Microwave-assisted modifications of polysaccharides

Jacques Desbrieres, Charlotte Petit, Stephanie Reynaud

HAL Id: hal-01564099

https://hal.science/hal-01564099

Submitted on 18 Mar 2021

Conference paper

Jacques Desbrières*, Charlotte Petit and Stéphanie Reynaud

Microwave-assisted modifications of polysaccharides

Abstract: Polysaccharides are a natural and renewable feed stock for synthesizing high performance macromolecular materials. However, their structure does not allow reaching all properties required for specific applications and chemical modifications are necessary to reach such objectives. Despite the use of natural polymers, the chemistry and processes employed are not environment-friendly due to the nature of chemicals, solvents or because the conventional chemical process are energy-consuming. On the other hand, microwave assisted processes were developed in organic chemistry since the 1980s and more recently for polymer chemistry (polymer formation and modification). Within the chemistry of natural polymers, the use of microwave irradiation has been exploited in the past two decades to alleviate limitations in the synthesis of graft modified polysaccharide materials. Microwave heating is described as more homogeneous, selective and efficient as compared to conventional heating resulting in faster reactions with fewer or no side products as example. Different results reported within the recent literature will be discussed considering the role of microwave irradiation and its consequence on the reaction parameters and properties of final materials. Grafting of polysaccharides, specific modification of polysaccharides or fibers particularly for preparing smart textiles or medical products as well as reactions of polysaccharides to valuable bio-platform molecule will be discussed.

Keywords: grafting; modifications; microwave chemistry; POC-2014; polysaccharides.

Introduction

Polysaccharides are a natural and renewable feed stock for synthesizing high performance macromolecular materials [1, 2]. They are abundant in nature, universally found in almost all living organisms. They are present in various tissues of seeds, stems and leaves of plants, body fluids of animals, shells of crustaceans and insects. They are also found in the cell walls and extra cellular fluids of bacteria, yeast and fungi. However their structure does not allow achievement of all properties required for specific applications and chemical or enzymatic modifications are necessary to reach such objectives. Modifications are often carried out through derivatization of functional groups, grafting of polymeric chains, oxidative, hydrolytic as well as

*Corresponding author: Jacques Desbrières, Université de Pau et des Pays de l'Adour/CNRS, Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les Matériaux (IPREM, UMR 5254), Helioparc Pau Pyrénées, 2 Avenue P. Angot, 64053 PAU cedex 9, France, e-mail: jacques.desbrieres@univ-pau.fr
Charlotte Petit and Stéphanie Reynaud: Université de Pau et des Pays de l'Adour/CNRS, Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les Matériaux (IPREM, UMR 5254), Helioparc Pau Pyrénées, 2 Avenue P. Angot, 64053 PAU cedex 9, France

enzymatic degradations…. Despite the use of natural polymers, the chemistry and the processes employed are no longer environment-friendly mainly due to the nature of chemicals, solvents and because the process is energy-consuming. To reduce these drawbacks, research groups studied environment-friendly processes during the last years with the objective to reach so many "green chemistry" principles [3] as possible. Among the processes, radiation-induced techniques (gamma rays, electron beam, Ultra Violet or microwave) show an increased development during the last decades. In particular, microwave assisted processes were developed in organic chemistry since the 1980s and for polymerization reactions only more recently [4]. The use of microwave irradiation as an energy source for polymer chemical reactions has been extensively investigated during recent years [5]. Specifically it has been exploited in the past two decades to alleviate limitations in the synthesis of graft modified polysaccharide materials [6].

