and functional properties of hydroxypropyl guar (HPG) are mainly dependent on the pattern of substitution, distribution of substituent and the

average length of hydroxypropyl substituents [Ho et al;1972]. The molar substitution (MS) of HPG can be easily determined by NMR analysis but the determination of the substitution pattern can be challenging. Reuben established a statistical kinetic model to describe the substituents of HPG. Gas liquid chromotagraphy with mass spectrometry has been employed for the determination of the substituent distribution in hydroxypropylated amylopectin   (Richardson et al; 2000). Wu X. et al., have developed a new method based on periodate oxidation combined with probability analysis to determine the degree of substitution at the secendory hydroxyl groups of hydroxypropyl guar gum. Y.Q. et al. have described a method for the determination of molar substitution at secendory hydroxyls of HPG by periodate oxidation. The rheological properties of HPG have been studied by several scientists using a capillary breakup extensional rheometer (caber) [Duxenneuner M.R. et al., 2008] and other rheometers [Zhang L.M. et al., 2007; Cheng Y. et al., 2002; Kesavan S. et al., 1992]. Cheng Y. et al have described the intermolecular interactions of HPG by studying the rheology.

Hydroxyethyl guar (HEG) is synthesised by reaction of ethylene oxide with guar gum and it exhibits excellent electrolyte resistance, viscosity stability and good shear stability. The methods developed for the determination of degree of substitution of   HEG are mainly based on cleavage of ether bonds in refluxing hydroiodic acid followed by quantification of the reaction product [Morgan, 1946; Lortz 1956]. He L.S. et al have described a chemical method for the determination of the degree of substitution of HEG using mixed p-toluene-sulfonic-acetic anhydride.

On carrying out the substitution of hydroxypropyl groups on guar gum, the intermolecular interactions change and as the level of substitution increases, the HPG chain stiffens [Cheng Y. et al., 2002]. HPG is widely used in many industrial sectors such as oil recovery, food systems, paints, mineral industry and personal care etc [Seaman, 1980].

5.4.5 Carboxymethylation :

The carboxymethylation of guar involves the reaction of guar gum with monochloroacetic acid or its sodium salt in presence of caustic. The carboxymethylation conditions with respect to the volume and concentration of caustic, amount of chloroacetic acid and reaction temperature were optimized by Dodi G. et al in their study. The various grades of carboxymethyl guar synthesized have been studied for their application as flocculants and viscosifiers [Pal S. et al., 2009]. The degree of substitution in carboxymethylated polysaccharides, such as guar gum can be determined by Raman & FTIR spectroscopy as shown by Yuen S.N. et al.

5.4.6 Cationization :

The cationic guar gum comprises of a cationic group, usually the quaternary ammonium group. These positively charged guar derivatives have been found to be suitable for use in personal care products, for treatment of industrial effluents, etc. Singh R.P. et al have developed a method for the incorporation of a cationic moiety N-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC) onto the backbone of guar gum in presence of caustic. It was found that the derivatives with longer CHPTAC chains show better performance as a flocculant. Patel S.P. et al have also described the synthesis and characterization of quaternary ammonium compounds of guar.

Another method used for cationisation of guar gum involves etherification reaction with the reagent 2,3 – epoxypropyl trimethylammonium chloride under alkaline conditions [Bigand V. et al., 2011]. The cationic derivatives of galactomannans are commercially available with D.S. lower than 0.1 [Dasgupta, 1994]. The higher D.S. of 0.2 – 1 have been obtained in isopropyl alcohol / water media [Cottrell et al., 2001] or in aqueous media [Pal, 2007] for potential use in cosmetic and food industries.

5.4.7 Methyl Ethers :

Methyl etherification of guar involves the replacement of hydrogen of the hydroxyl group with a methyl group. The reduction in the number of hydrogen atoms for H-bonding reduces the extent of hydrogen bonding giving rise to higher flexibility of the guar chains.

Methylation was carried out by the reaction of guar gum with dimethyl sulphate or methyl iodide in the presence of caustic. The process has been studied and optimized keeping in view its future scale – up for industrial production of methyl guar [Risica D. et al, 2005, Denham W.S. et al., 1913, Haworth W.N., 1915, Srivastava H.C. et al., 1963, Hakamori J., 1964, Hough L. et al., 1963, Singh V. et al., 2003, Manzi A.E. et al., 1986].

5.4.8 Sulphonation :

 Qing L.I. et al have reported a method for chemical modification of guar gum by sulphonation using chloro sulphonic acid as the sulphonating reagent. The structures of guar gum sulphate were investigated by GPC and spectroscopic analysis. It was observed that guar gum sulphate could inhibit the intrinsic coagulant pathway, thereby exhibiting anticoagulant activity. The guar gum sulphate with D.S. of 0.85 and the molecular weight of 3.40×10^4 had the best blood anticoagulant activity.

In a recent study it has been reported that the sulphonation of polysaccharides not only enhanced water solubility but also modified the chain conformation resulting in changes in the biological activities [Liu Y.H. etal., 2009]. Many studies have confirmed that the sulphated polysaccharides exert potential biological properties in comparison with non – sulphated polysaccharides, such as anti-coagulant, anti-virus, antioxidant and antitumor activities [Wang L. et al., 2009; Wang X. et al., 2010].

5.4.9 Amide formation :
 Das D. et al have developed a method for hydrophobic modification of guar gum by its reaction with chloroepoxypropane and benzoyl chloride to form guar gum benzamide, which was found to exhibit resistance to water and solubility in non-aqueous solvent like dimethyl sulphoxide. The films of guar gum benzamide were found to exhibit microbiocidal properties.

5.5 Esterification :
Guar gum as such has a very high viscosity and it does not possess any emulsifying activity. In order to use guar gum in microencapsulation application, it becomes necessary to bring down its viscosity and introduce some hydrophobic group on its backbone. Sarkar S. et al have developed a method for the esterification of guar gum hydrolysate (GGH) with n-octenyl succinic anhydride (OSA) and oleic acid. On evaluation of the esterified product for their applicability as a wall material in microencapsulation with respect to gum arabic (GA), it was found to follow the order : GA-OSA>GGH-OSA>GA>GGH-oleate. A simple and cost effective method for the preparation of galactomannan esters have been described by Sarkar S. et al. The introduction of bulky hydrophobic groups like octenyl succinate render guar hydrophobic and enhance its applications in certain areas.

5.5.1 Mixed Derivatives of Guar :
 Apart from single derivatives of guar, a few references are available on the synthesis of mixed or double derivatives of guar. Pasha M. et al have carried out the synthesis of a double derivative of guar gum. The derivative was analysed for its rheological behavior in detail. As compared to guar, it revealed a more controlled rate of hydration. The advantage of double derivatives is in imparting dual functionality to guar gum which leads to modification in its hydration, dissolution, rheology and thermal stability. The author of this chapter has experience of working on several mixed derivatives of guar, although references on them are not available in the literature.

5.5.3 By free radical generation :
This method used for the modification of guar is based on the generation of free radical sites on the guar backbone by either chemical method or by using radiation processing technology. Once a free radical is generated on the backbone, it can be reacted with a monomer species having desired functionality to carry out grafting / copolymerization and crosslinking of guar.

5.5.4 Grafting :
Grafting or graft copolymerization of natural polysaccharides, mainly guar, starch & cellulose, is becoming an important resource for developing advanced materials as it can improve their functional properties [Chen et al., 2005; Joshi & Sinha 2007; Ly et al., 2010; Meshram et al., 2009; Rui-He et al., 2006; Singh et al., 2009; Szamel et al., 2008; Zhu et al., 2010]. Srivastava A. et al have shown that the grafted polysaccharides (guar gum and xanthan gum) are thermally more stable than the pure polysaccharides. The grafted polymers are usually synthesized by using conventional initiators [Mundargi R.C. et al., 2006], redox initiators [daSilva et al., 2007; Hebeish A.E. et al., 2003; Kaith et al., 2007; Kang et al., 2006; Singh et al., 2005; Zahran M.K. et al., 2006; Pandey P.K. et al., 2006; taunk K. et al., 2002; Behari K. et al., 2001; Xiaofang W. et al., 2007; Chowdhury P. et al., 2007], by microwave irradiation [Kaith et al., 2007; Masuhiro et al., 2005; Singh et al., 2007], by γ-ray irradiation [Lokhande H.T., et al., 1993; Geresh S. et al., 2004; Wang et al., 2008; Xu et al., 2008, Biswal J. et al., 2007] or by using electron beam [Vahdat et al., 2007; Singh V. et al., 2006; Behari K. et al., 1999; Behari K. et al., 2000; Chowdhury P. et al., 2001; Behari K. et al., 1997].Graft copolymers of guar gum and poly(N-vinyl-2-pyrrolidone) have been synthesized using potassium persulphate and ferrous ammonium sulphate as redox pair initiator [Sharma R.K. et al., 2011] to develop low cost and environment friendly technologies for removal of metal ions from water systems. Graft copolymerization technique has also been used to synthesize electrically conducting biopolymer based materials [Tiwari A., Singh S.P., 2008].One of the major difficulties in preparing pure graft copolymer is the formation of homopolymers by conventional free radical polymerization [Banerjee etal., 2006; Behari et al., 2001a; Behari et al., 2001b; Kumar et al., 2009; Srivastava et al., 2010] which are difficult to remove [Jenkins & Hudson, 2001; Kumar R. et al., 2007, 2008; Srivastava et al., 2009; Tripathi et al., 2000] from the graft copolymer network.Another method as described earlier for carrying out graft copolymerization is the ATRP technique. The modification of

polysaccharides by graft copolymerization and atom transfer radical polymerization (ATRP) using hetero-aromatic monomers offers the opportunity to tailor their physical and chemical properties, yielding functional macromolecules that may find a wide range of applications [Matyjaszewski & Xia, 2001; Wang & Matyjaszewski, 1995; Wang et al., 1999].Mishra V. et al have studied ATRP graft copolymerization of 4-aminoantipyrine (AAP) from a guar gum based macroinitiator, Cu (I) Br and 2,2' – bipyridyl (bpy) as initiator, catalyst and ligand in water. The factors affecting the conversion and rate of graft copolymerization such as temperature, concentration of monomer, catalyst, ligand and initiator were studied and the graft polymer was characterized. The advantage of ATRP is that it allows great control over the molecular weight distribution and the architecture of polymers. It is very tolerant to a variety of functional groups and protic solvents, including water [Kamigaito etal., 2001; Matyjaszewski & Xia, 2001].Microwave initiated synthesis [Sen G. et al., 2009; Sen G. et al., 2010; Sen G. et al., 2010] is a recent technique for synthesis of grafted polysaccharides, where the free radical grafting reaction is initiated by microwave radiation in the absence of any chemical free radical initiator. This method gives maximum reproducibility and precise control of percentage grafting. Although the use of combination of microwave radiation and a chemical free radical initiator yields higher grafting percentage but it has lesser control & reproducibility [Mishra S. et al., 2011]. So, microwave initiated method is preferred in cases where precise control of grafting percentage is required such as matrix for controlled drug release [Sen G. et al., 2009; Sen G. et al., 2010].Mishra S. et al have reported a process for microwave initiated synthesis of polymethylmethacrylate grafted guar (GG-g-PMMA) alongwith its characterization and applications. GG – g – PMMA is expected to be a highly branched polymeric material having high hydrodynamic volume. Consequently, according to Singh's easy approachability model [Singh R.P., 1995 & Singh R.P. et al., 2000] these materials are expected to be a superior flocculant as compared to guar. Apart from guar gum, its partially carboxymethylated derivative [Sand A. et al., 2011; Trivedi J.H. et al., 2008; Trivedi J.H. et al., 2005; Trivedi J.H. et al., 2005; Trivedi J.H. et al., 2005; Thaker M.D. et al., 2005; Mishra M.M. et al., 2011; Tripathy J. et al., 2008] and hydroxypropyl derivatives [Nayak B.R. et al., 2001] have also been used as a base material for grafting of various monomers using redox initiator system. Wan X.F. et al have studied the synthesis of graft copolymers of acrylamide and cationic guar gum. Thaker M.D. et al. have attempted to modify the sodium salt of partially carboxymethylated guar gum by UV radiation induced graft copolymerization of methyl acrylate using ceric ammonium nitrate as a photoinitiator.

5.5.5 Crosslinking :
The applications of guar gum and its derivatives are based on their ability to modify the rheology of the system to which they are added. Their rheological properties, as described earlier are due to solvent – solute interactions based on their solubility. Another very interesting aspect is that of reducing the water solubility of guar and its derivatives to utilize them in areas where water solubility is not desirable.

The use of guar gum along with other polysaccharides is very well known as a thickening agent in food and drug industries. They are also used for the extended release of drugs after their oral administration but presently their use is being studied widely for targeted drug delivery. Guar gum is highly water soluble and this property has to be first controlled before it can be used for targeted drug delivery. This reduction in solubility is generally brought about by its crosslinking to form hydrogels. [Rubenstein A., 1995; Brondsted H., 1996; Rubinstein A. et al, 1993 and Gliko-Kabir I. et al, 1998]. The crosslinking of polysaccharides and in particular guar gum has been tried with a number of reagents. The most common ones are borate, phosphate, glutaraldehyde and epichlorohydrin.George et al have described a method for the preparation of alginate guar gum hydrogels with distinct alginate to guar gum weight percent ratios. Glutaraldehyde was added to the guar gum-alginite aqueous solution mixture in a specific ratio and then the mixture was precipitated to form beads. It was observed that increasing the concentration of glutaraldehyde leads to an increase in crosslink density causing a decrease in the buffer uptake. In case of glutaraldehyde based hydrogels, it has been observed that high amounts of glutaraldehyde are required for crosslinking reaction, suggesting low cross-linking efficiency. However, the crosslinked products retained the ability of guar gum to be degraded in vitro by a mixture of galactomannase and α-galactosidase [Kabir et al., 1998].Kumar S.R. et al have also made use of glutaraldehyde for the cross-linking of guar gum to get microspheres. These microspheres were prepared for colon specific delivery of ornidazole and it was observed that only a small fraction of the drug was released at acidic pH and mainly the drug was released in the colon. Soppirnath et al., 2002 have developed a method for the synthesis of crosslinked microspheres of polyacrylamide grafted guar. In a study carried out by Lang Y.Y. et al, the authors have developed a method for the synthesis of hydrogels based on block copolymers of poly (N-isopropylamide) & guar gum and glutaraldehyde. The effect of pH & temperature on the drug release characteristics of the hydrogel have been studied.Sandolo C. et al. have carried out a study to determine the dependence of crosslinking reaction between guar gum and glutaraldehyde on temperature of and concentration of crosslinker. Several important parameters such as activation energy, time to reach sol-gel transition phase, etc were detected on the basis of the results obtained from this study. The study revealed that the resulting hydrogel can be

considered as a potential material for design of medical devices due to its versatility that allows preparation of different hydrogels, with different number of crosslinks and consequently different pore size, by controlling the experimental conditions for the gelation of guar gum. Another crosslinking agent used to control the high swelling characteristics of natural gums is by phosphate crosslinking as reported by Kabir et al., 2000 and Dulong et al., 2004. Generally, phosphate crosslinked gums are prepared by dissolving trisodium trimetaphosphate in caustic solution and then mixing this solution with gum. After thorough mixing, the mixture is dried to get the hydrogel. Barium chloride (Ba^{2+}ions) has been studied as a crosslinking agent for sodium alginate and carboxymethyl guar gum mixture [Bajpai et al., 2006]. The crosslinking of guar gum has also been reported using polyethylene glycol diglycidyl ether as the cross-linking agent. The thixotropic and swelling behaviour of the hydrogel were evaluated. The hydrogel exhibited thixotropy unlike the hydrogels obtained by crosslinking of guar gum with glutaraldehyde and phosphate compounds [Barbucci R. et al., 2008]. Hongbo T. et al have used epichlorohydrin as a crosslinking agent for guar and have investigated the reaction parameters. The degree of crosslinking was found to be influenced by the pH, temperature and the amount of crosslinking agent. The crosslinking of guar improved its alkali and acid resistance, retrogradation and viscosity stability. Superabsorbent materials are polymers which have the ability to absorb and retain large quantities of solvents as compared to their weight. When the solvent is water, these materials are called hydrogels as they absorb and retain water molecules by way of hydrogen bonding. Guar gum and its derivatives are used to synthesize these hydrogel materials. The modification of partially carboxymethylated guar gum by grafting of vinyl monomers using redox intiators is one of the most convenient methods [Mishra et al., 2008; Mishra et al., 2008; Tripathy et al., 2009; Tripathy et al., 2010; Yadav M. et al., 2011] amongst the other approaches followed, such as AIBN [Abdel-Razik, 1997; Egboh et al., 1984] and use of high energy radiations such as x-ray or γ-ray [Cardona et al., 2002; Dargaville et al., 2003; Kabanov et al., 2003] for modifying guar gum to impart the property of swelling or superabsorbency.Crosslinking method is also used to synthesize superabsorbent polymers [Shi X. et al., 2011] and the degree of crosslinking decides the superabsorbancy [Wang W. et al., 2009, Wang W.B. et al, 2009]. Wang W. et al have developed a method for the synthesis of guar gum – g – poly (acrylic acid) while using N,N'- methylenebisacrylamide as a crosslinker. The superabsorbancy was evaluated in aqueous organic solvent mixtures and various anionic & cationic salt solutions and was found to be sensitive to the presence of organic solvents, cationic & anionic salts.Zhai N. et al have described a method for the synthesis of a series of superabsorbent composites by graft copolymerization of guar gum with partially neutralized acrylic acid and medicinal stone using ammonium persulphate as the initiator and N,N'-methylenebisacrylamide as the crosslinker. The composite showed excellent responsive properties and reversible on-off switching characteristics in various pH buffer solutions, which has presented a great possibility to extend the application of the superabsorbent composites.

