REVIEW ARTICLE

Microwave Assisted Grafting of Natural Polysaccharides

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Abstract
Polysaccharides are known as natural and renewable feed stock for synthesizing high performance macromolecular materials. The popular, versatile and convenient way to develop polysaccharide is being based on materials used for the grafting of synthetic polymers onto natural polysaccharides. Although the attractive chemical and physical properties of polysaccharide co-polymeric materials, undesired homopolymer formation in the concurrent competing reaction lowers the yield of copolymer, posing problems in the commercialization of the grafting procedures. In fact, the requirement for an inert atmosphere is an added disadvantage for many conventional grafting methods. The use of microwave irradiation has been exploited in the past two decades to alleviate these limitations in the synthesis of a range of graft modified polysaccharide materials. Whereas, increasing interest in clean and eco-friendly chemistry has motivated the use of microwaves in the polysaccharide grafting modification for various applications. More likely, microwave irradiation significantly decreases the use of toxic solvents, reaction time for almost all the grafting reactions of interest here, ensuring high yields, product selections and clean product formations. Moreover, in various examples, microwave synthesized polysaccharide copolymers comprises better properties for commercial exploitation rather than their conventionally synthesized intermediates. Recent applications of microwave heating in the grafting modifications of polysaccharides are reviewed and their mechanisms are discussed.
INTRODUCTION
In organic synthesis usage of microwave irradiation has become drastically popular within the pharmaceutical and academic domains. Therefore, it is a latest and advanced enabling technology for drug discovery and development. Advantage of microwave irradiation is compounded libraries for lead generation and optimization of compound can be assembled in a fraction of the time required by classical thermal methods.\(^1\) The frequency range of microwaves which generates electromagnetic radiation of 300 MHz to 300 GHz. Although exposure to microwaves, the polar or charge particles tend to align themselves with electric field component of the microwaves which reverses its direction. As the charged particles in a reaction medium fail to align themselves as fast as the direction of the electric field of microwaves changes, friction is created, due to which, the medium is heated.\(^2\) Microwave reactions have been done both in solution as well as in dry medium. Since in the dry medium reactions the mixing of reactants is not feasible, in homogeneous electric field of microwaves is created to produce localized superheating zones called hotspots measuring about 900–1000 m and having temperatures higher (~100–200 K) than the bulk temperature.\(^3\) These hot spots accelerate the solid supported reactions and make them more productive than solution phase reactions. In the earlier studies when microwaves were first used, by the using of domestic microwave ovens most of the chemical transformations were carried in which the irradiation power was generally controlled by on/off cycles of the magnetron. Due to their easy accessibility and low cost, these unmodified multimode microwave ovens were popular, their use was not much encouraged due to the safety concerns as they had insufficient control over the reaction temperature and pressure. To overcome these issues, several modifications to domestic microwave ovens were made over the past decade.\(^4\)

GRAFTED POLYSACCHARIDES
Polysaccharides such as cellulose, starch and chitin have been extensively graft modified to obtain macromolecular materials superior to the source polysaccharides, exhibiting better resistance to heat or abrasion, higher mechanical strength, greater oil/water repellant qualities, or antibacterial activity. In their native form polysaccharides are fairly resistant to degradation under shear and perform as useful flocculants [5], but have poor shelf life because of their susceptibility to biodegradation. Synthetic polymers on the other hand can be easily tailored, but they suffer from poor shear resistant properties. By grafting synthetic polymers, natural polysaccharides\(^6\)\(^,\)\(^7\) can be transformed into highly customizable matrices with hybrid properties suitable for different applications. Chemical grafting is thus one of the most effective methods to increase the compatibility between synthetic and natural polymers to obtain new materials with hybrid characteristics. It involves the attachment of polymer chains, usually a monomer, to the back-bone polymer. A variety of vinyl monomers, such as acrylamide, N-tert-butylacrylamide,\(^1\) methylmethacrylate,\(^2\) acrylonitrile\(^3\) and methacrylamide\(^4\) have been grafted to many industrial polysaccharides for optimizing their commercial utilization. Vinyl modification\(^5\)\(^,\)\(^9\) improves the flocculating characteristics of the polysaccharides wherein the dangling grafted chains are able to approach the contaminants more easily. Guargraft-poly(acrylamide) based anionic microgels have been reported for pH sensitive drug delivery.\(^10\) Besides guar derivatives, several polysaccharide-based graft copolymers are known for stimuli-dependent controlled drug release systems.\(^11\) Acrylamide-based homopolymer and copolymers have applications in petroleum and paper industries, in environmental protection and as biomaterials.\(^12\)