Microwave irradiation (MW) consists in electromagnetic waves and standard equipments operate at a frequency of 2.45 GHz to avoid interferences with radio and radar frequencies. Within this region of electromagnetic energy, only molecular rotation is affected, not molecular structure. The energy involved in matter-MW interactions (calculated from Planck's law) is much lower than the energy of Brownian motion, hydrogen interactions and those that induce chemical activation. As a direct consequence, no reaction exists that only proceeds in the microwave field but it occurs quicker and is more selective. They are always similar under classical reactions, i.e., thermal heating. Microwaves couple directly with the molecules that are present in the reaction mixture, leading to an instantaneous and localized rise in temperature. Microwave heating also offers facile reaction control, it can be described as "instant on – instant off". Under microwaves, polar molecules try to align themselves with the rapidly changing electric field of the microwave and results in a transfer of energy. Absorption of MW by materials is mainly connected with electromagnetic interactions which are specific to polar or ionic molecules. Up to now, some research teams still carry out assisted microwave chemistry using modified domestic ovens, the experimental conditions are then difficult to control and reproduce and the results have to be deeply analyzed to compare the results with those conducted under conventional heating. From the late 1990s, more reliable equipment with proper control over temperature (equipped with cooling system in most cases), stirring and pressure have been developed. Two types of microwave reactors are nowadays available for chemists; multi-mode and mono-mode (or single-mode). Within the later, the electromagnetic beam is focused and located in the center of the reaction vessel; therefore, the reactor cavity is designed for dedicated vessel. This enables the reactive medium to be placed in the position of maximum electric field for optimum transfer of the electromagnetic energy.

We present examples to illustrate the interest of such processes to modify the structure and/or the architecture of polysaccharides in relation with their applications without having the objective to be exhaustive and present a complete review of such a very wide domain.

Grafting of polysaccharides

Grafting of synthetic monomers onto natural polymers is of great interest because of its application in the biomedical and biodegradable materials, as examples. Synthetic protocols for graft polymerization can be classified into three main groups, free radical polymerization, ionic and ring opening polymerization and living radical polymerization. Polymer chains are grafted on polysaccharides through three main strategies: the "grafting through", the "grafting on" and the "grafting from" processes. The "grafting from" approach is one of the most commonly used and gives products with high graft density owing to easy accessibility of functional groups. It involves the use of a natural polymer with pendant functional groups which can be activated to initiate the tethering of an incoming monomer. Microwaves irradiation is one of the most contemporary techniques used in graft copolymer synthesis. Their utility stems from the fact they cause selective and targeted excitation of only polar bonds, resulting in their cleavage and consequent generation of radical sites [7]. The C–C backbone of the preformed polymer being relatively non polar remains unaffected by microwave irradiation. Thus, the structural integrity of the backbone remains intact. Microwave based graft copolymer synthesis is further classified into two types: microwave initiated synthesis (using microwave irradiation

alone to initiate grafting) and microwave assisted synthesis (using a synergism of microwave irradiation and chemical free radical initiator to initiate the grafting reactions) [8]. Moreover, taking into account environmental and safety considerations, attempts to replace organic solvents by safer and more environment friendly medium present a new, and now deeply developed interest. In this context, using a polar medium such as water appears to be an interesting option because of its abundance, non-toxic, non-corrosive and non-flammable nature [9].

A first example concerns polyacrylamide-grafted-tamarind kernel polysaccharide (TKP) [8] and its use as a biodegradable polymeric flocculant. Flocculation is a means of removing organic and inorganic contaminants from wastewater and involves the aggregation of dispersed particles into larger flocs that can be separated from the water. Organic or inorganic chemicals can be used for such an application. Natural flocculants have the advantage of low cost and biodegradability [10] but this latter character is also a drawback, since it potentially reduces storage life and the flocculation performance [10]. Grafting polyacrylamide chains onto polysaccharides allows developing efficient flocculants combining the best properties of both components [11, 12]. The grafted polymers are usually synthesized by conventional redox grafting methods [13], γ-ray irradiation [14] or by using electron beams [15]. Polyacrylamide-grafted-tamarind kernel polysaccharide was prepared by conventional redox grafting, microwave-initiated and microwave-assisted grafting. Flocculation efficiency was determined by the measurements of turbidity and the reduction of the total pollutant load of the different wastewaters. Under their experimental conditions, the authors noted the formation of free radicals from the polysaccharide backbone and acrylamide monomers. These free radicals would recombine with each other through initiation, propagation and termination steps to produce graft copolymers (Fig. 1).
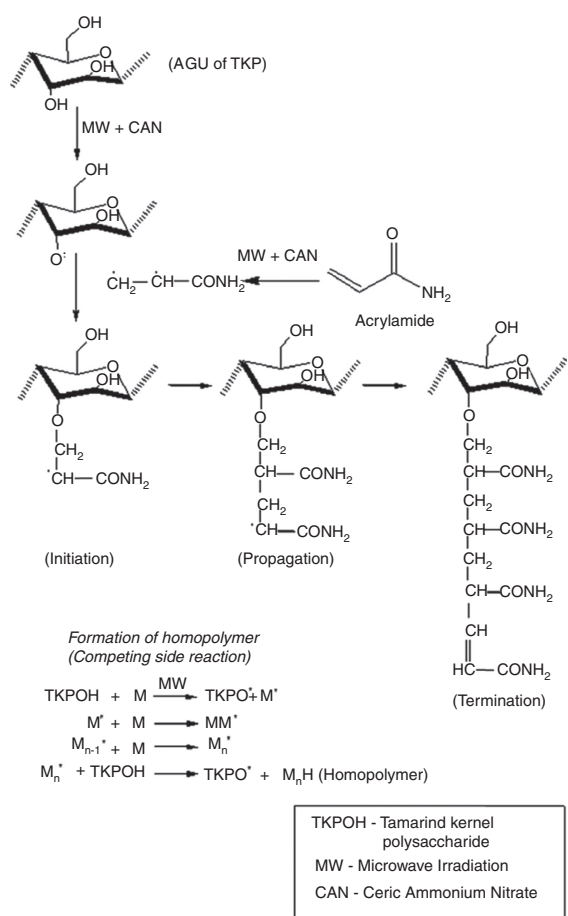