Li X. et al., have developed thermo-responsive guar gum / poly(N-isopropylacrylamide) hydrogels having interpenetrating polymer networks. The introduction of guar gum could reduce the total solid weight needed for gel formation from 43.5 g to 20 g /l. and lower the final water retention from 19.4 to 2.7%. It also improved the temperature sensitivity and permeability of hydrogels, which can be good candidates for controlled drug delivery system with both thermo-responsive and specific – colonic drug release behavior.
Li X.Y. et al have developed a process for the preparation of pH-sensitive guar gum /polyacrylic acid semi-interpenetrating polymer network hydrogels. The study has revealed that the maximum swelling ratio and diffusion exponent of hydrogels decreases with the increase in guar gum amount, but increases with enhanced acrylic acid amount and pH.
Hydrogels based on guar gum and other polysaccharides have also been developed for controlled drug release applications. Reddy K.M. et al have developed a blend microsphere of chitosan and guar gum and have studied it for its release properties of cefadroxil. The amount of drug loaded into microspheres, chitosan & guar gum composition of blend and the amount of cross-linking agent used have shown dependencies on the release of cefadroxil from semi-IPN microspheres.

5.5.6 Enzymatic Process :
 Enzymatic reactions catalyzed under mild process conditions, such as degradation / depolymerisation [Cheng Y. et al., 2000], debranching and oxidation represent a viable and eco-friendly alternative. Lavazza M. et al have described oxidation of guar galactomannan primary hydroxyl groups by a fungal laccase using the stable radical TEMPO as mediator. Oxidation of galactomannan by this process brought about a ten-fold increase in viscosity of a guar galactomannan solution and altered its rheological profile by converting a viscous solution to an elastic gel.
Shobha M.S. et al have carried out the modification of guar galactomannan by selective cleavage of galactose residue to obtain gum similar to locust bean gum by using pullulanase. This gum revealed enhanced rheological properties on co-gelation with xanthan and proved to be a cost effective replacement to locust bean gum.

5.5.7 Depolymerisation :
Guar gum solutions exhibit very high viscosity due to high molecular weight of guar galactomannan. In several of the industrial applications high viscosities are not desirable and in these cases hydrolysed or depolymerised guar gum is used.

Depolymerisation of guar gum to obtain a natural, water-soluble dietary fiber by partial hydrolysis of guar gum has been widely studied by several researchers. Approaches such as acid hydrolysis [Cheng et al., 2002; Wang et al., 2000], using specific enzymes such as mannosidase and or galactosidase [Mahammad et al., 2006; Reddy et al., 2004], hydrothermal degradation [Miyazaun et al., 2006], microwave mediated free radical degradation [Reddy et al., 2004] and irradiation [Jumel, Harding & Mitchel, 1996] have been used to depolymerize guar galactomannan. In case of the hydrolytic fragmentation of seed gums under microwave irradiation, the degradation of guar gum and other polysaccharides was carried out to oligo and monosaccharides [Singh V. et al., 2009]. A mechanism for the microwave induced hydrolytic degradation has also been proposed in the paper. The exposure time required for partial and complete degradation was found to be dependent on the type of linkages and degree of branching present in the gum. The partially hydrolyzed or depolymerized guar gum or guar gum hydrolyzate has a lower molecular weight and a markedly lower viscosity than the native guar gum [Slavin et al., 2003; Cheng Y. et al., 2002].

However, the drawback of these methods is that it is often difficult to make large quantity of depolymerized macromolecules with controlled degradation. In the recent years γ - irradiation induced depolymerisation of guar gum has also been tried [Dogan et al., 2007; Jumel et al., 1996; Sen M. et al., 2007]. The gamma irradiation of polysaccharides alters their rheological properties. Gupta S. et al have conducted a study on the effect of moisture content on rheological properties of guar. It was observed that high moisture content leads to less degradation of guar gum.

The hydrothermal treatment is a novel method being employed for the synthesis of mono & oligosaccharides from polysaccharides. Polysaccharides such as agar, guar gum, starch and xylan were hydrolyzed to produce mono- & oligosaccharides under hydrothermal conditions with and without carbon dioxide in a batch reactor [Miyazawa T. et al., 2005]. Polysaccharide hydrolysis under hydrothermal conditions in presence of carbon dioxide is an environmentally benign method to produce mono & oligosaccharides because the process does not require the use of conventional acids or bases followed by neutralization and separation.

5.5.8 Nanocomposites :
One of the latest development in the field of polysaccharides is the synthesis of nanocomposites using or based on polysaccharides. Zhu Y.G. et al have studied a method for the preparation of magnetic anionic guar gum microspheres by inverse – suspension crosslinking technique, using Fe_3O_4 as magnetic nucleus and glutaraldehyde as a crosslinker. The results of aspirin adsorption by magnetic microspheres showed that loading and encapsulation percentage of magnetic anionic guar gum microspheres were good.

The utilization of low cost, annually renewable and biodegradable polysaccharides for deriving superabsorbents has offered commercial and environmental advantages [Pourjavadi et al., 2006; Yoshimura et al., 2005] and the incorporation of inorganic clays or their modified products has also improved the performance of the resultant materials and further reduced the production cost [Zhang et al., 2007]. Presently, the natural polysaccharides, including starch [lanthong et al., 2006; Li et al., 2007], cellulose [Suo et al., 2007], chitosan [Chen et al., 2009; Liu et al., 2007b], alginate [Hua et al., 2009; Pourjavadi et al., 2007a] and gelatin [Pourjavadi et al., 2007 b] have been used for synthesis of superabsorbents, which have shown potential as substitutes for petroleum based superabsorbents. Keeping this in view, Wang et al. have prepared a series of guar gum – g – poly(sodium acrylate)/rectorite superabsorbent nanocomposites using guar gum, acidified or organified REC as the raw materials. The effect of HCl concentration, organification degree of REC and content of REC on swelling properties of the developed nanocomposites were investigated systematically. The organified REC was found to increase swelling capability to a greater extent than acidified REC. These nanocomposites exhibited improved swelling capability and swelling rate and can be used for several applications.

Singh V. et al. have developed a novel nanocomposite adsorbent out of polyacrylamide functionalized guar gum [Bajpai U.D.N. et al., 1990; Hongwen G. et al., 1995] and silica where the metal chelating capability of guar – g-polyacrylamide [Singh V. et al., 2004] and porosity & water insolubility of silica are jointly explored. The composite was found to be very stable and photoluminescent showing it to have great potential for optoelectronics.

5.5.9 Applications
Due to the immense potential and low price, this versatile macromolecule and its various derivatives find usage in several of the industrial sectors. Guar gum is used as a vehicle for oral controlled release purpose [Skinner, et al., 1998] and alongwith its derivatives, guar gum is used in oil industry, in drilling muds, textile industry to improve printing quality [Turk, et al., 2000].

5.6 Biocides :

Microbial contamination poses a threat to public health in areas such as water treatment, food packaging, hospital equipment, medical implants and devices. The disinfectants and synthetic polymers currently in use have residual toxicity and are not considered environment friendly. An alternative is the use of materials from bioresources. The current concept in the area of biocide materials is the adoption of a multifaceted approach towards molecularly designed surfaces that provide a hydrophobic surface and also exhibit biocidal activity by contact or by slow release of biocide molecules in the vicinity [Lichter et al., 2009].

Guar gum is being explored for its application in this area. It has a mannose backbone resistant to aerobic hydrolysis and only hydrolyses partially in anaerobic colonic micro flora. Thus guar gum provides an interesting backbone which can be modified to synthesize a new biomaterial biocide [Das D. et al., 2011].

5.6.1 Food :

The frying of food leads to an increase in its fat content due to oil absorption. The growing awareness amongst people about consuming fat in moderation has led the food industry to look for alternative methods of preparing fried food products so that their oil absorption is reduced. Food hydrocolloids, such as gums have been widely used as multifunctional additives in food processing to improve stability, modify texture and control the moisture content [Rimac-Brncic et al., 2004; Chaisawang & Suphantharika, 2005; Kaur A. et al., 2007]. In addition, hydrocolloids have the ability to form edible films and coatings with good oxygen, carbon dioxide and lipid barriers, which gives them potential to reduce oil absorption in deep fried products [Albert & Mittal, 2002]. Several hydrocolloids, including guar and xanthan gums at concentrations between 0.25% and 2.00% have been examined for their ability to reduce oil absorption in fried chickpea products [Annapure et al., 1999] and the results indicate that guar gum reduced the oil content by 30 – 33%. Sothornvit R. has described a method for reducing the oil absorption of banana chips by coating them with guar pr xanthan gum solutions prior to frying and then carrying out centrifugation of fried chips at high speed to reduce oil absorption.

Another application of guar gum is that it is incorporated into food products as it contains dietary fibers. Stewart M.L. have studied the effect of the molecular weight of guar gum on its physiological effects and it was concluded from the study that 400 kDa guar gum may be optimal for intestinal fermentability. Thus, it was concluded that the molecular weight of guar gum affects in vitro fermentability and should be considered when adding to a food or beverage. The effect of dietary fiber on blood cholesterol, etc has been studied [Jenkins D.J.A. et al., 1979; Simons L.A. et al., 1982].

The prediction of moisture exchange between food materials and surroundings is essential as it influences the physicochemical properties, drying process and the microbial safety [Rizvi, 1986]. The measurement and modeling of sorption isotherms of food materials have attracted numerous researchers because of their utility in industrial practice. Van den Berg & Bruin have compiled more than 200 isotherm equations. Vishwakarma R.K. et al. have determined the moisture absorption isotherms of guar grain and splits at 10 to 40°C and 23 – 96 % relative humidities using gravimetric method.

In dairy emulsions a non-fat phase, which is composed of polysaccharides, proteins and sugars is critical for the formation of the overall product microstructure [Vega & Goff, 2005]. The effect of additives, such as sugar & salt on the phase behavior of polysaccharides / protein aqueous two phase systems have been reported [Schorsch et al., 1999a, 1999b]. These detailed studies have demonstrated that sugar does affect phase behavior and as a result the emulsion – like structure of these systems. The effect of sucrose on the phase and flow behavior of polysaccharide / protein aqueous two – phase systems : locust bean gum/ sodium caseinate and guar gum / sodium caseinate have been investigated [Spyropoulos F., et al., 2010]. Guar gum has also been used to increase the thermogelation of whey protein isolates for various applications [Fitzsimons S.M., et al., 2008].

5.6.2 Hybrid Sorbents :

Singh V. et al have explored a new application of guar gum as a part of green absorbent hybrid. Native guar was used as a template for the polymerization of tetraethoxysilane giving rise to a hybrid nanocomposite. In an earlier publication by the same authors poly-acrylonitrile modified guar gum was used as a template to synthesize novel hybrid nanocomposites with excellent ability to bind Zn(II) [Singh V. et al., 2007 and Singh V. et al., 2008] and Cd (II) [Singh V. et al., 2009] but these nanocomposites involve synthetic ingredients which make them undesirable for biological applications. Keeping this in view, it is desirable to use guar gum in its native form as a template to obtain cost effective environmentally benign hybrid sorbent [Pavan F.A. et al., 2008 and Kuchma O.V. et al., 2006].

The depolymerised guar gum samples [Singh V. et al., 2006 & Singh V. et al., 2003] have also been used in templating the polymerization of tetraethoxysilane such that hybrids of controlled particle size and shape are formed to obtain maximum Zn (II) binding [Wright J.D., 2001].

5.6.3 Nanotechnology :
The guar gum – polyacrylamide graft copolymer has been used for the preparation of silver nanoparticles through the reduction of silver nitrate [Abdel – Halin E.S. et al., 2011] and for treatment of pulp and paper mill effluent [Masud H. et al., 2001]. With the increasing interest in minimization / elimination of waste and adoption of sustainable processes, the development of green chemistry approaches has become highly desirable. Other natural polymers like chitosan [Huang & yang, 2004], heparin [Yanli 1 & Hongtao, 2008], soluble starch [Vigneshwaran et al., 2006] and guar gum as such [Biswal J. et al, 2009] have been used as reducing and stabilizing agents for preparation of silver nanoparticles. Guar gum has also been for fabrication of green adsorbent hybrids for which guar gum was used as a template to polymerize tetraethoxysilane [Singh V. et al., 2011].

5.6.4 Packaging Film :
Chitosan and guar gum composite films have been developed for replacing the synthetic packaging material. The films comprising of 15% (v/v) guar gum showed very low oxygen permeability, good tensile and puncture strength and antimicrobial properties [Rao M.S. et al., 2010].

5.6.5 Metallurgy :
Guar gum is widely used in the metallurgical operations. It acts as a depressant of clays in silvite, talc in nickel and platinum floatation [Pearse, 2005]. The guar gum absorption mechanism onto pyrite was investigated by Rath et al. The laboratory tests have revealed that guar gum exhibits similar performance as starch while using it as an alternative depressant for iron ore floatation [Turrer H.D.G. et al., 2010]. The cationized guar gum synthesized by grafting with N-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride has been studied as a flocculating agent for coal fine suspensions alongwith several other cationized polysaccharides [Pal S., et al., 2008].Out of all the polysaccharides, cationized glycogen exhibited the best flocculation efficiency.
The grafting of guar gum helps in incorporation of a functional moiety on guar backbone, which enhances the application of guar gum. One such example is the grafting of poly(4-vinyl pyridine) on carboxymethylated guar gum. The pyridine functionality was chosen because it has the ability to bind hexavalent chromium and it also shows antibacterial property. The grafted polymer exhibited high water swelling capacity and can be used in the industry for metal ion sorption and flocculation.
The depression of pyrites, naturally occurring metal sulphide, is essential in concentration of base metal sulphides by floatation and this is achieved by floatation in alkaline medium in presence of cyanides. An environment friendly option for this is the use of polysaccharides. Bical O. et al have studied the depression of pyrite during sulphide floatation using carboxymethyl cellulose and guar gum. It was found from the study that guar gum depressed pyrites considerably even at very low concentration. There are various examples of the use of guar gum for stabilizing the mineral suspensions : potash ore floatation systems [Pawlik M. et al., 2006]. Nanthakumar B. et al have showed that guar gum is a better depressant of iron minerals than starch and it improves the floatation of high quality phosphate ores.

5.6.6 Building & Construction :
Guar and hydroxypropyl derivative of guar gum are used as water retainers in the cement mortars to improve the homogeneity of mortars, enhance the workability of the mortar and some properties in the hardened state [Cerulli T., 2003; Papayianni I., 2007 ; Izaguirre A., 2010].

5.6.7 Drag Reduction :
Guar gum have been examined as a turbulent drag reducer and was found to reduce friction drag tremendously under a turbulent flow even though it was used in very small concentration in the aqueous system [Choi H.J. et al., 2002; Lim S.T. et al., 2003; Hong C.H. et al., 2010].
Guar gum and hydroxypropyl gum have been studied for application as drag reducers [Shah S.N. et al., 2006] in coiled tubing. The graft copolymers of polysaccharides, such as starch & cellulose [Deshmukh S.R. et al., 1991] and guar gum [Deshmukh S.R. et al., 1987] have been found to be very effective drag reducers.

5.6.8 Pharmaceutical :
Nanoparticles of guar and other hydrocolloids are being studied as potential carriers of several drugs. Soumya R.S. et al have described a method for the preparation of guar gum nanoparticles involving cross linking reactions.

Hydrogels derived from biomacromolecules such as polysaccharides have emerged as promising scaffolding materials for tissue engineering applications owing to their three-dimensional porous structure, biodegradability & biocompatibility, ability to imbibe a large amount of water as well as biological fluids and good mechanical integrity [Halstenberg S., et al, 2002;]. The hydrogel material based on acryloyl guar gum (AGG) has been used as a carrier and slow release device for two pro-drugs, L-tyrosine and 3,4-dihydroxy phenylalanine (L-DOPA) [Thakur S. et al., 2009]. The acryloyl guar gum was functionalized by vinyl monomers; acrylic acid (AAc), methacrylic acid, 2-hydroxyethyl methacrylate and 2-hydroxypropyl methacrylate by grafting to get hydrogels. The maximum release of L-DOPA was observed from AGG-g-polyAAc and that of L-tyrosine from AGG – g – polymethacrylic acid.

Guar gum hydrogel has been used to cover the electrodes used in electrochemotherapy to facilitate the transfer of drugs to cancer cells and decreasing drug contact with healthy tissues [Fantozzi F. et al., 2010]. The hydrogel was swollen in a bleomycin sulphate solution and drug release took place only under the electric field.

A very important use of guar gum based hydrogels in the area of pharmaceuticals is as a carrier matrix for molecules which are unstable in the aqueous solution, such as ascorbic acid. Koop H.S. et al have studied the rheological behavior of xanthan – guar gum based hydrogels in the presence of ascorbic acid to find out whether this hydrogel can be used to minimize the instability of ascorbic acid. The improvement of gel like behavior of xanthan – guar gum in dispersions with buffer and 1,2 – propanediol and the stability tests performed suggest that these polysaccharide hydrogels represent a potential matrix for ascorbic acid formulations in pharmaceutical and cosmetic applications.