Conventional Grafting Procedures
Polymer chains are grafted on polysaccharides through three main strategies\(^13\): the ‘grafting through’, the ‘grafting on’ and the ‘grafting from’ processes. The ‘grafting through’ technique involves copolymerizing premade vinyl functionalized polysaccharide material with comonomers. Besides the conventional free radical processes, the ‘grafting from’ technique involving the growth of grafts directly from the polysaccharide backbones is the most extensively studied and used technique. Radicals can be conveniently generated along the polysaccharide backbone in the presence of chemical initiators.\(^14\) The synthesis of grafted polymers essentially involves free radicals which are generated in situ by radical/redox initiators such as ethylenediamine tetra acetic acid/ceric ammonium nitrate,\(^15\) ferrous ammonium sulfate/potassium persulfate,\(^16\) ceric ammonium nitrate/HNO\(_3\), potassium persulfate (KPS)/ N,N,N,N-tetramethylethylene diamine\(^18\) and K\(_2\)S\(_2\)O\(_8\)/ascorbic acid.\(^19\) The radical-initiated functionalization of
Polysaccharides have received considerable attention in recent years and has proven to be a useful method for the industrial production of modified polysaccharides. However, these transformations mostly require inert working conditions and are tedious and time consuming. In these conventional procedures the copolymer products are often accompanied by homopolymer formation which besides decreasing the yield also contaminates the copolymeric product. Other than by the use of radical initiators, free radicals are generated through X-rays, UV radiations, electron beam and microwave irradiation. Conventional grafting procedures may lead to polysaccharide backbone degradation and are not amenable to block copolymer formation. Their use may often be detrimental for some applications as they have limited control over graft molecular weight distribution. These problems have been addressed through the use of controlled/living radical polymerizations to obtain graft-functionalized polysaccharide based macromolecular materials. Carrying out controlled radical polymerization which is also known as ‘living’ radical polymerization in aqueous dispersed media opens the gate way to large-scale manufacture of products based on this technique. Nitroxide-mediated polymerization, atom transfer radical polymerization or reversible addition-fragmentation chain transfer techniques are used frequently for controlled/living radical polymerization. These techniques are tolerant to moisture and can be performed with the polymers having a range of functional groups and thus are very useful to precisely tailor the properties of the polysaccharide based materials where the synthetic graft length, chemical composition and product topology can be controlled and tailored. All these techniques use the concept of significantly reducing the concentration of propagating radical chain ends so as to minimize the irreversible termination reactions which form ‘dead’ polymer chains. This is done by addition of species that can reversibly trap the ‘active’ propagating radical species through reversible termination or reversible transfer.

**GRAFTING ON POLYSACCHARIDES UNDER MICROWAVES**

Grafting is an effective technique to modify the properties of synthetic and natural polymers. Using conventional redox grafting methods, synthetic grafts have been introduced in several natural polymers, including guar gum (GG), starch, cellulose/ cellulose derivatives and alginates. Polysaccharides are macromolecules having a number of polar functional groups, i.e., hydroxyl, amino, carboxylic acid and uronic acids, and they may be charged or electrically neutral depending upon the particular polysaccharide. Most of these polysaccharides are hydrophilic in their native form and are water soluble while some others like cellulose and chitosan are not soluble in water, requiring special conditions to dissolve them. While water is not a suitable solvent for most organic substrates, it dissolves majority of polysaccharides and derivatives. Thus, microwave grafting reactions of polysaccharides have been carried out mostly in aqueous conditions where the dominant source of dielectric heating is the dipolar polarization of water molecules present as solvent. Water is considered to be moderate microwave absorbing solvent, which like other solvents depends on temperature and dielectric loss. Presence of inorganic salts can enhance the ability of water to convert the microwave energy to heat energy since both dipolar polarization as well ionic conduction mechanisms now operate. Polysaccharide molecules being very large in size, cannot rotate or migrate under the influence of the changing electric field component of the microwaves but are capable of showing localized rotation of the pendant hydroxyl and other polar functional groups under its influence to contribute to the heating. For the microwave grafting, the polysaccharides are used either as their aqueous solution or suspension depending upon their solubility in water. However, even soluble polysaccharides are sometimes notoriously difficult to completely dissolve to form homogeneous solutions. The heterogeneity of the polysaccharide solutions often leads to hot spots which become hotter due to temperature dependence of loss tangent (tan ı) to enhance the grafting. Another available alternative is the grafting at solid support in which the reactants are impregnated on solid support before exposing to the microwaves. When the grafting is done in dissipative manner that is polysaccharide is dispersed in other reacting substances under non aqueous conditions or in dry medium, the localized rotations of the pendant groups of the polysaccharide are the major contributor to the dielectric heating. Polysaccharides are likely to differ in the extent to which they may be grafted under microwave conditions, depending upon the functionalities and the charge. Mostly inert atmosphere is a requirement for radical initiated conventional thermal grafting procedures as oxygen acts as radical inhibitor by adding to primary radicals, to produce stable free radicals which are unable to propagate the reaction. One of the major advantages of using microwaves in polysaccharide grafting is that unlike conventional methods, here the grafting reactions can be done under atmospheric conditions.
To date many polysaccharides have been grafted under microwave irradiation and the effect of microwaves on the properties of polysaccharide derivatives has been studied. A variety of procedures have been employed involving the use of microwaves in the grafting of polysaccharides, such as in open or closed vessel, either in a solution (homogeneous or heterogeneous) or in a dry medium. The most commonly used method is to perform grafting reactions under microwave irradiation in the presence of a free radical initiator and/ or catalyst and cross-linkers (microwave-assisted grafting). The lesser known method involves the use of microwave radiation in the absence of any free radical initiator (microwave-initiated grafting). Both the grafting mechanisms involve microwave-enhanced chemistry based on microwave absorption by the reactants or solvent which can be reactively inert but forms the microwave active component. Although both the aforesaid grafting methods lead to significant and rapid grafting of polysaccharides, grafting yields are usually higher in the microwave-assisted grafting. Microwaves have been extensively used in polysaccharide grafting but to fully understand the aforesaid grafting mechanisms and for deriving substantive advantage of grafting technique in obtaining macromolecular materials, more thorough study is needed. Available literature reveals that the majority of such grafting reactions have been attempted in multimode domestic ovens open vessels, where temperature and pressure of the reaction mixture were not controlled. These reactions have been performed in open vessels where the temperatures as measured by inserting thermometer to the reaction mixtures just after the exposure were not above the boiling temperature of water. However if such reactions can be repeated in mono mode cavity with exact control of temperature and pressure, useful inferences about the grafting mechanisms under various conditions can be drawn. In both types of the aforesaid grafting reactions, when performed under aqueous conditions, the dielectric heating takes place by dipolar relaxation of the water molecules and to some extent due to the localized rotation of the pendant polar groups at polysaccharide molecules. But in microwave assisted grafting reactions where radical initiators are added from outside, ions produced from these salts create ionic drift which results in Joule heating to expedite the heating. The microwave initiated grafting method is more attractive being more eco-friendly as it does not involve the usage of initiators and/or catalysts. A free radical mechanism has been postulated for such grafting reactions as in the presence of radical inhibitors such as hydroquinones, no grafting results. The following sections elaborate polysaccharide grafting modifications under microwave irradiation categorized by the individual polysaccharides considered. The conditions like: with or without initiator, solvent or dry media, usage of different microwave types and different microwave power and/ or temperature as adopted by different authors are reported in the present review with insight in the possible potential and future scope of this methodology.