Fig. 1 Schematic representation for the synthesis of TKP-*g*-PAM by microwave-assisted method ([8], reproduced from Bioresource Technology with permission from Elsevier).

Table 1 Synthesis parameters of TKP-*g*-PAM ([8], reproduced from Bioresource Technology with permission from Elsevier).

Polymer grade	Amount of TKP[a] (mol)	Amount of AM (mol)	Amount of CAN (mol×10⁻⁴)		% Grafting[b]	Intrinsic viscosity (dL/g)
Conventional synthesis						
TKP-g-PAM 1 (C)	0.0061	0.14	0.21		32	4.01
TKP-g-PAM 2 (C)	0.0061	0.14	0.525		36	4.226
TKP-g-PAM 3 (C)	0.0061	0.14	1.05		29	3.821
TKP-g-PAM 4 (C)	0.0061	0.17	0.525		38	4.37
TKP-g-PAM 5 (C)	**0.0061**	**0.21**	**0.525**		**45**	**4.7**
TKP-g-PAM 6 (C)	0.0061	0.28	0.525		41	4.45

Polymer grade	Amount of TKP[a] (mole)	Amount of AM (mol)	Exposure time (min)		% Grafting[b]	Intrinsic viscosity (dL/g)
Microwave-initiated synthesis						
TKP-g-PAM 1 (MI)	0.0061	0.07	1		18	3.02
TKP-g-PAM 2 (MI)	0.0061	0.07	2		22	3.42
TKP-g-PAM 3 (MI)	0.0061	0.07	3		28	3.75
TKP-g-PAM 4 (MI)	0.0061	0.07	4		24	3.6
TKP-g-PAM 5 (MI)	0.0061	0.14	3		30	3.9
TKP-g-PAM 6 (MI)	0.0061	0.17	3		37	4.2
TKP-g-PAM 7 (MI)	**0.0061**	**0.21**	3		53	**5.6**
TKP-g-PAM 8 (MI)	0.0061	0.28	3		46	4.9

Polymer grade	Amount of TKP (mol)	Amount of AM (mol)	Amount of CAN (mol×10⁻⁴)	Time (min)	% Grafting	Intrinsic viscosity (dL/g)
Microwave-assisted synthesis						
TKP-g-PAM 1 (MA)	0.0061	0.07	0.105	1	42	4.12
TKP-g-PAM 2 (MA)	0.0061	0.07	0.105	2	52	5.50
TKP-g-PAM 3 (MA)	0.0061	0.07	0.105	3	49	5.02
TKP-g-PAM 4 (MA)	0.0061	0.07	0.21	2	64	6.46
TKP-g-PAM 5 (MA)	0.0061	0.07	0.525	2	59	5.91
TKP-g-PAM 6 (MA)	**0.0061**	**0.14**	**0.21**	**2**	**87**	**S.98**
TKP-g-PAM 7 (MA)	0.0061	0.17	0.21	2	79	7.81
TKP	–	–	–	–	**0**	**2.8**

[a]Calculated on the basis of anhydroglucose unit (AGU). 1 mol of AGU=162 g.