In the area of pharmaceuticals, guar gum has been suggested as a vehicle for oral controlled release purposes [Baveja S.K. et al, 1991; Skinner G.W. et al., 1998] and also for colon targeting [Wong D. et al., 1997; Rubenstein A., 1995]. Since a major restriction in designing guar gum based matrices for drug delivery is its high swelling characteristics, chemical modification of guar is carried out to reduce its swelling property especially while using for orally administered colon – specific drug delivery systems.

Guar gum microspheres prepared by ionic gelation of cationic guar gum have been explored for application as a protein drug carrier [Qu F.et al., 2006]. From the loading experiments of bovine serum globulin at various concentrations, it was found that the encapsulating efficiency is more than 80%.

The water uptake behaviour of barium ions crosslinked sodium alginate / carboxymethyl guar gum biopolymeric beads has been studied in media of varying pH [Bajpai S.K. et al., 2006]. When loaded with the model drug Vitamin B_{12}, the total release in gastric fluid was found to be 20% in 3 hours and that in intestinal fluid was found to be 70% in 7 hours. Carboxymethyl guar has been explored for its application for oral drug delivery [Reddy T. et al., 2002].

It is a well known fact that the presence of proteins in polysaccharides can induce an inflammatory response in the tissues [Tuckova L. et al., 2002]. Also, the degree and kinetics of hydration or dissolution processes are critical variables influencing the biological activity of guar gum. Particle size, molar mass and presence of co-solutes and salts are some of the factors known to influence the hydration of this gum [Wang Q. et al., 2006].

Cunha P.L.R. et al. have carried out a study on the purification of guar gum for its utilization in biological applications. Four different methods were adopted to remove the proteins from guar and it was observed that purification first by dissolution followed by precipitation using Fehling's solution proved most efficient for protein removal.

One of the functions that guar gum plays in the tablet compositions is that of the release modulator [Senapati M.K. et al., 2006; Khullar P. et al., 1998; Altaf S.A., 1998]. A study carried out on in vitro release characteristics of the matrix tablets showed that a combination of karaya and guar gum shows better sustained release than the individual gums.

Li X.Y. et al have given a detailed description of the use of guar gum and its various derivatives in the controlled drug delivery systems. It has been observed that guar derivatives have better effect of controlling and releasing of drugs and are expected to be good candidates for controlled drug delivery systems, especially of the colon-specific drug delivery system after design of formulas.

5.6.9 Water Purification / Remediation :

Hydrogels find vast application in the area of water purification by acting as sorbents for heavy metal ions. Chauhan et al. have reported the synthesis and use of hydrogels based on crosslinked depolymerized and native guar gum. The guar was first subjected to acid hydrolysis and then depolymerised and native guar gums were oxidized to their respective polycarboxylic forms. The oxidation of guar gum to polycarboxylates has been reported previously by Frollini et al. and Varma et al. The polycarboxylic guar gums were crosslinked with N,N-methylenebisacrylamide and were then used as sorbents for Cu^{2+}. It was observed that the hydrogel prepared from oxidized guar gum offered maximum sorption and maximum sorption of 125.9 mg/g sorption capacity was achieved.

Crosslinked polyacrlamide – g- guar gum copolymer has also been used for the sorption of hexavalent chromium ion [Abdel-Halim E.S., et al., 2011]. It was found from the study that the hexavalent chromium sorption process is pH dependent and maximum sorption took place at pH 3 and the extent of crosslinking also effects the extent of sorption.

One of the technologies employed for groundwater remediation involves injection of nanoscale zero-valent iron into the groundwater. The efficiency of this process is hindered by the aggregation of the iron nanoparticles. Tiraferri A. et al have carried out a study on the use of guar gum for enhancing the colloidal stability of nanoparticles and the effect of guar gum on surface properties, particle size, aggregation and sedimentation of nanoparticles. The results obtained have suggested that guar gum can be used to effectively deliver stabilized zero-valent iron nanoparticles for remediation of contaminated groundwater.

Guar gum and its derivatives have been widely used as a flocculant in water treatment [Gupta B.S. et al., 2005; Levy N. et al., 1995]. The flocculation characteristics of cationic guar gum, synthesized by incorporating N-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride onto guar backbone in presence of caustic, has been studied for the treatment of highly negatively charged particle suspensions [Singh R.P. et al., 2006].Guar gum and its derivatives are used in cation exchange resins [Ahuja M. et al., 1997]. The chemically modified guar gum sulphonic acid finds usage as a cation exchanger for toxic metal ions as per the studies carried out by several scientists [Singh A.V., et al., 2011; Singh A.V., 1996]. Polysaccharides have come to be known as good flocculating agents and thus are used for water treatment. The graft copolymer of hydroxypropyl guar & acrylamide [Nayak B.R. et al., 2001] and cationic starch [Pal S. et al., 2005] have been explored for application as flocculating agent and have been found very effective.

5.7 Paints & Coatings :
The application of gums, especially guar gum, in paints & coatings has been known since ancient times. Colombini M.P.et al and Bonaduce I. et al have identified several gums, like Arabic, tragacanth, karaya, guar, locust bean and ghatty in the wall painting samples from ancient structures.

Guar and acrylate guar gum have been studied for their application in acrylic emulsions [Shenoy M.A. et al., 2008]. It was observed that these biodegradable additives like acrylated guar gum synthesized from renewable resources could be used to increase the mechanical strength, as UV stabilizers and as rheology modifiers.

5.7.1 Filler Material :
D'Melo D.J. et al have described a novel application of guar as a filler material in thermoset polymer composites. It was observed that unsaturated polyester composites comprising of acrylate derivatives of guar exhibited better mechanical properties and water resistance.

5.7.2 Magnetorheological Fluid :
The rheological properties of specially designed liquid formulations can be easily controlled by applying magnetic force on these fluids and this is the science of magnetorheology. Guar gum has been explored for its use in magnetorheological fluids [Fang C. et al., 2005]. Wu W.P. et al have proposed a novel approach for producing obvious strengthening of magnetorheological (MR) effect of MR fluids. Carbonyl iron powders coated with guar gum were used as magnetic particles in the MR fluids. The results showed that inducing a guar gum coating not only greatly improved the sedimentation stability but also strengthened the yield stress of the MR fluids.

5.7.3 Paper :
Guar gum and its derivatives are widely used in paper manufacturing industry as an additive. During the pulping process, most of the natural hemicelluloses present are lost alongwith lignin. Guar gum replaces and supplements these hemicelluloses in paper bonding. The gum is added into the pulp suspension just before the sheet is formed and it has several advantages : improved sheet formation with a more random distribution of pulp fibers, increased burst, fold & tensile strength, increased machine speed, increased retention of fines, improved finish and decreased porosity.

Wang L.J. et al have investigated the effect of three single, two dual and two triple systems, comprising of combinations of highly substituted cationic starch, highly substituted cationic guar gum and polyamide, in waste pulp stickies control. The study showed that the triple systems gave best stickies control effect and that the stickies control mechanism is based on hydrogen bonding effects.

Cationic hydroxypropyl guar (CHPG) derivatives were evaluated for their retention and drainage properties and it was inferred that with increasing dosage of CHPG, the fines retention increases and beating degree of the pulp increases [Wan X.F. et al., 2006]. The side chain of hydroxypropyl groups is found beneficial to adsorption bridge behaviour of fines suspension and better behaviour of CHPG with increase of N content in CHPG was observed.

5.7.4 Hydraulic Fracturing :

Hydraulic fracturing technology has been used in oil and natural gas production since more than fifty years. The fracturing fluids used now-a-days are water based polymer gels. Highly viscous fluids, based on guar gum and its derivatives are used to carry the proppants into a hydraulic fracture formed when this fluid is pumped into the well at high pressures. There are two major requirements of fracturing fluids : one is that they should be able to place the proppant deep in the formation and second is the ease of their removal afterwards. Bahamdan A. et al have followed a novel approach for the synthesis of polyoxyalkylene-g-guar derivatives by first carboxymethylation, then methylation and then reaction with poly oxyalkylene amines to get the grafted derivative with unique rheological properties for use in hydraulic fracturing fluids. These derivatives exhibit higher viscosity on crosslinking with zirconium based crosslinking agents. Also, their clean up could be facilitated using enzymatic process.

5.7.5 Media :

Jain R. et al have explored the possibility of using guar gum as an alternative to agar for gelling microbial culture media. The study has revealed that guar gum can be used as a gelling agent in place of agar and as the media made with guar does not melt at even $70^{o}C$, these can be used for isolation and maintenance of thermophiles.

5.7.6 Waste Disposal :

Kim D. et al have described a novel technology for the disposal of electronic waste using a concrete composite cross linked with biopolymers such as guar and xanthan gum and a crosslinking agent. This cathode ray tube – waste biopolymer – concrete composite showed higher compressive strength than the standard concrete and a marked decrease in lead leachability.

6. CONCLUSIONS

The naturally occurring hydrocolloids find application in almost all the industry sectors due to their excellent rheological properties. The major disadvantages attached with their use are their susceptibility to microbial attack and poor thermal resistance. In order to overcome these disadvantages and also to modify the hydration and dissolution kinetics of these hydrocolloids, their modification is carried out.

In the present paper, various aspects of two commercially important hydrocolloids have been described in detail. The process industrially followed for the modification of these two hydrocolloids are based on chemical routes. The steps of modification involve hydration and dehydration steps which are cumbersome and time inefficient. Some preliminary research work has been initiated for carrying out the grafting of monomers comprising of various functional groups on the guar gum, its derivatives and other polysaccharides, but so far the methods studied for this involve the use of redox initiator synthesis. These initiators are expensive as well as highly poisonous. Also, as described above, the reaction methodology involves hydration and subsequent dehydration steps. Although, a few attempts have been made for making use of gamma radiation processing technology for grafting of monomers on guar but so far, an in depth study on this aspect has not been carried out.

The crosslinking of guar chains has also been undertaken by chemical route using various reagents. In place of these crosslinking agents, difunctional monomers may also be taken for carrying out the crosslinking of guar macromolecular chains.

Another aspect of modification of guar gum is its depolymerisation to get low molecular weight product. In this case also, the chemical route is used for the depolymerisation of guar. An alternative route can be the radiation processing of guar for its depolymerisation. So far, this method has just been tried out at lab scale for research purposes and is to be commercially exploited.

Looking at the state – of – the – art existing presently, the present thesis work was undertaken to carry out the detailed study on the effect of radiation on guar and its various derivatives in order to show that :

➢ Radiation processing is a dry method and can be easily used for depolymerisation or modification of guar gum
➢ Radiation processing technology can be used as an effective tool for : (i) tailor making of molecular weight of guar and its derivatives and (ii) grafting of desired functional monomers on guar backbone.

7. REFERENCES

[1]. Abdel-Halim E.S., Al-Deyab S.S., 2011. 'Hydrogel from crosslinked polyacrylamide / guar gum graft copolymer for sorption of hexavalent chromium ion'. Carbohydrate Polymers, 86, 1306-1312

[2].   Abdel-Razik E.A., 1997. 'Photoinduced graft copolymerization of ethyl acrylate, methyl methacrylate and methyl acrylate onto ethyl cellulose in homogeneous media'. Journal of Photochemistryand Photobiology A : Chemistry, 107, 271-274

[3].   Abo-Shosha M.H., Ibrahim N.A., 1992. Starch/Staerke, 44(8), 296.

[4].   Achayuthakan P. , Suphantharika M., 2008. 'Pasting and rheological properties of waxy corn starch as affected by guar gum and xanthan gum'. Carbohydrate Polymers, 71, 9 – 17

[5].   Aguirre – Cruz A., Mendez-Monteavlo G., Solorza-Feria J., Bello-Perez L.A., 2005. 'Effect of carboxymethylcellulose and xanthan gum on the thermal, functional and rheological properties of dried nixtamalised maize masa'. Carbohydrate Polymers, 62, 222-231

[6].   Ahmed J., Ramaswamy H.S., Ngadi M.O., 2005. 'Rheological characteristics of Arabic gum in combination with guar and xanthan gum using response surface methodology : effect of temperature and concentration'. International Journal f Food Properties, 8 (2), 179-192

[7].   Ahuja M., Rai A.K.,1997. 'Adsorption studies with some chelating ion exchange resins derived from guaran'. Carbohydrate Polymers, 33 91), 57-62

[8].   Akiyama T., Yamazaki T., Tanamoto K., 2011. 'Analysis of thickening polysaccharides by the improved diethyldithioacetal derivatization method'. Journal of the Food Hygienic Society of Japan, 52(1), 40-46

[9].   Albert S., Mittal G.S., 2002. 'Comparitive evaluation of edible coatings to reduce fat uptake in a deep-fried cereal product'. Food Research International 35, 445-458

[10]. Alloncle M., Doublier J.L., 1991. 'Viscoelastic properties of maize starch / hydrocolloid pastes and gels'. Food Hydrocolloids, 5, 4550467.

[11]. Alloncle M., Lefebvere J., llamas G., Doublier J.L., 1989. 'A rheological characterization of cereal-galactomannan mixtures. Cereal Chemistry, 66, 90-93

[12]. Altaf S.A.m Yu K., Parasrampuria J., Friend D.R., 1998. 'Guar gum based sustained release diltiazem'. Pharmaceutical Research, 15 (8), 1196-1201

[13]. Annapure U.S., Singhal R.S., Kulkarni P.R., 1999. 'Screening of hydrocolloids for reduction in oil uptake of a model deep fat fried product. Fett/Lipid 101, 217-221

[14]. Athawale V.D., Rathi S.C., 1997. React. Funct. Polym., 34, 11

[15]. Athawale V.D., Rathi S.C., 1999. JMS-Rev Macromol Chem Phys, C39 (3), 445

[16]. Aziz, A., Daik R., Ghani M.A., Daud N.I.N. and Yamin B.M., (2004). 'Hydroxypropylation and acetylation of sago strach'. Malaysian J. Chem., 6 (48-54)

[17]. Bahamdan A., Daly W.H., 2006. 'Poly(oxyalkylene) grafts to guar gum with applications in hydraulic fracturing fluids'. Polymers for Advanced Technologies, 17 (9-10), 679-681

[18]. Bajpai S.K., Sharma S., 2006. 'Investigation of pH-sensitive swelling and drug release behaviour of barium alginate / carboxymethyl guar gum hydrogel beads'. Journal of Macromolecular Science, Part A : Pure and Applied Chemistry, 43 (10), 1513-1521

[19]. Banerjee J., Kumar R., Srivastava A., Behari K. 2006.'Graft copolymerization of 2-acrylamido-2-methyl-1-propanesulphonic acid onto carboxymethylcellulose (sodium salt) using bromated / thiourea redox pair. Journal of applied Polymer Science, 100, 26

[20]. Baranowska H.M., Sikora M., Kowalski, Tomasik P. et al., 2008. 'Interaction of potato starch with selected polysaccharide hydrocolloids as measured by low field NMR'. Food Hydrocolloids, 22, 336-345

[21]. Baranowska H.M., Sikora M., Krystyjan M., Tomasik P., 2011. ' Analysis of the formation of starch – Hydrocolloid binary gels and their structure based on the relaxation times of the water molecules'. Polymers, 56 (6), 478 – 483

[22]. Barbucci R., Pasqui d., Favaloro R., Panariello G., 2008. 'A thixotropic hydrogel from chemically crosslinked guar gum : synthesis, characterization and rheological behaviour'. Carbohydrate Research, 343, 3058-3065

[23]. Barre L.L., Vaughan A.S., Sutton S.J., 2007. 'On the solid – state ageing behavior of the polysaccharide'. Journal of Material Science, 42 (14), 5497-5507

[24]. Barros JAG, Fechine GJM, Alcantara MR, Catalani LH., 2006. Polymer, 47, 8414

[25]. Basu S., Bhattacharya A., Mondal P.C., Bhattacharya S.N., 1994. J Polym Sci Part A: Polym Chem, 32, 2251

[26]. Baveja S.K., Rao K.V.R., Arora J., Mathur N.K., Vinayak V.K., 1991. 'Chemical investigation of some galactomannan gums as matrix tablets for sustained drug delivery'. Indian Journal of Chemistry, 30, 133-137.

[27]. Be Miller, J.N. 1997. Styarch modification : Challenges and prospects. Staerke, 49 : 127 – 131.

[28]. Behari K., Kumar R., Tripathi M., Pandey P.K., 2001. 'Graft copolymerization of methacrylamide onto guar gum using potassium chromate/malonic acid redox pair. Macromolecular Chemistry & Physics, 202, 837

[29]. Behari K., Kumar R., Tripathi M., Pandey P.K., 2001. 'Graft copolymerization of methacrylamide onto guar gum using a potassium chromate / malonic acid redox pair'. Macromoleular Chemistry and Physics, 202 99), 1873 – 1877

[30]. Behari K., Pandey P.K., Kumar R., Taunk K.2001. 'Graft copolymerization of acrylamide onto xanthan gum using Fe^{2+}/BrO_3^- redox couple. Carbohydrate Polymers, 46, 185

[31]. Behari K., Taunk K., 1997. 'Graft copolymerization of methacrylamide on guar gum using PDP/malonic cid redox pair'. Indian Journal of Chemical Technology, 4(3), 141-144

[32]. Behari K., Taunk K., Tripathi M., 1999. 'Cu2+/mandelic acid redox pair initiated graft copolymerization acrylamide onto guar gum'. Journal of applied polymer science, 71 95), 739-745

[33]. Behari K., Tripathi M., Taunk K., Kumar R., 2000. 'Studies of graft copolym,erization of acrylamide onto guar gum using peroxydiphosphate – metabisulphite redox pair'. Polymer International, 49 (20, 153-157

[34]. Ben-Kerrour L., Duchene D., Puisieux F., Carstensen J.t., 1980. 'Temperature and concentration dependence in pseudoplastic rheological equations for guar gum solutions'. International Journal of Pharmaceutics, 5 (1), 59 – 65.