**Gum Acacia**

Gum acacia (GA) is a complex arabinogalactan containing a small proportion of proteinaceous materials, and has been classified as arabinogalactan–protein complex. The gum has a highly variable composition depending upon the source of the fruit pod nodules and thus its physical and chemical properties can vary considerably from source to source. It is composed of d-galactose, l-arabinose, l-rhamnose, d-glucuronic acid and 4-O-methyl-d-glucuronic acid. The grafting of conducting polymers such as polyaniline (PANI) on a flexible matrix of GA produces a material that is convenient to process and has electrical conductivity, chemical stability toward dopants and thermal stability. Although PANI grafted conducting biopolymers are interesting candidates for the development of biopolymer based electronic materials, their synthesis involves quite tedious and lengthy procedures. Recently, gum acacia has been grafted with PANI under microwave assisted irradiation using a catalytic amount of ammonium peroxysulfate (APS) as an oxidant/initiator under mild acidic conditions. The reaction mixture was homogeneous as all the reactants were soluble in water at acidic pH at which the grafting reaction was performed. The grafting product gum acacia-graft-polyaniline (GA-g-PANI) exhibited pH switching electrical conducting behavior which was found dependent on the extent of grafting and on the pH of the material. Microwave synthesized copolymer shows better conductivity than the conventionally synthesized copolymer due to the inclusion of extra PANI grafts. Role of PANI grafts in the electronic conduction in GA-g-PANI is evident by the increase in ionic conduction with the increase in the %G of the copolymer. Moreover the conductivity of GA-g-PANI increased on exposure to HCl vapor and decreased when exposed to NH3 vapors due to conversion of emeraldine salt to emeraldine base. The optimum grafted material with controlled multifunctional electronic properties was obtained when the
reaction mixture containing $40 \times 10^{-3}$ M (NH$_4$)$_2$S$_2$O$_8$; 0.1 M aniline; $2 \times 10^{-3}$ M hydrochloric acid and 8.0 g/L GA was exposed to 500W microwave power for 40 s.

**Alginate**

Sodium alginate is a sodium salt of alginic acid (empirical chemical formula is NaC$_x$H$_y$O$_z$) and is an important water soluble polysaccharide containing a linear unbranched chain of (1→4)-linked-d-mannuronic acid and (1→4)-linked-L-guluronic acid residues. It is extracted from the cell wall of brown algae and is extensively used by the food industries to increase viscosity and as an emulsifier, in indigestion tablets, preparation of dental impressions and in reactive dye printing in the textile industry. Very recently, poly(acrylamide)-graft-sodium alginate (SG-g-PAM), a commercially useful graft copolymer has been synthesized under homogeneous conditions using microwaves. The grafting was microwave initiated as no external initiators were used for this grafting in contrast to the grafting of PANI on gum acacia where the grafting was microwave assisted. Various grades of the graft copolymers were obtained by varying the acrylamide concentration (from 0.14 to 0.25 M) and microwave exposure time (1–4 min) at fixed sodium alginate (0.0062 M) and microwave power (900W). The optimized grafted grade determined by its higher percentage grafting (37%G) was obtained by using 0.21 M acrylamide, 0.0062 mol sodium alginate, 900W microwave power and 3 min exposure. Due to its high molecular weight ($4.3 \times 10^5$ Da) it proved to be a better flocculant in coal suspension compared with other grades of the grafted polymer and sodium alginate itself. The optimized grafting was obtained in 3 min when an aqueous solution of 0.21 M monomer and 0.0062 M alginate was exposed to 900W microwave power.