[b] % Grafting=$\dfrac{\text{wt. of graft copolymer - wt. of polysaccharide}}{\text{wt. of polysaccharide}} \times 100$.

The bold values are related to polymers considered for flocculation experiments in Figure 2.

Different reaction conditions allow the preparation of different graft copolymers (Table 1).

Grafting reaction over TKP has been studied by varying both the concentrations of TKP, the monomer to be grafted and the redox initiator under both conventional and microwave heating. The grafted TKP exhibiting the highest performances has been obtained under microwave assisted reaction (entry TKP-g-PAM 6 (MA), Table 1). The reaction has been let under microwave only for few minutes under 900 W below 70 °C, while it takes 24 h under conventional heating to get a grafted polymer with lower performances. TKP-g-PAM 6 exhibits the highest radius of gyration. Within this study the measurement of the intrinsic viscosity is directly related to the length of the graft chains. The flocculation characteristics of grafted copolymers were compared in a kaolin suspension (Fig. 2).

The optimized grades of graft copolymers show the best flocculation efficiency. These copolymers have the highest percentage of grafting, intrinsic viscosity and higher molecular weight. These properties result in a higher radius of gyration as well as pervaded volume and hence a higher flocculation efficiency [16]. The reason for the better flocculating power of the graft copolymers over the linear polymer is essentially due to the polymer bridging; the segments of a polymer chain adsorb onto different particles linking the particles together [17].
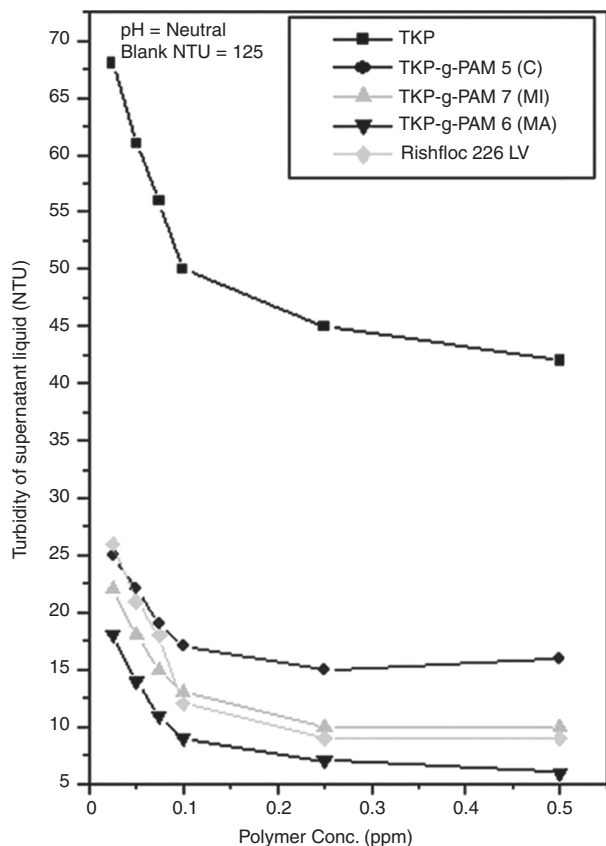
Fig. 2 Flocculation characteristics of kaolin suspension using various flocculants ([8], reproduced from Bioresource Technology with permission from Elsevier).

Another example in relation with similar applications is the grafting of methylmethacrylate onto *Cassia* seed gums [18]. Different species of Cassia with differences in the saccharide content were grafted with different acrylic monomers under conventional as well as under microwave heating in both aqueous and bulk media (Table 2).

Table 2 Grafting of acrylonitrile (AN), acrylamide (AM), methylmethacrylate (MMA) on various *Cassia* seed gums (CJ: *Cassia javanica*; CS: *Cassia siamea*; CM: *Cassia marbinata*) under conventional (CV) and microwave (Mw) conditions ([6], reproduced from Progress in Polymer Science with permission from Elsevier).