[35]. Bhattacharya A., 2000. Prog Polym Sci, 25, 371

[36]. Bhattacharya S.N., Maldas D., Pandey V.K., 1986. J Polym Sci Polym Chem, A 24, 2507

[37]. Bhattacharya S.N., Maldas D.,1983. Prog Polym Sci, 10, 171

[38]. Bhattacharyya S.N., Maldas D., 1984. Prog Polymer Science

[39]. Bical O., Ekmekci Z., Bradshaw d.J., Harris P.J., 2007. 'Adsorption of guar gum and CMc on pyrite'. Minerals Engineering, 20, 996 – 1002

[40]. Bigand V., Pinel C., Petrez D.D., Rataboul F., Huber P., Petit-Conil M. carbohydrate Polymers 85 (20110 138 – 148

[41]. Biswal J., Ramnani S.P., Shirolikar S., Sabharwal S., 2009. 'Synthesis of guar gum – stabilized nanosized silver clusters with gamma irradiation'. Journal of Applied Polymer Science, 114(4), 2348-2355

[42]. Bjorck I., Gunnarsson A., Ostergard K., 1988. 'A study of nativeand chemically modified potato starch Part II: Digestibility in the rat intestinal tract. Starch / Starke, 41, 128-134.

[43]. Bonaduce I., Brecoulaki H., Colombini M.P., Lluveras A., Restivo V., Ribechini E., 2007. 'Gas chromatographic – mass spectrometric characterization of plant gums in samples from painted works of art'. Journal of Chromatography A, 1175, 275-282

[44]. Bozzi A., Chapiro A., 1988. Rad Phys Chem, 32, 193

[45]. Bradley T.D., Bali A., Harding S.E., Mitchell J.R., 1989. 'Thermal degradation of guar gum'. Carbohydrate Polymers, 10 (3), 205-214

[46]. Bremner T., Rudin A., 1993. J.Appl. PolymSci, 49, 785

[47]. Bresolin T.M.B., Sander P.C., Reicher F., Sierakowski M.R., Rinaudo M., Ganter J.L.M.S., 1997. 'Viscometric studies on xanthan and galactomannan systems'. Carbohydrate Polymers, 32 (2-3), 131-138

[48]. Brockway C.E., 1964. J Polym Sci Part A: Polym Chem, 3721

[49]. Burdick J.A., Chung C., Jia X., Randolf M.A., Langer R, 2005. 'Controlled degradation and mechanical behavior of photopolymerized hyluronic acid networks. Biomacromolecules,6, 386-391

[50]. Cao B., Song R., 1992. Hauxe Shije, 33(1), 19; Chem Abstr., 115, 132035j

[51]. Cardona F., George G.A., 2002. 'Copolymers obtained by the radiation induced grafting of styrene onto poly (tetrafluoroethylene – co – perfluoropervinyl ether) substrates I. Preparation and structural investigation'. Macromolecules, 35, 355-364

[52]. Castillo G.E., Lopez Carballo G., Lopez castellano A., 2005. 'Guar gum characteristics and applications'. Ciencia y Tecnologia Pharmaceutica, 15 (1), 3-10

[53]. Chaisawang M., Suphantharika M., 2005. 'Effects of guar gum and xanthan gum additions on physical and rheological properties of cationic tapioca starch'. Carbohydrate Polymer 61, 288-295.

[54]. Chaisawang M., Suphantharika M., 2006. Food Hydrocolloids, 20 (5), 641-649

[55]. Chao A.C., Shyu S.S., Lin Y.C., Mi F.L., 2004. Bioresource Tech, 91, 157

[56]. Chauhan K., Chauhan G.S., Ahn J.-H., 2009. 'Synthesis and characterization of novel guar gum hydrogels and their use as Cu^{2+} sorbents'. Bioresource Technology, 100, 3599-3603

[57]. Chen L., Li X., Li L., Guo S., 2007. 'Acetylated starch-based biodegradable materials with potential biomedical applications as drug delivery systems'. Current Applied Physics, 7(supplement 1) E90-E93

[58]. Chen L., Ni Y., Bian X., Qiu X. Zhuang X., Chen X., et al., 2005. 'Approach to grafting polymerization of 3-caprolactone onto starch granules'. Carbohydrate Polymers, 60, 103-109

[59]. Chen L., Ni Y., Bian X., Qiu X., Zhuang X., Chen x., Jing X, Carbohydrate Polymers, 60, 103 (2005)

[60]. Chen Q., Guan Y., Min Zhang X., Peng X.X., Xu J., 2001. Chinese Chem Lett, 12 (11), 1029

[61]. Chen Y., Liu Y.F., Tan H.M., Jiang J.X., 2009. 'Synthesis and characterization of a novel superabsorbent polymer of N, o –carboxymethyl chitosan graft copolymerized with vinyl monomers'. Carbohydrate Polymers, 75, 287-292

[62]. Cheng Y., Brown K.M., Prudhomme r.K., 2002. 'Characterization and intermolecular interactions of hydroxypropyl guar solutions'. Biomacromolecules, 3 (3), 456-461

[63]. Cheng Y., Brown K.M., Prudhomme R.K., 2002. 'Characterization and intermolecular interactions of hydroxypropyl guar solutions'. Biomacromolecules, 3 (3), 456-461

[64]. Cheng Y., Brown K.M., Prudhomme R.K., 2002. 'Preparation and characterization of molecular weight fractions of guar galactomannans using acid and enzymatic hydrolysis'. International Journal of Biological Macromolecules, 31, (1-3), 29-35

[65]. Cheng Y., Prudhomme R.K., 2000. 'Enzymatic degradation of guar and substituted guar galactomannans'. Biomacromolecules, 1(4), 782-788

[66]. Chenlo F., Moreira R., Pereira G., Silva C., 2009. 'Rheological modeling of binary and ternary systems of tragacanth, guar gum and methyl cellulose in dilute range of concentration at different temperatures'. LWT-Food Science & Technology, 42, 519-524

[67]. Chenlo F., Moreira R., Pereira G., Silva C., 2011. 'Apparent viscosity of binary and ternary systems of tragancanth, guar gum and methylcellulose at semidilute range of concentration'. Journal of Food Process Engineering, 34 (2), 475-490

[68]. Chenlo F., Moreira r., Silva C. Journal of Food Engineering, 107 – 113.

[69]. Choi H.J., Lim S.T., Lai P.Y., Chan C.K., 2002. Phys. Rev. Lett. 89 (art no. 088302)

[70]. Choi H.M., Yoo B., 2008. Starch / Starke. 60 (5), 263-269

[71]. Choi H.M., Yoo B., 2009. 'Effect of various gums on flow properties and yield stress of Korean sweet potato starch' Journal of the Korean Society of Food Science and Nutrition, 38 (9), 1253 – 1257

[72]. Chor, s. G. and Kerr, W.L., 2003.'Water mobility and textural properties of native and hydroxypropylated wheat starch gels'. Carbohydrate Polymers, 51(1) : 1 – 8

[73]. Chowdhury P., Roy K., Ali M.D.A., Kundu T., Ghosh A.K., 2007. 'Graft polymerization of methyl methacrylate onto guar gum in presence of ammonium vanadate and hydrogen peroxide'. Journal of Polymer Materials, 24 93), 263-270

[74]. Chowdhury P., Samui S., Kundu T., Nandi M.M., 2001. 'Graft polymerization of methyl methacrylate onto guar gum with ceric ammonium sulphate / dextrose redox pair'. Journal of Applied Polymer Science, 82 914), 3520-3525

[75]. Christianson D.D., Hodge J.E., Osborne D., Detroy R.W., 1981. 'Gelatinization of wheat starch as modified by xanthan gum, guar gum and cellulose gum'. Cereal Chemistry, 58, 513-517

[76]. Comumbini M.P. Ceccarini a., 2002. Journal of Chromatography A, 968, 79-88.

[77]. Cottrell I.W., Martino G.T., Fewkes K.A., 2001. 'Keratin Treating cosmetic compositions containing high D.S. cationic guar gum derivatives' W.O. patent Int Publication No. 01/97761

[78]. Cunha P.L.R., de Paula R.C.M., Feitosa J.P.A., 2007. 'Purification of guar gum for biological applications'. International Journal of Biological Macromolecules, 41, 324-331

[79]. D'Melo D.J., Shenoy M.A., 2008. 'Evaluation of mechanical properties of acrylated guar gum – unsaturated polyester composites'. Polymer Bulletin 61 (2), 235 – 246

[80]. Daas P.J.H., Grolle K., Van Vliet T., Schlos H.A., De Jongh H.H.J., 2002.'Toward the recognition of structure – function relationships in galactomannans'. Journal of Agricultural and Food Chemistry, 50 (15), 4282 - 4289

[81]. Dargaville T.R., George G.A., Hill D.J.T., Whittaker A.K., 2003. 'High energy radiation grafting of fluoropolymer'. Progress in Polymer Science, 28, 1355-1376

[82]. Das D., Ara T., Dutta S., Mukherjee A. Bioresource Technology. (2011) 102, 5878-5883

[83]. Dasgupta S.P., 1994. "Enhancement of paper dry strength by anionic and cationic polymer combination". US Patent No. 5318669

[84]. DaSilva D.A., De Paula R.C.M., Feitosa J.P.A., 2007. ' Graft copolymerization of acrylamide onto cashew gum'. European Polymer Journal, 43, 2620-2629

[85]. Dea I.C.H., Morris E.R., Rees D.A., Welsh E.J., Barnes H.A. & Price J., 1977. Journal of Molecular Biology, 68, 153-172.

[86]. Degering E.F., 1953. 'Oxidized derivatives of starch' in Starch and its Derivatives, 3rd ed., Radley, J.A., Ed., Chapman and Hall, London, Chapter 16

[87]. Deng G., Cao M., Huang J., He L., Chen Y., 2005. Polymer, 26(15), 5698

[88]. Denham W.S., Woodhaouse H.J., 1913. Chemical Society, 103, 1735-1742

[89]. Deshmukh S.R., Singh R.P., 1987. 'Drag-reduction effectiveness, shear stability and biodegradation resistance of guar gum based graft copolymers'. Journal of Applied Polymer Science, 33 (6), 1963-1975

[90]. Deshmukh S.R., Sudhakar K., Singh R.P., 1991. 'Drag-reduction efficiency, shear stability and biodegradation resistance of carboxymethyl cellulose – based and starch – based graft copolymers'. Journal of Applied Polymer Science, 43 (6), 1091-1101

[91]. Dodi G., Hritcu D., Popa M.I. (2011), 45 (3-4), 171 – 176.

[92]. Dogan M., Kayacier A., Ic E., 2007. 'Rheological characteristics of some food hydrocolloids processed with gamma irradiation'. Food Hydrocolloids, 21, 392-396

[93]. Doner L.W., 2001. 'Determining sugar composition of food gum polysaccharides by HPTLC'. Chromatographia, 53 (9-10), 579 – 581

[94]. Doyle J.P., Lyons G., Morris E.R., 2009. 'New proposals on "hyperentanglement" of galactomannans : Solution viscosity of fenugreek gum under neutral and alkaline conditions'. Food Hydrocolloids, 23, 1501-1510

[95]. Duke F.R., Froist A.A., 1949. J.Am.Chem. Soc.,71, 2790

[96]. Duxenneuner M.r., Fischer P., Windhab E.J., Cooper-White J.J., 2008. 'Extensional properties of hydroxypropyl ether guar gum solutions'. Biomacromolecules, 9(11), 2989-2996

[97]. Dworjanyn P.A., Garnett J.L. in Radiation Processing of Polymers, A Singh. J Silvermann, eds. (Munich : Hanser Publishers, 1992)

[98]. Egboh S.H., George M.H., Barrie J.A., 1984. 'The γ-radiation induced grafting of unsaturated segmented polyurethanes with N-vinyl pyrrolidone'. Polymer 25, 1157-1160

[99]. Elfak A.M., Pass G., Philips G.O., Molley R.G., 1977. Journal of Science, Food & Agriculture, 28 (10), 895

[100]. Fang C., Zhao B.Y., Chen L.S., Wu Q., Liu N., Hu K.A., 2005. 'The effect of the green additive guar gum on the properties of magnetorheological fluid'. Smart Materials and Structures, 14 (1), N1-N5

[101]. Fanta G.F., Bagley E.B., 1977. Encycl. Polym. Sci. Technol. Suppl. No. 2, 665

[102]. Fanta G.F., Bangley E.B. Encycl. Polym. Sci. Technol. Suppl. No. 2, 665 (1997)

[103]. Fanta G.F., Burr R.C., Richard C.R., Rist C.E., 1969. J. Polym. Sci Part A-1, 7(7), 1675

[104]. Fanta G.F., Burr R.C., Richard C.R.,Doane W.M., 1983. J. Polym. Sci., Poly. Chem. Ed., 21(7), 2095

[105]. Fanta G.F., Doane W.M., 1987. Modified Starches:Properties and uses (O.B. Wurzburg, Ed.), CRC Press, Boca Raton, FL, 1987, 149

[106]. Fantozzi F., Arturoni E., Barbucci R., 2010. 'The effects of the electric fields on hydrogels to achieve antitumoral drug release'. Bioelectrochemistry, 78, 191-195

[107]. Fares, M.M., El-Faqeeh, A.S. and Osman, M.E., 2003, 'Graft copolymerization onto starch – I. Synthesis and Optimization of starch grafted with N-tert-butylacrylamide copolymer and its hydrogels'. Journal of Polymer Research, 10 (2) : 119 – 125.

[108]. Fitzsimons S.M., Mulvihill D.M., Morris E.R., 2008. 'Large enhancements in thermogelation of whey protein isolate by incorporation of very low concentrations of guar gum'. Food Hydrocolloids, 22, 576-586

[109]. Frollini E., Reed W.F., Milas M., Rinaudo M., 1995. 'Polyelectrolytes from polysaccharides: selective oxidation of guar gum – a revised reaction'. Carbohydrate Polymers, 27, 129 – 135

[110]. Funami T Kataoka Y., Omoto T., Goto Y., Asai I., Nishinari K., Food Hydrocolloids 19 (2005), 25 - 36

[111]. Funami T., Kataoka Y., Noda S., Hiroe M., Ishihara S., Asai I., Takahashi R., Nishinari K., 2008. 'Functions of fenugreek gum with various molecular weights on the gelatinization and Retrogradation behaviours of corn starch – 1 : Characterizations of fenugreek gum composite system at a relatively high starch concentration; 15 w/v%'. Food Hydrocolloids, 22, 763-776

[112]. Funami T., Kataoka Y., Noda S., Hiroe M., Ishihara S., Asai I., Takahashi R., Inouchi N., Nishinari K., 2008. 'Functions of fenugreek gum with various molecular weights on the gelatinization and Retrogradation behaviours of corn starch – 2 : Characterizations of fenugreek gum composite system at a relatively high starch concentration; 15 w/v%'. Food Hydrocolloids, 22, 777-787

[113]. Funami T., Kataoka Y., Omoto T., Goto Y., Asai I., Nishinari K., Food Hydrocolloids 19 (2005), 1-13

[114]. Fuongfuchat A., Seetapan N., Makmon T., Pongjaruwat W., Methacanon P., Gamonpilas c., Journal of food engineering, 109 (2012), 571 – 578

[115]. Galmarini M.V., Baeza R., Sanchez V., Zamora M.C., Chirife J., 2011. LWT-Food Science and Technology, 44, 186 – 190

[116]. Gamze G., Sibel K., J. Appl. Polym. Sci, 106, 2422 (2007)

[117]. Garti N., Leser M., 2001. 'Emulsification properties of hydrocolloids'. Polymers for Advanced Technologies, 12, 123-135.

[118]. George M., Abraham T.E. (2007). International Journal of Pharmaceutics, 335, 123 – 129.

[119]. Geresh S., Gdalevsky G.Y., Gilboa I., Voorspoels J., Remon J.P., Kost J., 2004. 'Bioadhesive grafted starch copolymers as platforms for peroral drug delivery : A study of theophylline release'. Journal of Controlled Release, 94, 391-398

[120]. Ghosh R. N., Jana T., Ray B.C. and adhikari B., Polym. Int., 53, 339 (2004)

[121]. Gittings M.R., Cipelletti L., Trappe V., Weitz D.A., In M., Lal J., 2001. 'The effect of solvent and ions on the structure and rheological properties of guar solutions'. Journal of Physical Chemistry A, 105 (40), 9310 – 9315

[122]. Goto A. Fukuda T., 2004. Prog Polym Sci, 29, 329

[123]. Goycoolea F.M., Morris E,R., Gidley M.J., 1995. 'Viscosity of galactomannans at alkaline and neutral pH : evidence of hyperentanglement in solution'. Carbohydrate Polymers, 27 (1), 69 – 71.