**Artemisia Seed Gum**

Artemisia seed gum is composed of l-arabinose, dxylose, d-lyxose, d-mannose, d-glucose and d-galactose. The polysaccharide has a linear backbone with side branches and its molecular weight is reported to be about $1.42 \times 10^5$ Da. A super-absorbent polymer was prepared by grafting of acrylic acid on Artemisia seed gum under homogeneous conditions. For the grafting, an aqueous solution containing Artemisia seed gum, partially neutralized acrylic acid and controlled amount of ammonium persulfate was exposed to 180W microwave power. The grafted gum was found to be more thermally stable than the parent seed gum due to the incorporation of the synthetic grafts. Both the seed gum and the monomer were water miscible and the grafting was performed in the aqueous solution, using small amount of APS. Exposure to microwave irradiation facilitated the free radical generation from APS and thus the grafting. The water absorbency of the graft copolymer was used as a criterion for the optimization of the copolymer synthesis. The optimal reaction conditions were reached in 3 min at 180W microwave power, 70% neutralization degree of acrylic acid and 2% initiator on the basis of the mass of acrylic acid used. When the mass ratio of acrylic acid to Artemisia seed gum was 10:1, the product had high water absorbency close to 400 times (at room temperature) in distilled water.

**Chitin and Chitosan**

Chitin is the important natural polymer which is found in shrimp and crabs. Chitin can be converted to chitosan through deacetylation using a strong aqueous alkali solution. Although chitosan has potential use in many areas, it is insoluble in water, brittle in nature and tends to absorb moisture from the air. However, on vinyl grafting many of its properties are enhanced and the vinyl grafted chitosan materials behave as efficient flocculant, paper strengthener, drug-releaser, etc. Vinyl modification is quite a popular route for changing the solubility and morphological characteristics of chitosan and is conventionally done under thermal conditions using various redox systems. The microwave synthesis of a water absorbent copolymer of chitosan and acrylic acid has been reported, in which ceric ion was used as an initiator in the presence of N,N-methylene-bis-acrylamide as a cross-linker. Microwave assisted grafting takes place under heterogeneous environment as the reactants are not miscible. Though both chitosan and acrylic acid dissolve in water under slightly acidic condition, the cross-linker used had very low solubility in water. The grafting efficiency was found to be largely dependent on the amount of chitosan and the irradiation power of the microwave. Using 0.3 g chitosan, 5 mL of 0.01 M cross-linker, 2.5 mL of 0.01 M initiator, when the grafting was done at 260W microwave power, a copolymer having 680 g/g water absorbency was obtained in 30 min. Under identical conditions, the reaction rate under microwaves was eight times higher than that observed under traditional heating conditions which required 240 min for the grafting to complete. The copolymer so produced had 665 g/g water absorbency which...
was only slightly less than that of microwave synthesized copolymer. When microwave power was lowered to 120W, a copolymer having even better water absorbency (704 g/g), better grafting degree (0.986) and grafting efficiency (0.865) was obtained as homopolymerization becomes insignificant at such low microwave power. In microwave assisted grafting reactions, the presence of catalyst or initiators not only facilitates the dielectric heating, but also generate primary free radicals for propagation of the grafting reactions as observed by many researchers for a number of polysaccharides and monomers. However, there are recent reports from our group about the microwave initiated vinyl grafting which takes place in the absence of any initiator or catalysts. Grafting of acrylonitrile, acrylamide and methylmethacrylate on chitosan has been done in the absence of any redox initiating system under aqueous conditions in very short reaction time. Optimum copolymer sample having 170%G and 49.4% efficiency was obtained in the microwave initiated grafting of chitosan with poly(acrylonitrile) at 80% microwave (960W) power in 1.5 min. In all these studies, the reactions were performed under homogeneous conditions in open glass vessels using domestic microwave ovens. Though precise temperature and pressure control was not possible in the domestic oven used, the temperature of the reaction mixture was monitored by inserting a thermometer in the reaction mixture just after the microwave exposure, and was found to be ∼95 °C. Further increase in the microwave power (>80%) led to a decrease in the grafting, which can be attributed to the increased homopolymerization and some decomposition of the grafted copolymer at high microwave power, though experimental evidence for such conclusions is still lacking.