PS	Structure	Monomer (M)	Optimum conditions	Mode	%G	%E
CJ	Gal:Man (1.02:3.20)	AA (26×10^{-2})	CV (Aq)	Initiator (Aq)	110	23
			Mw: (640 W, 40 s	(AQ)	130	27
CS	Gal:Man:Xyl (3:6:2)	AN (26×10^{-2})	CV (Aq)	Initiator (Aq)	82	23
			Mw: 800 W, 120 s	(Aq)	150	43
CM	Gal: Man (1:2.7)	MMA (18×10^{-2})	CV (Aq)			
			Mw: 480 W, 40 s	(Aq)	270	59
		AN (18.2×10^{-2})	CV (Aq)	Initiator (Aq)	110	45
			Mw: 960 W, 80 s	(S)	184	76
			Mw: 960 W, 80 s	(Aq)	45	18
		AM (3.52×10^{-2})	CV (Aq)	Initiator (Aq)	200	40
			Mw: 480 W, 50 s	(S)	288	57
			Mw: 480 W, 50 s	(Aq)	132	57

%G percentage grafting.
%E percentage efficiency.

Though the *Cassia* seeds gums 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. It is clear that, at the same monomer concentration, the microwave power and exposure time required to reach the optimal grafting depends on the polysaccharide type, i.e., the ratio of the sugar components in the macromolecular backbone, the molecular weight and the secondary structure. This observation suggests that by controlling the molecular size of the polysaccharide (by partial depolymerization), the grafting efficiency under microwave irradiation can be controlled to target a material with specific properties. Microwave grafting was carried out in microwave initiated process in absence of initiator and the resulting copolymer was used for the Cr(VI) removal from solution (Table 3). The conventionally prepared copolymer was found less efficient in Cr(VI) removal as compared to the microwave synthesized one. As above, the grafting efficiency is better under microwave, and the modified polymer obtained under this experimental condition offers extra sites for the surface adsorption of cations.

The last example dealing with the modification of polysaccharides concerns the grafting of poly(*N*-vinyl-2-pyrrolidone) onto alginate and its application in controlled drug release [19]. *N*-vinyl-2-pyrrolidone is a hydrophilic and nonionic monomer and its polymerization may be easily initiated through thermal or photochemical free radical routes [20]. Poly(*N*-vinyl-2-pyrrolidone) (PVP) shows excellent biocompatibility with living tissues and low cytotoxicity, which makes it an excellent candidate as a carrier of some hydrophilic or hydrophobic drugs [21]. As an example, the grafting reaction of PVP onto alginate allows the preparation of pH-responsive beads containing Ibuprofen with high entrapment efficiency. PVP was grafted onto sodium alginate through microwave irradiation and the grafting mechanism is based on free radical mechanism using microwave irradiation in synergism with an azo-initiator (AIBN) to generate free radical sites on the polymer backbone. Ibuprofen was loaded within the hydrogel beads previously crosslinked with glutaric aldehyde. Beads formed are almost spherical in shape and showed rough and porous surface by comparison with smooth surface of sodium alginate beads, which is also a proof of PVP grafting onto alginate. The release results are in accordance with the equilibrium swelling degree, diffusion constant observations. The drug release mechanism from the grafted beads was found to be non-Fickian transport from the analysis using the Peppas model [22].

Specific modifications on polysaccharides

Polysaccharides possess functional groups (hydroxyl, amino...) which allow specific reactions either using any chemical or enzymatic process. The first example concerns the reductive amination of chitosan to prepare amphiphilic polysaccharides. Chitosan is a *N*-deacetylated derivative of chitin, which is one of the most abundant organic materials found in crustacean, mollusks and insects where it is an important constituent of the exoskeleton. Chitosan (Chi) is biodegradable, biocompatible, non-irritant [23] and exhibits good

Table 3 Cr(VI) removal by Microwave and Conventionally synthesized graft copolymer using 0.1 g/20 mL adsorbent dose at pH 1.0; $T = 30\ °C$, 150 rpm, and contact time 18 h (from [18]).