[124]. Grasdalen H., Painter T., 1980. 'N.M.R. studies of composition and sequence in legume-seed galactomannans'. Carbohydrate Research, 81(1), 59-66

[125]. Grubbs R.B., Hawker C.J., Dao J., Frechet J.M., 1997. J Angew Chem Int Ed Engl, 36, 270

[126]. Gugliemelli L.A., Swanson C.L., Doane W.M., Russell, C.R., 1977. J. Polym. Sci. Polym. Lett. Ed., 15 (12), 739

[127]. Gujral H., Guardiola I., carbonell J.V., Rosell C.M., 2003. 'effect of cyclodextrin glycoxyl transferase on dough rheology and bread quality from rice flour'. Journal of Agriculture and Food Chemistry, 51, 3814-3818

[128]. Gupta B., Buchi F.N., Scherer G.G., 1994. J Polym Sci Polym Chem,32, 1931

[129]. Gupta B.S., Ako J.E., 2005. 'Application of guar gum as a flocculant aid in food processing and potable water treatment'. European Food Research and Technology, 221 (6), 746-751

[130]. Gupta S., Shah B., Sanyal B., Variyar P.S., Sharma A. 2009. Food Hydrocolloids 23, 1785 – 1791.

[131]. Hakamori J., 1964, Biochemistry (Tokyo), 55, 205-208

[132]. Halstenberg S., Panitch A., Rizzi S., Hall H., Hubbell J.A. 'Biologically engineered protein-graft-poly(ethyleneglycol) hydrogels: a cell adhesive and plasmin-degradable biosynthetic material for tissue repair'. Biomacromolecules, 3, 710-723.

[133]. Hawker C.J., Bosman A.W., Harth E., 2001. Chem. Rev., 101, 3661

[134]. Hawker C.J., Mercerreyes D., Elce E., Dao J., Hedrick J.L., Barakat I., Dubious P., Jerome R., Volksen W., 1997. Macromol. Chem and phys., 198 (1), 155

[135]. Haworth W.N., 1915. Chemical Society, 1915, 107, 8-12

[136]. He D., Ulbricht M., 2006. J Mater Chem, 16, 1860

[137]. He L.S., Jiang B., Wang K., 2008. 'Determination of the degree of the substitution of hydroxyethyl guar gum'. Carbohydrate Polymers, 72, 557-560

[138]. Hebeish a., Aly A.A, El-Shefei A.M., Zaghloul S., Starch, 60, 97 (2008)

[139]. Hebeish A., Bayazeed A., El-Alfy E., Khalil M.I., 1988. Starch/Staerke, 40(6), 223

[140]. Hebeish A., Beliakova m.K., Bayazeed A., J. Appl. Polym. Sci., 68, 1709 (1998)

[141]. Hebish A., Abd El Thalouth I., EI-Kashouti M.A., Abdel –Fattah S.H., 2003. 'Graft copolymerization of acrylonitrile onto starch using potassium permanganate as initiator.' Angwandte Macromolekulare Chemie, 78, 101 – 108

[142]. Hegazy E.A., Ishigaki I., Desouki A.M., Rabie A., Okamoto J., 1982. J Appl Polym Sci, 27, 535

[143]. Heinze, T., 2005.'Carboxymethyl ethers of cellulose and starch – a review'. Chemistry of plant raw materials., 3 : 13 – 29

[144]. Ho F.F.L., Kohler R.R. & Ward, G.A., 1972. 'Determination of molar substitution and degree of substitution of hydroxypropyl cellulose by nuclear magnetic resonance spectrometry'. Analytical Chemistry, 44(1), 178-181.

[145]. Hong C.H., Zhang K., Choi H.J., Yoon S.M., 2010. 'Mechanical degradation of polysaccharide guar gum under turbulent flow' Journal of Industrial and engineering Chemistry, 16, 178-180

[146]. Hong C.H., Zhang K., Choi H.J., Yoon S.M., 2010. 'Mechanical degradation of polysaccharide guar gum under turbulent flow'. Journal of Industrial and Engineering Chemistry, 16, 178-180

[147]. Hong S.C., Jia S., Teodorescu M., Kowalewski T., Matyjaszewski K., Gottfried A.C., Brookhart M., 2002. Journal of Polymer Science Part A: Polym Chem, 40, 2736

[148]. Hong S.C., Pakula T., Matyjaszewski K., 2001. Macromol. Chem. And Phys., 202, 3392

[149]. Hoover, R. and Vasanthan, T. 1994. The effect of annealing on the physicochemical properties of wheat, oat, potato and lentil starches. J. Food Biochem, 17 : 303 – 311.

[150]. Hough L., Theobald R.S., 1963. Methods Carbohydrates Chemistry, 2, 162-166

[151]. Huang C.C., 2009. 'Physicochemical, psting and thermal properties of tuber starches as modified by guar gum and locust bean gum'. International Journal of Food Science and Technology, 44, 50-57

[152]. Huang H., Yang X., 2004. 'Synthesis of chitosan – stabilized gold nanoparticles in the absence or presence of tripolyphosphate'. Biomacromolecules, 5, 2340 – 2346

[153]. Huang J.X., Yuan X.Y., Yu X.L., Zhang H.T., 2003. Polym Int, 52(5), 819

[154]. Huang W., Baker G.L., Bruening M.L., 2001. Angew Chem Int Ed, 40, 1510

[155]. Irwan G.S., Kuroda S.I., Kubota H., Kondo T., 2002. J Appl Polym Sci, 83(11), 2454

[156]. Ishigaki I., Sugo T., Takayama T., Okamoto J., 1982. J Appl Polym Sci, 27, 1043

[157]. Izaguirre A., Lanas J., Alvarez J.I., 2010. 40, 1081-1095.

[158]. Jain r., Anjaiah V., Babbar S.B., 2005. 'Guar gum : A cheap substitute for agar in microbial culture media'. Letters in applied Microbiology, 41 94), 345-349

[159]. Janata M., Masar B., Toman L. Vleck P., Policka P., Brus J., Holler P., 2001. React & Funct Polym, 50, 67

[160]. Jarwrenko, W., (1986). 'Pregelatinised starches'. In O.B. Wurzburg (Ed.), Modified starches : Properties and uses, Boca Raton, FL:CRC Press : 71

[161]. Jayakumar R., Prabaharan M., Reis R.L., Mano J.F., 2005. Carbohydrate Polymers, 62, 142

[162]. Jenkins D.J.A., Leeds A.r., Slavin B., 1979. 'Dietary fiber and blood lipids : Reduction of serum cholesterol in type II hyperlipidemia by guar gum'. American Journal of Clinical Nutrtion, 32 (1), 16-18

[163]. JenkinsD.W., Hudson S.M. 2001. 'Review of vinyl graft copolymerization featuring recent advances toward controlled radical – based reactions and illustrated with chitin/chitosan trunk polymers. Chemical Reviews, 101, 3245

[164]. Jia X., Burdick J.A., Kobler J., Cliffton R.J., Rosowski J.J., Zeitels S.M., et al., 2004. 'Synthesis and characterization of in situ crosslinkable hyluronic acid-based hydrogels with potential application for vocal fold regeneration'. Macromolecules, 7, 3239-3248

[165]. Jia Z. and Du S.Y., Fibers, Polym., 7, 235 (2006)

[166]. Jiang J.X., Zhu L.W., An X.N., Zhang W.M., 2006. 'NMR studies on chemical structures of polysaccharides of the main plant – gum resources in China'. Chemistry and Industry of Forest Products, 26 (1), 41-44

[167]. Jin R., Hiemastra C., Zhong Z., Feijen J., 2007. 'Enzyme mediated fast in situ formation of hydrogels from dextran-tyramine conjugates'. Biomaterials, 28, 2791-2800

[168]. Joshi J.M., Sinha V.K., 2007. 'Cerric ammonium nitrate induced grafting of polyacrylamide onto carboxymethyl chitosan'. Carbohydrate Polymers, 67, 427-435

[169]. Jumel K., Harding S.E., Mitchell J.R., 1996. 'Effect of gamma irradiation on macromolecular integrity of guar gum'. Carbohydrate Research, 282, 223-236

[170]. Jyothi A.N., M.S.S., Moorthy S.N., Sreekumar J. and Rajasekharan K.N., 2008. 'Microwave – assisted synthesis of cassava starch phosphates and their characterization'. Journal of root Crops, 34 (1) : 34 – 42

[171]. Kabanov V.Y., Kudryavtsev V.N., 2003. 'A review modification of polymers by radiation graft polymerization'. High Energy Chemistry, 37, 1-5

[172]. Kabir I.G., YagenB., Penhase A., Rubenstein A. (1998) Pharmaceutical Research, 15 (7), 1019 – 1025

[173]. Kabir I.G., YagenB., Penhase A., Rubenstein A. (2000). 'Phosphated crosslinked guar for colon specific drug delivery I. Preparation and physicochemical characterization' Journal of Controlled release 63, 121 – 127

[174]. Kaith B.S., Singha A.S. ., Kalia S., 2007. 'Grafting MMA onto flax under the influence of microwave radiation and the use of flax – g – poly(MMA) in preparing PF composites.' Autex Research Journal, 7, 119 – 129

[175]. Kalai S., Kaith b.s., Charma S., Bhardwaj B., Fibers Polym., 9, 416 (2008)

[176]. Kamigaito M., Ando T., sawamoto M., 2001.'Metal catalyzed living radical polymerization'. Chemical Reviews, 101, 3689

[177]. Kampouris E.M., Andreopolous A.G., 1987. J Appl Polym Sci, 34, 1209

[178]. Kang H.M., Cai Y.L., Liu P.S., 2006. 'Synthesis, characterization and thermal sensitivity of chitosan based graft copolymers'. Carbohydrate Research, 11, 2851-2855

[179]. Kaur A., Singh N., 2007. "Effect of guar gum coating on moisture content, oil uptake and textural properties of fried (French fries) potato from different cultivars'. Journal of Food Science and Technology, 44 91), 115 – 117

[180]. Kautharapu K., Pujari N.S., Golegaonkar S.B., Ponrathnam s., Nene S.N., Bhatnagar D., 2009. 'Vinyl-2-pyrrolidone derivatized guar gum based aqueous two-phase system'. Separation and Purification Technology, 65, 9-13

[181]. Kesavan S., Prudhomme R.K.,1992. 'Rheology of guar & HPG cross-linked by borate'. Macromolecules, 25 (7), 2026-2032

[182]. Khalil M.I., Mostafa K.M., Hebeish A., 1990.Starch/Staerke, 42, 107

[183]. Khouryieh H.A., Herald T.J., Aramouni F., Bean S., Alavi S., 2007. 'Influence of deacetylation on the rheological properties of xanthan – guar interactions in dilute aqueous solutions'. Journal of Food Science, 72(3), C173-c181

[184]. Khullar P. Khar R.K., Agarwal S.P., 1998. 'Evaluation of guar gum in the preparation of sustained release matrix tablets'. Drug development and Industrial Pharmacy, 24 (11), 1095-1099

[185]. Kim C., Lee S.P., Yoo B., 2006. 'Dynamic rheology of rice starch – galactomannan mixtures in ageing process'. Starch / Starke, 58 (1), 35 - 43

[186]. Kim C., Yoo B., 2006. 'Rheological properties of rice starch-xanthan gum mixtures'. Journal of Food Engineering, 75, 120-128

[187]. Kim D., Quinlan M., Yen T.F., 2009. 'Encapsulation of lead from hazardous CRT glass wastes using biopolymer cross-linked concrete systems'. Waste Management, 29, 321-328

[188]. Kim W.W., Yoo B., 2011. LWT – Food Science and Technology, 44, 759 – 764

[189]. Kim Y._k., Robyt, J.F., 1999. 'Enzyme modification of starch granules:in situ reaction of glucoamylase to give complete retention of glucose – inside the granule'. Carbohydrate Research, 318(1-4), 129-134

[190]. Kim Y.K., Robyt J.F., 1999. 'Enzyme modification of starch granules:in situ reaction of glucomylase to give complete retention of glucose inside the granule'. Carbohydrate Research, 318 (1-4), 129-134

[191]. Kim, H.R., Muhrbeck, P. and Eliasson, A. – c., 1993. 'Changes in rheological properties of hydroxypropyl potato starch pastes during freeze – thaw treatments. III. Effects of cooking conditions and concentration of the starch paste'. Journal of the Science of Food and Agriculture, 61 (1) : 109 – 116.

[192]. Kok M.S., 2010. Carbohydrate Polymers 81, 567 – 571

[193]. Kok M.S., Hill S.E., Mitchel J.R., 1999. 'Viscosity of galactomannans during high temperature processing : influence of degradation and solubilisation'. Food Hydrocolloids, 13 (6), 535 – 542

[194]. Koninck P.D., D.A., Hamel f., Sachan F. & Mateescu M.A., 2010.'Carboxymethyl – starch excipients for gastrointestinal stable oral

[195]. Koop H.S., Praes C.E.O., Reicher F., Petkowicz C.L.O., Silveria J.L.M., 2009. 'Rheological behavior of gel of xanthan with seed galactomannan : Effect of hydroalcoholic – ascorbic acid'. Materials Science and Engineering C, 29, 559-563

[196]. Kubota H., Fukushima Y., Kuwabara S., 1997. Eur Polym J, 33 (1), 67

[197]. Kuchma O.V., Yu L., Zub A., Dabrowski, 2006, Colloid Journal, 68, 721-728

[198]. Kukuri M.D., Lee J.R., Han J.H., Lee I., 2006. Smart Material Structure, 15, 417

[199]. Kumar D., Singh N.B., 2002. 'Guar – an introduction'. In Kumar D. & Singh N.B. (Eds.) Guar in India, Jodhpur: Scientific Publishers (India)

[200]. Kumar G., Smith P.J. Payne G.F., 1999. Biotech Bioeng, 63(2), 154

[201]. Kumar R, Srivastava A. & Behari K., 2007. 'Graft copolymerization of methacrylic acid onto xanthan gum by Fe^{2+} / H$_2$O$_2$ redox initiator'. Journal of Applied Polymer Science, 105, 1922.

[202]. Kumar R., Srivasatava A., Behari K., 2008. 'One-pot synthesis of a polysaccharide based graft copolymer with an efficient redox pair (Fe^{2+}/BrO$_3^{-}$). Journal of Applied Polymer Science, 107, 2883

[203]. Kumar R., Srivastava A. Behari K., 2009.'Synthesis and Characterrisation of Polysaccharide based graphcopolymer by using potassium peroxi mono sulpahte/ascorbic acid as an efficient redox intiator in inert atmosphere.' Journal of Applied Polymer Science,112,1407

[204]. Kumar S.R., Piyush T., Suman R., Akanksha T. Chemical & Pharmaceutical Bulletin. 59 (2), 185 – 190, 2011

[205]. Lai V., Lii C., Hung W., Lu T., 2000. 'Kinetic compensation effect in depolymerisation of food polysaccharides'. Food Chemistry, 68, 319-325

[206]. Lang Y.Y., Li S.M., Pan W.S., Zheng L.Y., Journal of Drug Delivery Science and Technology, 16 (1), 2006, 65 – 69

[207]. Lapasin R., Lorenzi L.D., Pricl S., Torriano G., 1995. 'Flow properties of hydroxypropyl guar gum and its long chain hydrophobic derivatives'. Carbohydrate P{olymers,28, 195-202.

[208]. Lavazza M. at al., Journal of Biotechnology 156 (2011) 108 – 116

[209]. Lawal O.S., Lechner M.D., Hartmann B., Kulicke w.M., 2007. 'Carboxymethyl cocoyam starch : synthesis, characterization and influence of reaction parameters'. Starch/Starke, 59, 224-233.

[210]. Lemieux M., Gosselin P., Mateescu M.A., 2009. 'carboxymethyl high amylase starch as excipient for controlled drug   release ; mechanistic study and the influence of degree of substitution. International Journal of Pharmaceutics, 382 (1-2), 172-182

[211]. Levesque S.G., Lim R.M., Shoichet M.S., 2005. 'Microporous interconnected dextran scaffolds of controlled porosity for tissue – engineering applications'. Biomaterials, 26, 7436-7446

[212]. Levesque S.G., Schoichet M.S., 2006. 'Synthesis of self adhesive dextran hydrogels and macroporous scaffolds'. Biomaterials, 27, 5277-5285

[213]. Levy N., Garti N., Magdassi S., 1995. 'Flocculation of bentonite suspensions with cationic guar'. Colloids and Surfaces A : Physicochemical and Engineering Aspects, 97 (2), 91-99.