**Guar Gum**

Guar gum (GG) has a straight chain of mannose units joined by β-d-(1→4) linkages having galactopyranose units attached to the linear chain by (1→6) linkages. Galactose to mannose ratio in guar gum is reported to be 1:2. The prime interest in the modification of GG is due to its utility as a water binder in many industries like mining, textile, explosive, paper, petroleum and food where it is used as drag reducer and flocculant. However, GG undergoes fast biodegradation in aqueous medium and is therefore rarely used in its natural form. Both conventional as well as microwave irradiation methods have been used for the modification of GG by grafting of some hydrophilic as well as hydrophobic monomers to improve or induce certain desired properties. As in the case of chitosan, guar gum was graft copolymerized under the influence of microwaves with several monomers like acrylamide, acrylonitrile and ethylacrylate in the absence of radical initiator or catalyst. Using 0.16 M acrylamide and 0.1 g guar gum in 25 mL of water, persulfate/ascorbic acid initiated Ag+ catalyzed conventional thermal grafting reaction at ±35 °C resulted in guar-graft-poly(acrylamide) with 140%G and 45% efficiency in 90 min. Both the grafting reaction rate and %G (in the copolymer) were significantly high when the reaction was performed in a domestic microwave oven, with or without the initiator. In microwave assisted grafting (with an initiator), optimum copolymer had 182%G and 63% efficiency and was obtained in 1.6 min using 960W microwave power. However, when the grafting reaction was performed in a microwave initiated manner, where no outside initiator was used, optimum copolymer had %G and %E (120% and 42%, respectively) even lower than that with conventional grafting, though in much lesser time (0.33 min) and at lower microwave power (840W). Using the same persulfate/ascorbic acid redox initiator, when poly(acrylonitrile) was grafted on guar gum under thermal conditions at ±35 °C, the optimum copolymer sample had 177%G and 51% efficiency. However, in this reaction, Ag+ catalyst was not used. When the grafting reaction was carried out under the influence of 100% (1200W) microwave power at same monomer (0.26 M) and guar gum (0.1 g/25 mL) concentrations, 188%G and 54% efficiency were obtained in 1.66 min. Though there was not much increase in the %G and %E of the copolymer on exposing to microwave irradiation, the time for completion of the reaction was much reduced when grafting acrylamide and acrylonitrile monomers on guar gum. Poly(ethylacrylate) was also grafted on to guar gum in microwave initiated manner without using initiator/catalyst. The optimum sample was synthesized at 0.16 M ethylacrylate, 0.1 g guar gum/25 mL water, 1200W microwave power and 15 sec exposure time. The copolymer had 295%G and 73% efficiency which were significantly higher than the %G and %E obtained with other monomers like acrylamide and acrylonitrile as described above. Both acrylamide and acrylonitrile monomers have good miscibility in the aqueous solution of the guar gum, thus creating a homogeneous environment for the grafting. On the contrary, being immiscible in the aqueous solution of the guar gum, ethylacrylate creates a heterogeneous environment and the grafting takes place in a dissipative manner. The high %G copolymer was indicative of the incorporation of higher
and larger graft chains in the copolymer, as more active binding sites were available in the more thermostable microwave synthesized copolymer. TGA thermograms of guar-graft-poly(acrylonitrile) synthesized thermally and under microwaves. Cd(II) from an aqueous solution. The adsorption process is described through an isotherm, that is, the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at a fixed temperature. The quantity adsorbed is nearly always normalized by the mass of the adsorbent for comparisons among different materials. The Langmuir isotherm is valid for monolayer sorption on a surface with a number of identical sites. Based on Langmuir model, monolayer adsorption capacity (Qmax) for microwave synthesized sample was calculated to be 714 mg/g as compared to 270 mg/g for conventionally synthesized copolymer, showing the advantage of using microwaves in the adsorbent synthesis. For these grafting reactions, 960W microwave power was found to be the most suitable, while the optimum exposure time varied from few seconds to minutes according to the monomer type. Thus, it was observed that the grafting reactions, when done under microwaves become more productive though the grafting yield varied with the type of monomer used differing in their bond polarity.