Polymer	Standard solution		Waste water	
	Cr(VI) (ppm) concentration	Removal (mg/g)	Cr(VI) (ppm) concentration	Removal (mg/g)
CM-*g*-PMMA (microwave synthesized)	10	1.99	9.09	1.68
	1000	124.40	909.5	104.41
CM-*g*-PMMA (conventionally synthesized)	10	1.02	9.09	0.58
	1000	13.06	909.5	8.91

CM, *Cassia marginata* seed gum; PMMA, poly(methylmethacrylate).

film-forming properties and high mechanical strength and adhesion [24, 25]. All these characteristics make it suitable for a wide range of applications such as controlled delivery systems [26–29], wastewater treatments [30, 31], packaging [32–34], separation membranes [35, 36], biosensors [37–39].

However, to improve its physico-chemical properties and widen the domain of applications it is possible to modify its structure due to the presence of hydroxyl and amino groups on the macromolecular chain. The presence of amino groups gives the opportunity of specific reactions such as N-alkylation, N-carboxylation or crosslinking... [40].

N-alkylation allows preparing amphiphilic derivatives of chitosan which possess specific properties such as rheological (and their autoassociative character) [41] or surface active characteristics [42]. This class of polymers has found a widespread use in technical formulations. Their main function is as rheology modifiers (particularly thickening agents) especially in aqueous based formulations within numerous industrial domains such as paints, oil recovery, cosmetic or foods [43], or emulsion stabilizers [44]. However, their elaboration process presents disadvantages considering environmental point of view either from the energy needs or the number and/or nature of chemicals involved. The alkylated chitosan derivatives were obtained by reductive amination following the procedure described by Yalpani and Hall [45]. The scheme of the reaction is given in Scheme 1.

A study has been conducted to compare conventional and microwave heating [46]. Whatever the chitosan sample, the target degree of alkylation and the temperature are, the yields obtained under microwave irradiation are larger than those obtained with conventional heating (Fig. 3). It is worth noticing that the microwave assisted reactions have been done within a monomodal mode and specific attention has been dedicated to the control of the irradiation and temperature profiles in order to have an accurate comparison between both types of heating.

The sample related to the 10 % alkylation of the larger molar mass chitosan can be specially considered: the microwave assisted reaction at 40 °C for 1 h allows a 35 % increase in the yield. When the different
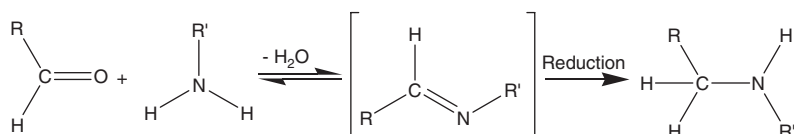
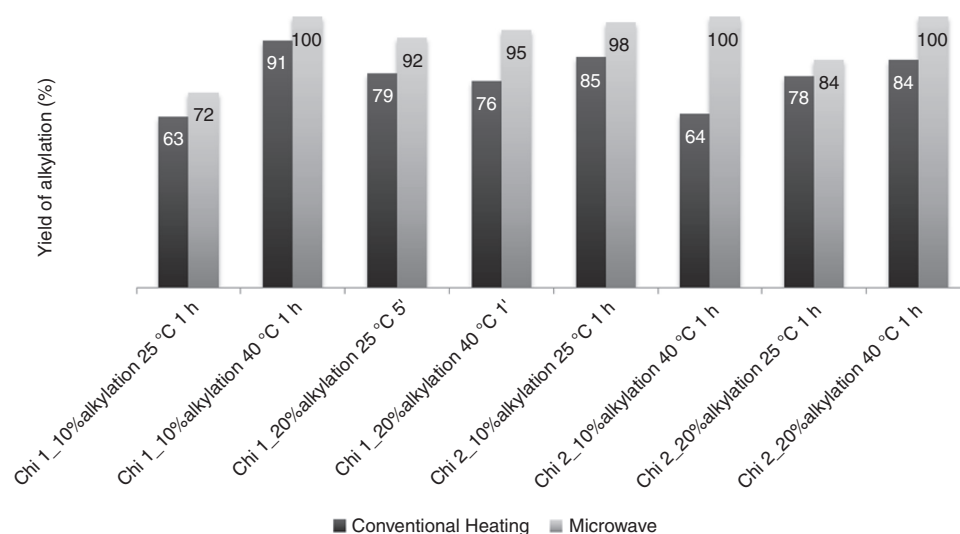**Scheme 1** Synthesis of amphiphilic derivative of chitosan.