[214]. Li M., Zhu Z., Jin E. Fibers and Polymers 2010, Vol. 11, No. 5, 683 – 688

[215]. Li M., Zhu Z., Jin E., 2010. 'Graft copolymerization of granular allyl starch with carboxyl-containing vinyl monomers for enhancing grafting efficiency'. Fibers and Polymers, 22(5), 683-688

[216]. Li X. – Y., Wu W.H., 2007.'Research progress in guar gum and its derivatives for controlled drug delivery system'. Xiandai Huagong / Modern Chemical Industry, 27 (1), 23-28

[217]. Li X., Wu W., Liu W., 2008. 'Synthesis and properties of thermo-responsive guar gum/poly(N-isopropylacrylamide) interpenetrating polymer network hydrogels'. Carbohydrate Polymers, 771, 394 – 402

[218]. Li X.Y., Wu W.H., Wang J.Q., Wang Z., Niu C.M., 2006. 'Swelling dynamics of pH-sensitive GG/PAA semi-IPN hydrogels'. Polymeric Materials Science and Engineering, 22 92), 177-180

[219]. Lichter J.A., Vlite K.V. J., Rubner M.F., 2009. 'Design of antibacterial surfaces and interface. Polyelectrolyte multilayers as a multifunctional platform'. Biomacromolecules, 42, 8573-8586

[220]. Lim S.T., Choi H.J., Lee S.Y., So J.S., Chan C.K., 2003. Macromolecules, 36, 5348

[221]. Liu H., Eskin N.A.M., Cui S.W., 2003. 'Interaction of wheat and rice starches with yellow mustard mucilage'. Food Hydrocolloids, 17, 863-869

[222]. Liu J., Ming J., Li W., Zhao G., 2012. 'Synthesis, characterization and in vitro digestibility of carboxymethyl potato starch rapidly prepared with microwave-assistance'. Food Chemistry, 133, 1196-1205.

[223]. Liu Q., Zhu Z., Yang X., Chen x, Song Y., 2007. Rad Phys Chem, 76(4), 707

[224]. Liu, H., Ramsden, L. and Corke, H., (1999). 'Physical properties and enzymatic digestibility of hydroxypropylated ae, wx and normal maize starch'. Carbohydrate Polymers, 40 (3) : 175 – 182

[225]. Lokhande H.T., Vardarajan P.V., Nachane N.D., 1993. 'Gamma-radiation induced grafting of acrylonitrile onto guar gum : Influence of reaction conditions on the properties of the grafted and saponified products'. Journal of applied Polymer Science, 48 (3), 495-503

[226]. Lu S. J., Lin S.B., Yao K.D., starch, 56, 138 (2004)

[227]. Ly E.B., Bras J., Sadocco P., Belgacem M.N., Dufresne A.N., Thielemans W., 2010. 'Surface functionalization of cellulose by grafting oligoether chains'. Materials Chemistry & Physics, 120, 438-445

[228]. Ma X., Pawlik M., 2007. 'Intrinsic viscosities and Huggins constants of guar gum in alkali metal chloride solutions'. Carbohydrate Polymers, 70, 15 – 24

[229]. Manzi A.E., Cerezo A.S., 1986. Carbohydrate Polymers, 6, 349-350

[230]. Marco C., Rosell C.M., 2008. 'Breadmaking performance of protein enriched, gluten-free breads'. European Food Research Technology, 227, 1205-1213

[231]. Masato T., Li Q., Mika K., Tatsuko H., Hyoe H., 2006. 'Viscoelasticity and thermal properties of xanthan gum / galactomannan / water systems'. Polymer Preprints, Japan, 55 (1), 1067

[232]. Mason W.R., 2009. 'Starch use in foods'. In J BeMiller & R.Whistler (Eds.), Starch: Chemistry and technology (3rd ed., pp. 745-795)

[233]. Massicott L.P. Baille W.E., Mateescu M.A., 2008. 'carboxylated high amylase starch as pharmaceutical excipient:structural insights and formulation of pancreatic enzymes'. International Journal of Pharmaceutics, 356 (1-2), 212-223

[234]. Masud H.S.K., Das M., 2001. 'Studies on synthesis and application of guar gum – graft polyacrylamide copolymer for the treatment of pulp and paper mill effluent'. Indian Journal of Environmental Protection, 2001, 21 (7), 611-617

[235]. Masuhiro T., Shafiul I., Takayuki A., Alessandra B., Giuliano F., 2005. 'Microwave irradiation technique to enhance protein fiber propertioes'. Autex Research Journal, 5, 40 – 48

[236]. Matyjaszewski K.,Beers K.L., Kern A., Gaynor S.G., 1998. Journal of Polym Sci Part A:Polym Chem, 36, 823

[237]. Matyjaszewski K.Xia J., 2001 'atom transfer radical polymerization,' chemical reviews, 101,2921

[238]. McCleary B.V., Clark a.H., Dea I.C.M., Rees D.A., 1981. 'The fine structure of carob and guar galactomannans'. Carbohydrate research, 92, 269-285

[239]. Mehrotra R., Ranby B., 1977. . J Polym Sci, 21(6), 1647

[240]. Meshram M.W., Patil V.V., Mahaskae S.T., Thorat B.N., 2009. 'Graft copolymers of starch and its application in textiles'. Carbohydrate Polymers, 75, 71-78

[241]. Mino G., Kaizerman S., 1958. J.Polym. Sci. 31(122), 212

[242]. Mishra D.K., Tripathy J., Behari K., 2008. 'Synthesis of graft copolymer (κ-carrageenan-g-N,N-dimethylacrylamide) and studies of metal ion uptake, swelling capacity and flocculation properties'. Carbohydrate Polymers, 71, 524-534

[243]. Mishra D.K., Tripathy J., Shrivastava A., Mishra M.M., Behari K., 2008. 'Graft copolymer (chitosan-g-N-vinylformamide):Synthesis and study of its properties like swelling, metal ion uptake and flocculation'. Carbohydrate Polymers, 74, 632-639

[244]. Mishra M.M., Yadav M., Mishra D.K., Behari Kunj, 2011. 'Synthesis of graft copolymer (CmgOH-g-NVP) and study of physicochemical properties : Characterization and application'. Carbohydrate Polymers, 83, 1749-1756.

[245]. Mishra S., Sen G., 2011. 'Microwave initiated synthesis of polymethylmethacrylate grafted guar (GG-g-PMMA), characterization and applications. International Journal of Biological Macromolecules, 48, 688-694

[246]. Mishra V. et al., 2011. Carbohydrate Polymers 86, 29-303

[247]. Misra B.N., 1985. J Polym Sci Polym Chem, 23, 307

[248]. Misra B.N., Mehta I.K., Khetrpal R.C., 1984. Journal of Polymer Science and Polymer Chemistry, 22, 2767

[249]. Miwa Y., Yamamoto K., Skaguchi M., Shimada S., 2001. Macromolecules, 34, 2089

[250]. Miyazaea T., Funazukuri T., 2005. 'Polysaccharide hydrolysis accelerated by adding carbon dioxide under hydrothermal conditions'. Biotechnology Progress, 21 (6), 1782-1785

[251]. Moller S., Weisser J., Bischoff S., Schnabeirauch M., 2007 'Dextran and hyluronan methacrylate based hydrogels as matrices for soft tissue reconstruction'. Biomolecular Engineering, 24, 496-504

[252]. Momose T., Kitazame T., Ishigaki I., Okamoto J., 1990. J Appl Polym Sci, 39 (6), 1221

[253]. Morris g.A., Patel T.R., Picout D.R., Ross-Murphy S.B., Ortega A., de la Torre J.G., Harding S.E., 2008. 'Global hydrodynamic analysis of the molecular flexibility of galactomannans'. Carbohydrate Polymers, 72, 356-360

[254]. Mostafa K.M., El-Sanabary A.a., Polym. Degrad. Stab., 55, 181 (1997)

[255]. Mundargi R.C., Agnihotri S.A., Patil S.A., Aminbhavi T.M., 2006. 'Graft copolymerizationof methacrylic acid onto guar gum using potassium persulphate as an initiator'. Journal of Applied Polymer Science, 101 91), 618-623

[256]. Nagamori M., Funazukuri T., 2004. 'Glucose production by hydrolysis of starch under hydrothermal conditions'. Journal of Chemical Technology and Biotechnology, 79 (3), 229-233

[257]. Naghash H.J., Massah A., Erfan A., 2002. Eur Polym J., 38, 147

[258]. Nanthakumar B., Grimm D., Pawlik M., 2009. 'Anionic flotation of high-iron phosphate ores – Control of process water chemistry and depression of iron minerals by starch and guar gum'. International Journal of Mineral Processing, 92, 49-57

[259]. Nayak B.R., singh r.P., 2001. 'Development of graft copolymer flocculating agents based on hydroxypropyl guar gum and acrylamide'. Journal of Applied Polymer Science, 81 (7), 1776 – 1785

[260]. Nayak B.R., Singh R.P., 2001. 'Synthesis and characterization of grafted hydroxypropyl guar gum by ceric ion induced initiation'. European Polymer Journal, 37 (8), 1655-1666

[261]. Nayak B.R., Singh R.P.,2001. 'Development of graft copolymer flocculating agents based on hydroxypropyl guargum and acrylamide'. Journal of Applied Polymer Science, 81 (7), 1776 – 1785

[262]. Neukom H., 1993. 'Galactomannans : properties and applications'. Lebenson. Wiss. Technol. 22, 41-45

[263]. Newton J.M., Peckham G.T., 1950. 'Oxidation of starch'. In Chemistry and Industry of Starch, 2nd ed., Kerr R.W., Ed., Academic Press, New York, Chapter 11

[264]. Ng D., Coventry K., Lim Pearl, Wiltshire J., Qiao G.G., Buolton A., Senior G., 2009. 'An improved technique for concentration measurement of galactomannan solutions by differential refractive index'. Carbohydrate Polymers, 77, 150-153

[265]. Nguyen C.C., Martin V.J., Parley E.P., US Patent 5003022 (1991)

[266]. Nho Y.C., Garnett J.L., Dworjanyn P.A., Jin J.H., 1992. J Korean Ind Eng Chem, 3(3), 491

[267]. Norman B.E., 1981. 'New developments in starch syrup technology'. W:Enzymes and Food Processing, G.G. Birch, N. Blakeborough, K.J. Parker eds., Applied Science Publishers, London, 15-50

[268]. Nutan, M.T.h., Soliman, M.S., Taha, E.I. and Khan, M.A., (2005). 'Optimization and characterization of controlled release multi – particulate beads coated with starch acetate'. International Journal of Pharmaceutics, 229 (1-2) : 155 – 162

[269]. Ochubiojo E.M., Rodrigues A. Starch: From Food to Medicine. Scientific, Health and Social Aspects of the Food Industry, 355-380

[270]. Onfre F.O., wang Y.J., 2010. 'Hydroxypropylated starches of varying amylase contents as sustained release matrices in tablets'. International Journal of Pharmaceutics, 385(1-2), 104-112

[271]. Orozco R.L., Redwood M.D., Leeke G.A., Bahari A., Santos R.C.D., MacAskie L.E., 2012. 'Hydrothermal hydrolysis of starch with CO_2 and detoxification of the hydrolysates with activated carbon for bio-hydrogen fermentation'. International Journal of Hydrogen Energy, 37 (8), 6545-6553

[272]. Ostergard K., Bjorck I., Gunnarsson A., 1988. 'A study of native and chemically modified potato starch PartI:Analysis and enzymic availability in vitro. Starch/Starke, 40, 58-66.

[273]. Painter T.J., Gonzalez J.J., Hemmer P.C., 1979. 'The distribution of d-galactosyl groups in guaran and locust bean gum: new evidence from periodate oxidation'. Carbohydrate Research, 6991), 217-226

[274]. Pal S., 2007. 'Synthesis and characterization of cationic guar gum: A high performance flocculating agent.' Journal of applied Polymer Science, 105 (6), 3240 – 3245

[275]. Pal S., 2009. 'carboxymethyl guar : Its synthesis and macromolecular characterization'. Journal of Applied Polymer Science, 111 (5), 2630-2636

[276]. Pal s., Mal D., Singh R.P., 2005. 'Cationic starch : An effective flocculating agent'. Carbohydrate Polymers, 59 (4), 417-423

[277]. Pal S., Sen G., Karmakar N.C., Mal D., Singh R.P., 2008. 'High performance flocculating agents based on cationic polysaccharides in relation to coal fine suspension'. Carbohydrate Polymers, 74, 590-596

[278]. Pandey P.K., Srivastava A., Behari K., 2006. 'Graft Co-polymerization of 2-acrylamido-2-methyl-1-propane sulphonic acid onto guar gum by the bromated / mandelic acid redox pair'. Designed Monomers and Polymers, 9 (3), 247-260

[279]. Park S., Chung M.G., Yoo B., 2004. 'Effect of octenyl suucinylation on rheological properties of corn starch' Starch / Starke, 56 (9), 399 – 406

[280]. Pasha M., Swamy N.G.N., 2008. 'Derivatisation of guar to sodium carboxymethyl hydroxypropyl derivative; characterization & evaluation'. Pakistan Journal of Pharmaceutical Sciences, 21 (1), 40-44

[281]. Patel S.P., Patel R.G., Patel V.S. (1988). Thermochemica Acta, 127, 141

[282]. Pavan F.A., Dias S.L.P., Lima E.C., Benvenutti E.V., 2008, Dyes Pigments, 76, 64-69

[283]. Pawlik M., Laskowski J.S., 'Stabilization of mineral suspensions by guar gum in potash ore floatation systems'. Canadian Journal of Chemical Engineering, 84 (5), 532-538

[284]. Pearse M.J., 2005. Minerals Engineering, 18, 139 – 149

[285]. Peng T., Cheng Y.L., 2001. Polymer 42, 6811

[286]. Percec V., Barbolu B., Bera T.K., Van der Sluis M., Grubbs R.B., Frecht J.M.J., 2000. J Polym Sci Polym Chem, 38, 4776

[287]. Perera, c., Hoover, R. and Martin, A. M., 'The effect of hydroxypropylation on the structure and physicochemical properties of native, defatted and heat – moisture treated potato starches'. Food Research International, 30 (3-4) : 235 – 247.

[288]. Pinheiro A.C., Buorbon A.I., Rocha C., Riberio C., Maia J.M., Gonclaves M.P., Teixeira J.A., Vicente A.A., 2011. Carbohydrate Polymers 83, 392 – 399

[289]. Pitchon, E, O.R.J.D. & Joseph T. h (1981), 'Process for cooking or gelatinizing materials'. US Patent 4280851

[290]. Pongsawatmanit R., Temsiripong T., Ikeda S., Nishinari K., 2006. 'Influence of tamarind seed xyloglucan on rheological properties and thermal stability of tapioca starch'. Journal of Food Engineering, 77, 41-50

[291]. Ptaszek P., Grzeslik M., 2007. 'Viscoelastic properties of maize starch and guar gum gels'. Journal of Food Engineering, 82, 227-237

[292]. Qiu H.Y., He L.M., 1999. 'Synthesis and properties study ofcarboxymethyl cassava starch'. Polymers for Advanced Technologies, 10, 468-472

[293]. Qu F., Zhang L., Chen R., 2006. 'Study on modified guar gum microsphere as a protein drug carrier'. Journal of biomedical engineering, 23 (6), 1267-1270

[294]. Rao M.S., Kanatt S.R., Chawla S.P., Sharma A. 2010. Carbohydrate Polymers 82, 1243-1247.

[295]. Reddy K.M., Babu V.R., Sairam M., Subha M.C.S., Mallikarjuna N.N., Kulkarni P.V., Aminabhavi T.M., 2006. 'Development of chitosan-guar gum semi-interpenetrating polymer network microspheres for controlled release of cefadroxil'. Designed Monomers and Polymers, 9 (5), 491-501

[296]. Reddy T., Tammishetti s., 2002. 'Gastric resistant microbeads of metal ion cross-linked carboxymethyl guar gum for oral drug delivery'. Journal of Microencapsulation, 19 (3), 311-318

[297]. Reddy T.T., Tammishetti S., 2004. 'Free radical degradation of guar gum'. Polymer Degradation and Stability, 87, 403-410

[298]. Reid g.J.S., in : P.M. Dey, R.A. Dixon (eds.0, Biochemistry of Storage carbohydrates, Acaedemic Press, London, 1985, 265-286

[299]. Richardson S., Nilsson G.S., Bergquist K.E., Gorton L., Mischnick P., 2000. 'Characterisation of the substituent distribution in hydroxypropylated potato amylopectin starch'. Carbohydrate Research, 26, 125-132.

[300]. Rimac-Brncic S., Lelas V., Rade D., Simundic B., 2004.'Decreasing of oil absorption in potato strips during deep fat frying' Journal of Food Engineering 64, 237-241

[301]. Risica D., Dentini M., Crescenzi V., 2005. Polymer (46), 12247 – 12255.

[302]. Rizvi S.S.H., 1986. 'Thermodynamic properties of foods in dehydration'. In M.A. Rao & S.S.H. Rizvi (Eds.), Engineering properties of foods (pp. 133-214)

[303]. Robinson G., Ross-Murphy S.B., Morris E.R., 1982. 'Viscosity-molecular weight relationships, intrinsic chain flexibility and dynamic solution properties of guar galactomannan'. Carbohydrate Polymers, 107 (1), 17-32

[304]. Rohr T., Ogletree D.F., Svec F., Frecht M.J., 2003. Adv Func Mat, 13 (4), 264

[305]. Rojas J.A., Rosell C.M., Benedito C., 1999. 'Pasting properties of different wheat flour-hydrocolloid systems'. Food Hydrocolloids, 13, 27-33

[306]. Rosell C.M., Gomez M., 2006. Rice. In Y.H. Hui (Ed.), Bakery products : Science and Technology, 123-133. Ames,Iowa, USA:Blackwell Publishing

[307]. Rubinstein A., Gliko-Kabir I., 1995. 'Synthesis and swelling dependent enzymatic degradation of borax modified guar gum for colonic delivery purposes'. S.T.P. Pharm. Sci., 5, 41-46.