**Cassia Seed Gums**

Cassia seeds are non-conventional renewable source of galactomannan polysaccharides; they have close structural resemblance to commercial seed gums such as guar and locust bean gums. Cassia seed gums differ from guar gum in their galactose to mannose ratio, molecular sizes and secondary structures, which may vary from source to source. Therefore, on vinyl modification they are expected to furnish copolymers of different properties and characteristics than that of the guar gum. Different species of Cassia with differences in their galactose, mannose, and xylose ratios were grafted with different vinyl monomers conventionally as well as under microwave in both aqueous and dry media. The microwave grafting reactions were carried out in the absence of any initiator, in a domestic microwave oven in microwave initiated manner. To obtain the optimal conditions, various reaction parameters were varied, one at a time while keeping the others fixed and a comparative evaluation was made on the basis of %G and %E. Though the Cassia seeds gums under study had the same constituent monosaccharides, their behavior to accept vinyl grafts on microwave grafting was very different as reflected by the difference in grafting yields and efficiencies in different sets of experiments. Thus, it is clear that at the same monomer concentration, the microwave power and exposure time required to reach the optimum grafting depends on the polysaccharide type i.e. ratio of the component sugars in them, their molecular weight and the secondary structures. This observation also suggest that by controlling the molecular size of the polysaccharide (by partial depolymerization), the grafting under microwave can be controlled to bestow the desired properties in the copolymeric materials. However, this is an area for future research in high performance biomaterials. *Cassia marginata* seed gum was grafted with poly(methylmethacrylate) using both conventional and microwave procedure. Microwave grafting was done in microwave initiated manner in the absence of initiator or catalyst and the resulting copolymer was used for the Cr(VI) removal from solution. The conventionally prepared copolymer was found less efficient in Cr(VI) removal (from solution) as compared to the microwave synthesized copolymer. This is due to the incorporation of extra grafts under microwave conditions, which in turn offer extra sites for the surface adsorption of the cation. No direct evidence is available for the presence of extra grafts except the gravimetric increase of the polysaccharide weight after grafting due to the incorporation of larger and/or more frequent grafts of same size at the polysaccharide back bone. This difference is due to the enhanced reaction rate under microwave dielectric heating conditions.

Acrylonitrile and acrylamide have been grafted on *C. marginata* seed gum using a microwave initiated method without initiator or catalyst on neutral alumina support. Acrylonitrile was grafted on *C. marginata* very efficiently using neutral alumina support in microwave initiated grafting (without initiator/catalyst) while under same conditions %G and %E were poor in microwave initiated aqueous grafting though such grafting reactions were found quite successful in guar gum and chitosan. This difference can be attributed to the structural differences of the polysaccharides/monomers used. Aqueous grafting in *C. marginata* was more facile under conventional (in presence of initiator) conditions than under MWs. Similarly acrylamide was also very effectively grafted on *C. marginata* seed gum using neutral alumina support while the respective aqueous (microwave initiated and conventional thermal) grafting were much less efficient. However, no grafting was observed under microwave assisted grafting.

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conditions when an initiator was used in a alumina supported microwave grafting reaction of \emph{C. marginata}, rather a pink coloration was observed along the sides of the reaction vessel, possibly due to decomposition of the polysaccharide in pink colored furfural derivatives as a result of superheating which results due to the uncontrolled dielectric heating in the presence of a radical initiator.

Though the microwave grafting on a solid support can be generalized, the grafting yield can differ for different monomer types and gum-to-alumina ratios used. The type of microwave oven used could also be one of the deciding factors. Due to the easy availability and low cost, studies have been conducted in a multimode domestic oven, even though the monomode microwave oven could have an edge over this mode of oven. Owing to the non-homogeneous distribution of the energy throughout the cavity, it is possible that some areas receive higher amounts of energy (hot spots) whereas others receive less energy (cold spots), which may also affect the grafting efficiency. Though comparative evaluation of the work has not been carried out in mono and multimode oven, it is possible that the grafting efficiency could be further enhanced using the monomode microwave oven, giving a further scope to this line of work.

It was evident that the method was fairly applicable for both the monomers under study. After each cycle, the alumina support could be recovered, and the reaction was found to be reproducible on the recovered alumina which did not lose much of its efficiency. Further, the use of a solid support in the copolymer synthesis did not add much to the cost. The absence of solvents coupled with the high yields and short reaction times makes the procedures very attractive for polysaccharide grafting.