[308]. Rui-He Y., Wang X., Wang Y., Yang J., Ding S., 2006. 'A study on grafting poly(1,4- dioxan –2-one) onto starch via 2,4-tolylene diisocyanate'. Carbohydrate Polymers, 65, 28-34

[309]. Rutenberg, M.W.a.D.S., Whistler, R.L., J.N. Be Miller and E.F. Paschall(eds.), 1984.'Starch Derivatives : Production and uses in starch : Chemistry and Technology'. 'Acaedemic Press, New York, 312 – 388

[310]. Saboktakin M.R., Tabatabaie R.M., Maharramov A., Ramazanov M.A., 2010. 'Synthesis and in vitro evaluation of carboxymethyl starch – chitosan nanoparticles as drug delivery system to the colon'. International Journal of Biological Macromolecules, 48 (3), 381-385

[311]. Sajilata, M.G., Singhal, R.S. and Kulkarni, P.R. (2006).Resistant Starch – A Review. Comprehensive Reviews in Food Science and Food Safety, 5 (1) : 1- 17

[312]. Samutsri W., Suphantharika M., Carbohydrate Polymers, 87 (2012) 1559-1568

[313]. Sand A., Yadav M., Mishra M.M., Tripathyl J., Behari K., 2011. Carbohydrate Polymers 83, 14 – 21.

[314]. Sanda F., Takata T., Endo T.T., 1994. J Polym Sci Part A:Ploym Chem, 32(13), 2517

[315]. Sandolo C., Matricardi P., Alhaique F., Coviello T., 2009. 'Effect of temperature and cross-linking density on rheology of chemical cross-linked guar gum at the gel point'. Food Hydrocolloids, 23, 210-220

[316]. Sapaio S., Taddei P., Monti P., Buchert J., Freddi G., 2005. J. Biotech, 116, 21

[317]. Sarkar S. etal., Carbohydrate Polymers (2011), 86, 1723 – 1731

[318]. Schellekens M>A.J., Klumperman B.J.M.S., 2000. Rev Macromol Chem Phys, C40 (2-3), 167

[319]. Seaman J.K., 1980. Handbook of water-soluble gums and resins. In R.L. Davidson (Ed.). New York:McGrawHill.

[320]. Sen G. Singh R.P., Pal S., 2010. Journal of Applied Polymer Science, 115, 63-71

[321]. Sen G., Kumar R., Ghosh S., Pal S., 2009. Carbohydrate Polymers, 77, 822-831

[322]. Sen G., Mishra S., Jha U., Pal S., 2010. 'Microwave initiated synthesis of polyacrylamide grafted guar gum (GG-g-PM)-characterizations and applications as matrix for controlled release of 5-amino salicyclic acid'. International Journal of Biological Macromolecules, 47, 164-170

[323]. Sen G., Mishra S., Jha U., Pal S., 2010. International Journal of Biological Macromolecules, 47, 164-170

[324]. Sen G., Mishra S., Jha U., Pal S., 2011. InternationalJournal of Biological Macromolecules, 48, 106-111

[325]. Sen G., Pal S., 2009, International Journal of Biological Macromolecules, 45, 48 – 55

[326]. Sen M., Yolacan B., Guven O., 2007. 'Radiation induced degradation of galactomannan polysaccharides'. Nuclear Instruments and Methods in Physics Research B, 265, 429-433

[327]. Senapati M.K., Srinatha A., Pandit J.K., 2006. 'In vitro release characteristics of matrix tablets : Study of Karaya gum and Guar gum as release modulators'. Indian Journal of Pharmaceutical Sciences, 68 (6(), 824-826

[328]. Seok Kim H., Be Miller J.N., Carbohydrate Polymers, 88 (2012), 1164 – 1171

[329]. Shah S.N., Zhou Y., 2006. 'Maximum drag reduction asymptote of polymeric fluid flow in coiled tubing'. Conference paper. American Society of Mechanical Engineers International Mechanical Engineering Congress and Exposition, IMECE 2006, Chicago, IL 5

[330]. Sharma R.K., Lalita, 2011. 'Synthesis and characterization of graft copolymers of N-vinyl-2-pyrrolidone onto guar gum for sorption of Fe^{2+} and Cr^{6+} ions'. Carbohydrate Polymers, 83, 1929-1936

[331]. Shenoy M.A., D'Melo D.J., 2008. 'Effect of modified galactomannan on acrylic film properties'. Pigment and Resin Technology, 37 (5), 284 – 290.

[332]. Shinoda H., Matyjaszewski K., 2001. Macromolecules, 34, 6243

[333]. Shobha M.S., Tharanathan R.N., 2009. 'Rheological behavior of pullulanase treated guar galactomannan on co-gelation with xanthan'. Food Hydrocolloids, 23, 749-754

[334]. Shorgen, R.L. (2000). 'Modification of maize starch by thermal processing in glacial acetic acid'. Carbohydrate Polymers, 43 (4) : 309 – 315

[335]. Shorgen, R.L. (2008). 'Scandiumtriflate catalysed acetylation of starch at low to moderate temperatures'. Carbohydrate Polymers, 72 (3) : 439 – 443

[336]. Shorgen, R.L., (2003). 'Rapid preparation of starch esters by high temperature pressure reaction'. Carbohydrate Polymers, 52 (3) : 319 – 326

[337]. Simons L.A., Gayast S., Balasubramanian S., Ruys J., 1982. 'Long – term treatment of hypercholestrolaemia with a new palatable formulation of guar gum'. Atherosceloris, 45 (1), 101-108

[338]. Singh A. Sharma N.K., 2011. 'Characterisation and applications of synthesized cation exchanger guar gum sulphonic acid (GSA) resin for removal and recovery of toxic metal ions from industrial waste water'. Water SA, 37 93), 295 – 302

[339]. Singh A.V., Gupta S., Gupta S.C., 1996. 'Synthesis of guaran – sulphonic acid cation exchanger and its application in metal ion removal from underground mine water of the Rajpura dariba Mines, Udaipur, India'. Desalination, 104 93), 235 – 238

[340]. Singh R.P., in : Prasad P.N., Mark J.E., Fai T.J. (Eds.), 1995. Polymers and other advanced materials : Emerging technologies and Buisness opportunities, Plenum Press, New York, pp. 227 – 249

[341]. Singh R.P., Karmakar G.P., Rath S.K., Lan N.T., 2000. Polymer Engineering Science, 40, 46-60

[342]. Singh R.P., Pal S., Mal D., 2006. 'A high performance flocculating agent and viscosifiers based on cationic guar gum'. Macromolecular Symposia, 242, 227-234

[343]. Singh R.P., Pal S., Mal D., Macromolecular Symposia, 242, 2006, 227-234

[344]. Singh V., Pandey S., Singh S.K., Sanghi R., 2008. Journal Sol-Gel Science Technology, 47, 57-58

[345]. Singh V., Pandey S., Singh S.K., Sanghi R., 2009. 'Removal of cadmium from aqueous solutions by adsorption using poly(acrylamide0 modified guar gum – silica nanocomposites'. Separation and Purification Technology, 67, 251-261

[346]. Singh V., Pandey S., Singh S.K., Sanghi R., 2009. Sep. Purif. Technol. 67, 251-261

[347]. Singh V., Sethi R., Tiwari A., Srivastava V., Sanghi R., 2003. Carbohydrate Polymers, 54, 523-525

[348]. Singh V., Sharma A.K., Tripathy D.N., sanghi R., 2009. 'Poly(methylmethacrylate) grafted chitosan : An efficient absorption for anionic azo dyes'. Journal of Hazardous Materials, 161, 955-966

[349]. Singh V., Singh S.K., Pandey S., Sanghi R., 2011. 'Synthesis and characterization of guar gum tempelated hybrid nanosilica'. International Journal of Biological Macromolecules, 49, 233-240

[350]. Singh V., Tiwari A., Kumari P.L., Tiwari S., 2006. Carbohydrate Research, 341, 2270-2274

[351]. Singh V., Tiwari a., 2009. 'Hydrolytic fragmentation of seed gums under microwave irradiation'. International Journal of Biological macromolecules, 44, 186-189

[352]. Singh V., Tiwari A., Pandey A., Singh S.K., 2007. 'Peroxydisulphate initiated synthesis of potato starch – graft – poly(acrylonitrile) under microwave irradiation'. Express Polymer Letters, 1, 51-58

[353]. Singh V., Tiwari A., Pandey S., Singh S.K., Sanghi R., 2007. Journal of Applied Polymer Science, 104, 536-544

[354]. Singh V., Tiwari A., Sanghi R., 2005. 'Studies on $K_2S_2O_8$/Ascorbic acid initiated studies of Ipomoea dasysperma seed gum-g-poly(acrylonitrile): A potential industrial gum'. Jpurnal of applied Polymer Science, 98, 1652-1662

[355]. Singh V., Tiwari A., Shukla P., Singh s.P., Sanghi R., 2006. 'Grafting of methylmethacrylate onto the plant seed galactomannans using potassium persulphate / ascorbic acid redox pair'. Reactive and Functional Polymers, 66 (11), 1306-1318.

[356]. Singh V., Tiwari A., Tripathi D.N., Malviya T., 2003. Tetrahedron Letters, 44, 7295-7297

[357]. Singh, J., Kaur, L. and Mc Carthy, O.J., 2007. 'Factors influencing the physico-chemical, morphological, thermal and rheological properties of some chemically modified starches for food applications – A review'. Food Hydrocolloids, 21 (1) : 1 – 22

[358]. Sitochy, M.Z., Ramadan, M.F., 2001. 'Degradability of different phosphorylated starches and thermoplastic films prepared from corn starch phosphomonoesters'. Starch – Starke, 53 (70 : 317 – 322.

[359]. Skinner G.W., Harcum W.W., Barnum P.E., Guo J.H., 1998. Proceedings of annual meeting of the American Association of Pharmaceutical Scientists, 514

[360]. Soppirnth K.S., Aminabhavi T.M., 2002. European Journal of Pharmaceutics, 53 (1), 87 – 98

[361]. Sothornvit R. Journal of Food Engineering (2011), 107, 319 – 325

[362]. Spyropoulos F., Portsch A., Norton I.T., 2010. 'Effect of sucrose on the phase and flow behavior of polysaccharide / protein aqueous two-phase systems'. Food Hydrocolloids, 24, 217-226

[363]. Srivastava A., Mishra V., Singh P., Srivastava A., Kumar R., 2012. 'Comparitive study of thermal degradation behavior of graft copolymers of polysaccharides and vinyl monomers'. Journal of Thermal Analysis and Calorimetry, 107 (1), 211-223

[364]. Srivastava A., Mishra V., Singh S.K., Kumar R., 2009.'one pot synthesis and characterization of industrially important graft copolymer (GOH-g-ACM) by using proxy mono sulpahte/mercaptosuccinic acid redox pair.' E-polymers, no.006,1

[365]. Srivastava A., Mishra V., Singh S.K., Kumar R., 2010.'Vanadium (V)/Mandelic acid initiated graft copolymerization orf acrylamide onto guar gum in an aqueous medium.' Journal of Applied Polymer Science, 115, 2375, 1002/app31172

[366]. Srivastava H.C., Harche S.N., 1963. Tetrahedron Letters, 27, 1869-1873

[367]. Stewart M.L., Slavin J.L., 2006. 'Molecular weight of guar gum affects short – chain fatty acid profile in model intestinal fermentation'. Molecular Nutrition and Food Resewarch, 50 (10), 971-976

[368]. StojanovicZ., Jeremic K., Jovanovic S., 2000. 'Synthesis of carboxymethyl starch'., Starch/Starke, 52, 413-419.

[369]. Stute, R., Heilbronn, Klinger, R.W., Boguslawski, S., Eshtiaghi, m.N. and Knorr, D. (1996). 'Effects of high pressure treatment of starches'. Starch – Starke, 48 (11-12) : 399 – 408.

[370]. Sudhakar V., Singhal R.S., Kulkarni P.R., 1996, Food Chemistry, 55 (3), 259 – 264

[371]. Swamy n.N.g., dharmarajan T.S., Paranjothi K.L.K., 2006. '---'. Indian Drugs, 43 (9), 756-759

[372]. Swamy N.N.G., Dharmarajan T.S., Paranjothi K.L.K., 2006. 'Derivatization of guar to various hydroxy alkyl derivatives and their characterization'. Indian Drugs, 43 (9), 756-759

[373]. Szamel G., Domjan A., Klebert S., Pukanszky B., 2008. 'Molecular structure and properties of cellulose acetate chemically modified with caprolactone'. European Polymer Journal, 44, 357-375

[374]. Takacs E., Wojnarovits L., Borsa J., Papp J., Hargittai P., Korcez L., 2005. Nuclear instruments and methods in physics Research B, 236, 259

[375]. Taniguchi M., Pieracci J., Samsonoff W.A., Belfort G., 2003. Chem Mater, 15, 3805

[376]. Tapie N., Malhiac C., Huchner N., Grisel M., 2008. 'Determination of galactose and mannose residues in natural galactomannans using a fast and efficient high – performance liquid chromatography / UV detection'. Journal of Chromatography A, 1181, 45 – 50

[377]. Tatsumi D., Kourogi H., Chen B., Matsumoto T., 2008. 'Effect of natural additives on the rheological properties of cellulose fiber disperse systems'. Colloids and Surfaces A : Pysicochemical engineering Aspects, 316, 151 – 158

[378]. Taunk K., Behari K., et al., 2002. 'Studies on graft copolymerization of 4-vinylpyridine onto guar gum'. Journal of Applied Polymer Science, 84 (13), 2380 – 2385

[379]. Techawipharat J., Suphantharika M., BeMiller J.N., 2008. 'Effects of cellulose derivatives and carrageenans on the pasting, paste and gel properties of rice starches'. Carbohydrate Polymers, 73, 417-426

[380]. Thaker M.D., Trivedi H.C., 2005. 'Ultraviolet – radiation induced graft copolymerization of methyl acrylate onto the sodium salt of partially carboxymethylated guar gum'. Journal of applied Polymer Science, 97 95), 1977-1986

[381]. Thakur S., Chauhan G., ahn J.H., 2009. 'Synthesis of acryloyl guar gum and its hydrogel materials for use in the slow release of L-DOPA and L-tyrosine'. Carbohydrate Polymers, 76, 513-520

[382]. Tharanthara, R.N. 1995 Starch – The Polysaccharide of high abundance and usefulness. Journal of Scientific & Industrial Research, 54:452 – 458

[383]. Thomas D.J., Atwell W.A., 1999. Starches. St paul: Eagan Press

[384]. Thomas T.L., Mishra a.K., 2002. Eur Polym J, 38(9), 1805

[385]. Tijsen C.J., Kolk H.J., Stamhuis E.J., Beenackers A.A.C.M., 1999. 'Optimisation of the process conditions for the modification of starch'. Chemical Engineering, 54, 2765-2772

[386]. Tijsen C.J., Kolk H.J., Stamhuis E.J., Beenackers A.A.C.M., 2001a. 'An experimental study on the carboxymethylation of granular potato starch in non-aqueous media'. Carbohydrate Polymers, 45, 219-226

[387]. Tijsen C.J., Kolk H.J., Stamhuis E.J., Beenackers A.A.C.M., 2001b. 'Design of acontinuous process for the production of highly substituted granular carboxymethyl starch'. Chemical Engineering Science, 56, 411-418.

[388]. Tiraferri A., Chen K.L., Sethi R., Elimelech M., 2008. 'Reduced aggregation and sedimentation of zero-valent iron nanoparticles in the presence of guar gum'. Journal of Colloid and Interface Science, 2008, 324, 71-79

[389]. Tiwari A., Singh S.P., 2008. Journal of Applied Polymer Science, 108 (2), 1169-1177.

[390]. Touvien L., Peltonen S., Jarvinen K., 2003. 'Drug release from starch-acetate films'. Journal of Controlled Release, 91 (3), 345-354

[391]. Touvien L., Peltonen S.,Liikola M., Hotakainen M., Lahtela-Kakkaonen M., Poso A., Jarvinen K., 2004a. 'Drug release from starch acetate microparticlesand films with and without incorporated [alpha]-amylase'. Biomaterials, 25(18), 4355-4362

[392]. Touvinen L., Ruhanen E., Kinnarinen T., Ronkko S., Pelkonen J., Urtti A., Peltonen S., Jarvinen K., 2004 b. 'Starch acetate microparticles for drug delivery into retinal epithelium – in vitro study'. Journal of Controlled Release, 98 93), 407-413

[393]. Tripathi M., Behari K., Taunk K., Kumar R., 2000. 'Studies of graft copolymerization of acrylamide onto guar gum using peroxy diphosphate / metabisulphite redox pair. Polymer International, 49, 153

[394]. Tripathy J., Mishra D.K., Behari K., 2009. 'Graft copolymerization of N-vinylformamide onto sodium carboxymethyl cellulose and study of its swelling, metal ion absorption and flocculation behaviour'. Carbohydrate olymers, 75, 604-611

[395]. Tripathy J., Mishra D.K., Shrivastava A., Mishra M.M., Behari K., 2008. 'Synthesis of partially carboxymethylated guar gum-g-4-vinyl pyridine and study of its water swelling, metal ion sorption and flocculation behaviour'. Carbohydrate Polymers, 72, 462-472

[396]. Tripathy J., Mishra D.K., Srivastava A., Mishra M.M., Behari K., 2008. 'Synthesis of partially carboxymethylated guar gum – g – 4-vinyl pyridine and study of its water swelling, metal ion sorption and flocculation behaviour'. Carbohydrate Polymers, 72, 462-472

[397]. Trivedi J.H., Bhatt T.A., Kalia K., Patel N.K., Trivedi H.C., 2008. 'Grafting of ethyl methacrylate onto sodium salt of partially carboxymethylated guar gum by tetravalent cerium ion'. Journal of Polymer Materials, 25(4), 541 – 555.

[398]. Trivedi J.H., Bhatt T.A., Kalia K., Patel N.K., Trivedi H.C., 2005. 'Cerric induced grafting of acrylonitrile onto sodium salt of partially carboxymethylkated guar gum'. Carbohydrate Polymers, 60 (1), 117 – 125.

[399]. Trivedi J.H., Kalia K., Patel N.K., Trivedi H.C., 2005. 'Graft copolymerization of sodium salt of partially carboxymethylated guar gum with methyl methacrylate : An examination of the reaction variables'. Journal of applied Polymer Science, 96 (5), 1855-1864

[400]. Trivedi J.H., Patel N.K., Trivedi H.C., Kalia K., 2005. 'Grafting of vinyl monomers onto sodium salt of partially carboxymethylated guar gum : Comparison of their reactivity'. Polymer – Plastic Technology and Engineering, 44 (3), 407-425

[401]. Trivedi J.H., Patel N.K., Trivedi H.C., Kalia K., 2005. 'Modification of sodium salt of partially carboxymethylated guar gum by graft copolymerization with methyl acrylate'. Polymers and Polymer Composites, 13 (3), 301-312

[402]. Trubianco Paolo, c., (1997). 'The role of speciality food starches in flavor encapsulation'. Flavour Technology : American Chemical Society, 244 – 253.

[403]. Trubiano, P.C., (1987). 'Succinate and substituted succinate derivatives of starch'. Modified starches : Properties and uses, CRC Press, Boca Raton, Florida, In : Wurzburg, O.B., Editor, 1987 : 131 – 148

[404]. Tsoukatos T., Pispas S., Hadjichristidis N., 2000. Macromolecules, 33, 9504

[405]. Tukomane, T. and Varavinit, s., (2008). 'Influence of octenyl succinate rice starch on rheological properties of gelatinized rice starch before and after retrogradation'. Starch – Staerke, 60 (6) : 298 – 304.

[406]. Turk S.S., Reinhold S., 2000. 'Printing properties of a high substituted guar gum and its mixture with alginate'. Dyes and pigments, 47, 269-275

[407]. Turrer H.D.G., Peres A.E.C. et al., 2010. Minerals Engineering, 23, 1066 – 1069.

[408]. Vahdat A., Bahrami H. Ansari N., Ziaie F., 2007. 'radiation grafting of styrene onto polypropylene fibers by 10 MeV electron beam .' radiation Physics 7 Chemistry, 76, 787-793

[409]. Varma A.J., Kokane S.P., Pathak G., Pradhan S.D., 1997. 'Thermal behavior of galactomannan guar gum and its periodate oxidation products.' Carbohydrate Polymers, 32, 111-114.

[410]. Vazquez B., Goni I., Gurruchaga M., Areizaga J., Valero M., Guzman G.M., 1992. Makromol. Chem., 193(9), 2189

[411]. Vazquez B., Goni I., Gurruchaga M., Valero M., Guzman G.M., 1989. . J Polym Sci Part A: Polym Chem, 27(2),595

[412]. Vega-Cantu Y.I., Hauge R.H., Norman L.R., Powell R.J., Billups W.E., 2006. 'Effect of magnesium and iron on the hydration and hydrolysis of guar gum'. Biomacromolecules, 7(2), 441-445

[413]. Vigneshwaran N., Nachane R.P., Balasubramania R.H., Vardarajan P.V., 2006. 'A novel one pot green synthesis of stable silver nanoparticles using soluble starch'. Carbohydrate Research, 341, 2012-2018

[414]. Vishwakarma R.K., Shivhare U.S., Nanda S.K., 2011. . LWT-Food Science and Technology, 44, 969-975

[415]. Viturawong Y., Achayuthakan P., Suphantharika M., 2008. 'Gelatinization and rheological properties of rice starch / xanthan mixtures : effect of molecular weight of xanthan and different salts'. Food Chemistry, 111, 106-114

[416]. Wan X.F., Li Y.M., Song L.L., Chen C.X., Wang Y.X., 2006. 'Research on application of CHPG in the ONP furnish system'. China Pulp and paper, 25 (11), 32-34

[417]. Wan X.F.., Li Y.M., Hu Q.X., Wang Y.Y., 2008. 'Graft copolymerization of acrylamide onto cationic guar gum at low temperature with high grafting effiociency'. Polymeric Materials Science and Engineering, 24 (7), 40-43

[418]. Wang A.R., Zhu S., 2002. Macromolecules, 35, 9926

[419]. Wang A.R., Zhu S., 2005. J Polym Sci Part A: Polym Chem, 43(22), 5710

[420]. Wang F., Wang Y.J., Sun Z., 2002. 'Conformational role of xanthan gum in its interaction with guar gum'. Journal of Food Science, 67 (9), 3289 – 3294.

[421]. Wang J.P., Chen Y.Z., Zhang S.H., Yu H.Q., 2008. 'A chitosan – based flocculant prepared with gamma - irradiation - induced grafting.' Bioresource Technology, 99, 3397-3402

[422]. Wang J.-S., Metyjaszewski K., 1995. 'Controlled / living radical polymerization atom transfer radical polymerization in the presence of transition – metal complexes'. Journal of Americal Chemical Society, 117, 5614

[423]. Wang L.J., Chen F.S., Qin L.J., Zhou L.J., 2006. 'application of high substituted cationic starch and guar ghum in waste pulp stickies control'. China Pulp and paper, 25 91), 17-20

[424]. Wang Q., Ellis P.R., Ross-Murphy S.B., 2000. 'the stability of guar gum is an aqueous system under acidic conditions'. Food Hydrocolloids, 14 (2), 129 – 134.

[425]. Wang Q., Ellis P.R., Ross-Murphy S.B., 2000. 'The stability of guar gum in an aqueous system under acidic conditions'. Food Hydrocolloids, 14, 129-134

[426]. Wang Q., Ellis P.R., Ross-Murphy S.B., 2002. 'Dissolution kinetics of guar gum powders. I. Methods of commercial polydisperse samples'. Carbohydrate Polymers, 49 92), 131 – 137

[427]. Wang q., Ellis P.R., Ross-Murphy, S.B., 2003. 'Dissolution kinetics of guar gum powders – II. Effects of concentration and molecular weight'. Carbohydrate Polymers, 53 91), 75-83

[428]. Wang Qi, Ellis P.R., Ross-Murphy S.B., 2008. 'Disolution kinetics of water-soluble polymers : the guar gum paradigm'. Carbohydrate Polymers, 74, 519-526

[429]. Wang W., Wang A. (2008). 'Preparation, swelling behavior and water – retention properties of superabsorbent based on guar gum'. Journal of Chemical Industry and Engineering, 59 (11), 2916 – 2921

[430]. Wang W., Wang A., 2009. 'Preparation, characterization and properties of superabsorbent nanocomposites based on natural guar gum and modified rectorite'. Carbohydrate Polymers, 77, 891-897

[431]. Wang W.B., Wang A.Q., 2009. 'Effects of crosslinking degree on the properties of guar gum – g – poly(acrylic acid) / sodium humate superabsorbents'. Polymeric Materials Science & Engineering, 25 912), 41-44

[432]. Wang X., Qi J., Xue H., 1997.Gaofenzi Cailiao Kexue Yu Gongcheng, 13(1), 135, 1997; Chem Abstr, 126, 144851w

[433]. Wang X., Wang J., Zhang J., Zhao B., Yao J., Wang Y., 2010. 'Structure – antioxidant relationships of sulfated galactomannan from guar gum'. International Journal of Biological Macromolecules, 46, 59-66.

[434]. Wang X.S., Lascelles S.F., Jackson R.A., Armes S.P., 1999. 'Facile synthesis of well defined water soluble polymers via atom transfer radical polymerization (ATRP) in aqueous media at ambient temperature. Chemical Communications, 1817

[435]. Whistler R.L., Bemiller J.N., Paschall E.F., (eds) 1984. Starch : Chemistry and Technology, 2nd edn, Academic Press, New York

[436]. Whitcomb P.J., Gutowski J., Howland W.W., 1980. 'Rheology of guar solutions'. Journal of Applied Polymer Science, 25(12), 2815 – 2827

[437]. Wienties R.H.W., Duits M.H.G., Jongschaap, R.J.J., Mellema J., 2000. 'Linear rheology of guar gum solutions'. Journal of Macromolecules, 33 (26), 9544-9605

[438]. Willett J.L., Finkenstadt V.l., J. appl. Polym, Sci., 99, 52 (20060

[439]. Wong D., Larabee S., Clifford K., Tremblay J., Friend D.R., 1997. ' USP Dissolution apparatus III (reciprocating cylinder) for screening of guar-based colonic delivery formulations'. Journal of Contr. Rel., 47,173-179

[440]. Woo K.S., Seib P.A., 2002. 'Crosslinked resistant starch :Preparation and properties'. Cereal Chemistry, 79, 819-825.

[441]. Wootton M., Chaudhy M.A., 1981. 'In vitro digestion of hydroxypropyl derivatives of wheat starch'. Starch/Starke, 33, 135-137

[442]. Wootton, M. and Manatsathit, A., (1983). 'The influence of molar substitution on the water binding capacity of hydroxypropyl maize starches' Starch – Starke, 35 (3) : 92 – 94.

[443]. Wright J.D., 2001. 'Silica sol-gels: reaction mechanism in sol-gel materials'. Chemistry and Applications, Chapter 2, Gordon and Beach Science Publisher, 33-51.

[444]. Wu G., Sun S., 1991. Shiyou Huagong, 20 (4), 242; Chem Abstr 115, 257313 p

[445]. Wu G., Zhou L., 1994. Shiyou Huagong, 22(5), 287; Chem Abstr 121, 256894r

[446]. Wu M., 2009. 'Shear thining and viscosity synergism in mixed solution of guar gum and its etherified derivatives'. Polymer Bulletin, 63 (6), 853-863

[447]. Wu W.P., Zhao B.Y., Wu Q., Chen L.S., Hu K.A., 2006. 'The strengthening effect of guar gum on the yield stress of magnetorheological fluid'. Smart Materials and Structures, 15 (4), N94-N98

[448]. Wu X., Ye Y., Chen y., Ding B., Cui J., Jiang B., 2010. '------'. Carbohydrate Polymers 80, 1178 – 1182

[449]. Wurzburg O.B., 1986, Modified Starches:Properties and Uses, CRC Press, Florida

[450]. Xiaofang W., Youming L., Xiaojun W., Yanxia W., Linlin S.,2007. 'Ceric ion – induced graft copolymerization of acrylamide on cationic guar gum at low temperature'. Journal of Applied Polymer Science, 104 (6), 3715 – 3722

[451]. Xu Q., Wang Q.R., Liu L.J., Journal of Applied Polymer Science, 107, 2704 (2008)

[452]. Xu Z., Yang Y., Jiang Y., Sun Y., Pang S.Y., 2008. 'Synthesis and characterization of konjac glucomannan – graft – polyacrylamide via c-irradiation'. Molecules, 13, 492-500

[453]. Yadav M., Mishra D.K., Behari K., 2011. 'Synthesis of partially hydrolyzed graft copolymer 9H-partially carboxymethylated guar gum – g – methacrylic acid) : A superabsorbing Material'. Carbohydrate Polymers, 85, 29-36

[454]. Yamagishi H., Cricvello J.V., Belfort G., 1995. J Memb Sci, 105, 237

[455]. Yan Y., Yang H.Y., Liu W.Y., Zhu P.P., He P.S., 2005. 'Intermolecular and intramolecular interactions of polymer guar gum in solutions'. Chinese Journal of Polymer Science, 23 (5), 557-559

[456]. Yanli1 G., Hongtao Y., 2008. 'Properties and characterization of heparin stabilized gold nanoparticles'. Journal of Carbohydtrate Chemistry, 27, 309-319

[457]. Ye Y.Q., Ding B., Wang K., He J.P., Cui, J.J., Jiang B., 2009. 'Determination of the degree of substitution at secendory hydroxyls of hydroxypropyl guar gum by periodate oxidation'. Chemical journal of Chinese Universities, 3(4), 835-840

[458]. Yener K.M., Oguz O., 2003. Polymer, 44, 5239

[459]. Yoo D., Kim C., Yoo B., 2005.'Steady and dynamic shear rheology of rice starch – galactomannan mixtures'. Starch, 57 (7), 310-318

[460]. You Y.C., Zhu C.Y., Jiao J.L., Shen X., Acta Polym. Sinica, 6, 746 (2000)

[461]. Yu Q., Zhang J., Cheng M., Zhu S., 2006. Macromol Chem Phys, 207 (3), 287

[462]. Yuen S.N., Choi S.M., Phillips D.L., Ma C.Y., 2009. 'Raman and FTIR spectroscopic study of carboxymethylated non-starch polysaccharides'. Food Chemistry, 114, 1091-1098

[463]. Zahran M.K., Mahmoud R.I., 2006. 'Synthesis and charcatreization of polyacrylamide guar gum graft copolymers'. Journal of the Textile association, 66 (6), 273-281

[464]. Zhai N., Wang W., Wang A., 2011. 'Synthesis and swelling characteristics of a pH-responsive guar gum – g – poly(sodium acrylate) / medicinal stone superabsorbent composite'. Polymer Composites, 32 (2), 210 – 218

[465]. Zhang B., Zhou Y.Y., J. Donghua Univ. Nat. Sci. Ed., 31, 86 (2005)

[466]. Zhang B., Zhou Y.Y., Polym. Compos., 29, 506 (2008)

[467]. Zhang l.M., Kong T., 2006. 'Aqueous polysaccharide blends based on hydroxypropyl guar gum and carboxymethyl cellulose : Synergistic viscosity and thixotropic properties'. Colloid and Polymer science, 285 (2), 145-151

[468]. Zhang L.M., Kong T., Hui P.S., 2007. 'Semi-dilute solutions of hydroxypropyl guar gum:Viscosity behavior and thixotropic properties'. 87(4), 684-688

[469]. Zhang X.D., Li W.Y., Liu X., j. Appl. Polym. Sci, 88, 1563 (2003)

[470]. Zhao J., Fan G., Guo Z., Xie Z., Liang G., 2005. Polym Bull, 55, (1-2), 1

[471]. Zhao J.C., Xie Z.H., Gio Z.A., Liang G.J., Wang J.L., 2004. Appl. Surf Sci, 229, 124

[472]. Zhu J., Dong X., Wang X., Wang Y., 2010. 'Preparation and properties of a novel biodegradable ethyl cellulose grafting copolymer with poly(p-dioxanone) side chains'. Carbohydrate Polymers, 80, 352 - 359

[473]. Zhu R.T., Yang y., Guo J.Q., Wang X., Zhang J., 2009. 'Rheological properties of an anionic guar gum solution and its weakly acidic gel'. Oilfield Chemistry, 26 (4), 382 – 386

[474]. Zhu Y.G., Lin W.H., Li W., Zhang L.M., 2007. 'Study on the preparation and characterization of magnetic guar gum composite microspheres'. Zhongshan Daxue Xuebao, 2007, 46 (3), 55-58

[475]. Fox, J. E. (1992). In A. Imeson (Ed.), Thickening and gelling agents for food (pp.

a.   153–169). London: Chapman & Hall

[476]. Doublier, J. L. & Launay, B., 1981. Journal Of Texture Studies, 12, 151-72

[477]. Kok, M. S.; Hill, S. E.; Mitchell, J. R., 1999. Food Hydrocolloids, 13, 535

[478]. Morris, E.R., Cutler, A.N., Ross-Murphy, S.B., Rees, D.A. & Price, J., 1981. Carbohydrate Polymers, 1, 5-21.

[479]. Lapsin, R.& Pricl, S. 1995 Rheology of industrial polysaccharides: Theory and applications.Blackie Academic, London.

[480]. Yun-fei Yan et al, 2005. 'Intermolecular and intramolecular interactions of polymer guar gum in solutions' *Chinese J. Polym. Sci.* **23**, 557 (2005).

[481]. Sarkar S., Singhal R.S., 2011. 'Esterification of guar gum hydrolysate and gum Arabic with *n*-octenyl succinic anhydride and oleic acid and its evaluation as wall material in microencapsulation'. Carbohydrate Polymers, 86(4), 1723-1731

[482]. Rubenstein A., Gliko-Kabir I., 1995. 'Synthesis and swelling dependent enzymatic degradation of borax modified guar gum for colonic delivery purposes'. STP Pharma Sci, 5, 41.

[483]. Brondsted H., Anderson C., Hovgaard L., 1998. 'Crosslinked dextran – a new capsule material for colon targeting of drugs'. Journal of Controlled Release, 53, 7-13

[484]. Phillips G.O. and Williams P.A., 2000. Handbook of Hydrocolloids, CRC Press, Cambridge, England

[485]. Torres M.D., Moreira R., Chenlo F., Vazquez M.J., 2012. 'Water absorption isotherms of CMC, guar, locust bean, tragacanth and xanthan gums'. Carbohydrate Polymers, 89, 592-598