**Starch**

Starch is a low cost abundantly available renewable biopolymer having a source dependent structure like Cassia seed gums and has a wide range of applications in its native and modified form. In its crude form, starch is a mixture of two polymers of anhydrous glucose units, i.e., amylose and amylpectin.\(^2\) Amylose is present at levels up to 25% depending upon the source and amylpectin is the major fraction with levels up to 95%. Amylose is essentially a linear polymer of 1,4-linked α-d-glucopyranosyl units with molecular weight ranging from 10,000 to 60,000 g mole\(^{-1}\). On the other hand, amylpectin is a highly branched polymer of α-d-glucopyranosyl residues linked together mainly by 1–4 linkages with 1–6 bonds at the branch points\(^2\) \(^6\) with a high molecular weight, between 105 and 107 g mole\(^{-1}\). Besides the synthesis of biodegradable polysacrylates and chemically modified starch\(^6\) in solvent-free or aqueous-based reaction systems, microwave irradiation has also been used for the grafting modification of starch. Polycaprolactone was successfully grafted on starch under heterogeneous conditions in 3 min, yielding as high as 24% grafting efficiency and 25% grafting degree.\(^6\) Similarly, acrylonitrile\(^2\) and acrylamide\(^2\) were grafted on soluble potato starch in high yield in very short time using very low concentration of potassium persulfate as initiator in a microwave assisted homogeneous grafting experiment. Optimum sample of starch-graft-poly(acrylamide) (St-g-PAM) had 160%G with 89% efficiency and the reaction was carried out using 0.1 M acrylamide, 0.0025 M potassium persulfate, 0.1 g soluble starch/25 mL (H\(_2\)O), 720W microwave power in 60 s (temperature 98 °C). However, when acrylonitrile was grafted on starch, the optimum copolymer sample (St-g-PAN) had 225%G and 98% efficiency at 0.17 M acrylonitrile, ammonium persulfate (0.0014 M), 0.1 g soluble starch/25 mL (H\(_2\)O) at 100% power in 70 s (temperature 98 °C). These graftings could be accomplished quite quickly and the process did not require an inert atmosphere, both being major advantages. It was observed that even at higher temperatures, the same amount of potassium persulfate was not capable of initiating grafting under conventional thermal grafting reactions. Sodium acrylate has been grafted on corn starch,\(^6\) with potassium persulfate (KPS) as initiator and polyethylene glycol diacrylate (PEGD) as the cross-linker in a microwave assisted grafting. Microwave power was believed to be the most significant factor affecting the swelling ratio and solubility of the product. Optimized experimental results showed that 10 min of microwave irradiation at 85-90 W could produce a corn starch-based belonging to the family Araceae. Chemically it consists of mannose and glucose in a molar ratio of 1.61, respectively, with an 1–4 linkage. The native polysaccharide contains an acetyl group per 12 or 18 repeating units. Konjac acetate is obtained by acetylation Konjac glucomannan with acetic anhydride.\(^6\) The microwave assisted ring-opening polymerization of cyclic monomers like caprolactone was successfully extended to grafting reactions between different biodegradable polymers, such as starch and Konjac in the presence of Sn (Oct). Konjac acetate has been
Xanthan Gum

Xanthan gum is a polysaccharide produced by the fermentation of the bacterium *Xanthomonas campestris*. This organism is found in nature on the leaf surfaces of green vegetables, particularly the cabbage family. The gum is used as a food additive and rheology modifier. The %G of poly(acrylamide) on xanthan gum under microwave-initiated grafting has been found to be much higher (190%G in 100 s, 100% power) as compared to ceric-induced conventional grafting (62.87%G). The grafting yield was found directly proportional to the microwave power and exposure time. The swelling of the xanthan gum was found to vary inversely with the %G, while erosion varied directly with the %G. The microwave-assisted graft copolymerization was used as an efficient tool to modify the release properties of xanthan gum by the grafting of acrylamide on xanthan gum.

Xyloglucan

Xyloglucan (XG), a water-soluble food grade polysaccharide, extracted from tamarind seed mucilage has been reported as a substrate for the graft copolymerization of acrylonitrile. Polymerization was initiated with XG both conventionally by ceric ions in an aqueous medium under N2 atmosphere and also under microwave irradiation. In the microwave initiated grafting reaction where no initiator was used, 92.5%G was achieved using 0.5 M acrylonitrile, XG (1 g/200 mL (H2O)), temperature 60 ◦C, microwave power 150W in 120 s. Conventionally, under same monomer and polysaccharide concentration, 76%G was achieved in 24 h using ceric ammonium nitrate (0.001 M) as initiator at 40 ◦C.

EFFECT OF POLYSACCHARIDE TYPE ON GRAFTING

It is difficult to compare and contrast the polysaccharides in terms of the ease with which they can be grafted, as different parameters and reaction conditions have been used by different workers for the grafting of the polysaccharides, and for most such studies, domestic microwave ovens have been used, for which temperature cannot be monitored very precisely. However, the %G in uncharged polysaccharides such as glactomannans depends on the ratio of the constituent monosaccharides and also on the monomer type being grafted. As the branching increases, the optimum grafting is obtained at lower microwave power, e.g., for obtaining optimum grafting (130%) of AM at CJ (Gal:Man = 1:3), 40 s exposure of 640 W microwave power was required, while in the case of guar gum (Gal:Man = 1:2 ratio), optimum grafting (288%) was achieved in 50 s using 480 W microwave power. This is explained by the increase in galactose content since galactose is present as side chains and higher branching offer more sites for the generation of macro free radicals which in turn results in higher %G. *C. marginata* when grafted with MMA, AN and AM under aqueous microwave conditions, also show difference in optimum %G, which is highest for MMA and lowest for AN. The higher microwave power (960 W) needed for grafting AN on CM gum correlates with differences in the polarity of the monomer type. The comparison of the behavior of different polysaccharides with reference to their chemical structure is difficult to make and the effect of polysaccharide charge type on the microwave grafting reactions is still a matter of future research and require much thorough investigations using monomode cavity where precise control of the temperature and pressure is possible.

MECHANISM

Microwave-enhanced chemistry is based on the efficiency of the interaction of molecules in a reaction mixture (substrates, catalyst and solvents) with electromagnetic waves generated by a “microwave dielectric effect” depending upon the specific polarity of the molecules. Polysaccharide grafting reactions when performed under the influence of microwaves become more productive and selective. Conventional thermal grafting reaction usually results in low grafting yields due to the competing homopolymerization but under microwaves, copolymerization is the favored reaction. This difference in the product selectivity results due to the different heating rates under the two conditions, microwave or thermal. In microwave reactions, while the microwave power is dissipated over the whole volume of the reaction mixture, the heat loss occurs at the outer surface, only where the nucleation points for boiling are available. This sets up a reverse thermal gradient to induce super boiling as the loss of excess of thermal
energy by boiling is possible only at the side of the reactor or at the solvent–air interface. However this volumetric heating does not always translate into homogeneous temperature distribution as different constituents of the reaction mixture convert the microwave field energy into heat by different amounts. In most polysaccharide grafting reactions, water is the solvent of choice, as many polysaccharides are soluble in water. Water being polar in nature, has a good potential to absorb microwaves and convert them to heat energy. Therefore, aqueous grafting reactions when performed under microwaves are much more accelerated then those done under conventional grafting reactions and this accounts for the high yield in the microwave grafting reactions. It is well known that water can be rapidly heated to high temperatures in the presence of salts when exposed to microwaves and because of the very high heat capacity of water, there is a certain control on the reaction temperature.31

Depending on the overall miscibility of the monomers, catalyst and cross-linkers that are used as reactants in a grafting reaction, the system may be homogeneous or heterogeneous. Even for the reactions where polysaccharides are used in solution form, heating will not be homogeneous as polysaccharides usually do not form true solutions. Polysaccharide solutions along with other additives such as redox initiator and/or monomer form a heterogeneous system which being anisotropic in terms of the loss tangents of the components, result in inhomogeneous energy dissipation leading to temperature gradient. The presence of higher temperature zones (hot spots) results in the heat transfer processes between the different domains of the reaction system. In a system where the heat transfer is slow, a steady state hot spot is possible that may enhance the rate of the chemical reaction within that hot zone.

The use of microwaves can significantly reduce the reaction time besides eliminating the requirement of radical initiators and/or catalyst.59 While under thermal conditions, no grafting takes place without an initiator, under microwave conditions it takes place without the addition of an initiator. In contrast to conventional grafting reactions in which oxygen acts as an inhibitor and has to be expelled before performing the grafting reaction, microwave irradiation could substantially accelerate the synthesis with no need of O2 removal.59,60 Though the reason for this difference has not been established experimentally, an assumption may be made that under microwave conditions, the inactive free radicals that are formed by the combination of oxygen with the primary radicals are unstable and therefore reverse back to the primary radicals for further propagation of the grafting reaction. This could also be related to the higher temperatures generated under microwaves,60 or perhaps to the shorter reaction times associated with higher temperatures, such that O2 initially present and consumed in scavenging radicals is not replaced faster than the radicals formed, which in turn can react with the monomers.

FUTURE ASPECTS

Researchers worldwide are interested in the area of biopolymer development. The German government has stringent regulations in place regarding acceptable emission levels. In 1990, the German government published a call for research and development of biodegradable thermoplastics. For this reason, many German material scientists and engineers have focused their work on environmentally stable biodegradable plastics. Various materials have been created by these researchers, including the Bayer BAK line which was introduced in extrusion and injection moulding grades in 1996. Novamont, an Italian company, introduced the Mater-Bi line for similar reasons. Queen Mary University in London, England, has a plastics department which is actively working on biocomposite development. As a whole, all European nations are expected to follow the European Packaging directive, which expects a material recovery of packaging waste. Organic recovery (composting spent materials) is the most commonly applied waste reduction method. European nations are also expected to incorporate 15% w/w of recycled plastics into the manufacture of packaging materials. Germany aims to better that level, as they set tier goal in 2001 for a 60% incorporation of recycled plastics into new packaging materials.

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CONCLUSION
There are a seemingly limitless number of areas where biodegradable polymer materials may find use. The sectors of agriculture, automotives, medicine, and packaging all require environmentally friendly polymers. Because the level of biodegradation may be tailored to specific needs, each industry is able to create its own ideal material. The various modes of biodegradation are also a key advantage of such materials, because disposal methods may be tailored to industry specifications. Environmental responsibility is constantly increasing in importance to both consumers and industry. For those who produce biodegradable plastic materials, this is a key advantage. Biopolymers limit carbon dioxide emissions during creation, and degrade to organic matter after disposal. Although synthetic plastics are a more economically feasible choice than biodegradable ones, an increased availability of biodegradable plastics will allow many consumers to choose them on the basis of their environmentally responsible disposal. The processes which hold the most promise for further development of biopolymer materials are those which employ renewable resource feedstocks. Biodegradable plastics containing starch and/or cellulose fibres appear to be the most likely to experience continual growth in usage. Microbially grown plastics are scientifically sound, and a novel idea, but the infrastructure needed to commercially expand their use is still costly, and inconvenient to develop. Time is of the essence for biodegradable polymer development, as society’s current views on environmental responsibility make this an ideal time for further growth of biopolymers.

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DECLARATION OF INTEREST
It is hereby declared that this paper does not have any conflict of interest.

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