Fig. 3 Comparison of yields obtained in synthesis of alkylchitosan using conventional heating or microwave irradiation (SPS mode, Irradiation power 30 W) ([46], reproduced from Carbohydrate Polymers with permission from Elsevier).

parameters (molar masses of chitosan to be modified, temperature and reaction duration) are considered it is observed that the molar mass has not a significant effect within the studied range (up to 200 000 g mol^{-1}). Moreover neither polymer degradation not deacetylation was observed during the reaction proceeded under microwave irradiation. The physico-chemical properties, either rheological or interfacial, are similar to those obtained with derivatives prepared using a conventional heating [46].

The enzymatic reactions may be also performed under microwave irradiation. Lukasiewicz and Kowalski [47] have carried out the low power microwave-assisted esterification of starch with acetic, lauric or stearic acid in presence of lipase. Lipases are a class of biocatalysts that may be employed in esterification, ester hydrolysis or transesterification processes [48]. Enzymes are known as very thermostable and active, even if an organic solvent is used as a reaction medium. Low power (80–160 mW/g of sample) microwave irradiation was used to allow the action of hog pancreas lipase on starch considering two solvents, DMSO known as a very good starch solvent and DMF as effective solvent for lipase meditated reactions. Using DMF suspensions result in higher degree of substitution and lower degradation. The application of DMSO as the reaction medium is also possible. But the differences probably rely on the nature of the solvent. More polar ones, like DMSO, seem to have stronger influence on the steric structure of the lipase molecules [49]. The conformation changes of the enzyme might affect its catalytic mechanism. The solvent effect does not depend on a heating method that additionally testifies its strong effect. Another explanation may be the solubility of starch in DMSO. After dissolution, the accessibility of hydroxyl groups for enzymatic reaction increases but the process causes a dramatic increase in the viscosity of the solution. In highly viscous solutions the diffusion process will reduce the overall reaction rate. Finally, due to the solubilization of the polysaccharide in DMSO, the final product lost its granular structure. The thermal effects are responsible for activation of the reaction at low power of microwaves but may also cause the inactivation of the enzyme when higher power is applied. Application of microwaves allows shortening the reaction times of about 2.5 times with slight increase in substitution. Shortening of the process has influence on degradation susceptibility, so the molecular parameters of the product, by means of average molar mass are higher than those observed at conventional conditions.

Fibers and microwaves

In the past decade, the demands on textile fibers have significantly increased. Large efforts have been made to implement additional functionalities on fibers which can be summarized by the term "smart textiles". Such smart textiles can offer thermo-responsive behavior, conductivity, self-cleaning effects... and for some of these applications fibers are modified with nanoparticles exhibiting specific properties. Among them, the incorporation of silver nanoparticles has proven to induce antimicrobial activity [50, 51]. In most of the cases, the manufacturing process involves a separate silver nanoparticle synthesis step followed by a loading of the particles onto the fibers using crosslinking agents or adsorption via electrostatic interactions as an example. For preparing silver nanoparticles, the reduction of silver (I) species is usually achieved using an excess amount of an external reducing agent such as $NaBH_4$, hydrazine...using elevated temperatures [52]. The high cost and the environmental impact caused by the use of reducing agents can be avoided by the replacement with reducing polysaccharides for silver nanoparticles synthesis. Using microwave irradiation the nanocomposite fibers may be obtained by an in situ process where silver nanoparticles are generated by the reduction of $AgNO_3$ in the presence of chitosan sulfate acting as a reducing agent in close spatial proximity to the fiber where adsorption takes place [53]. All nanocomposites exhibit similar mechanical strength compared to the unmodified fibers and show excellent microbial activity toward *E. coli* bacteria. Carefully conducted control experiments involving the generation of colloidal silver nanoparticles under microwave and conventional heating under otherwise identical reaction conditions demonstrate that no appreciable differences between particle size and morphology are found comparing both heating methods. However, the silver content of the modified fibers may be the same when the two heating processes are compared but with a reaction duration of 2 h in conventional heating conditions and only 5 min when microwaves are used (Fig. 4).
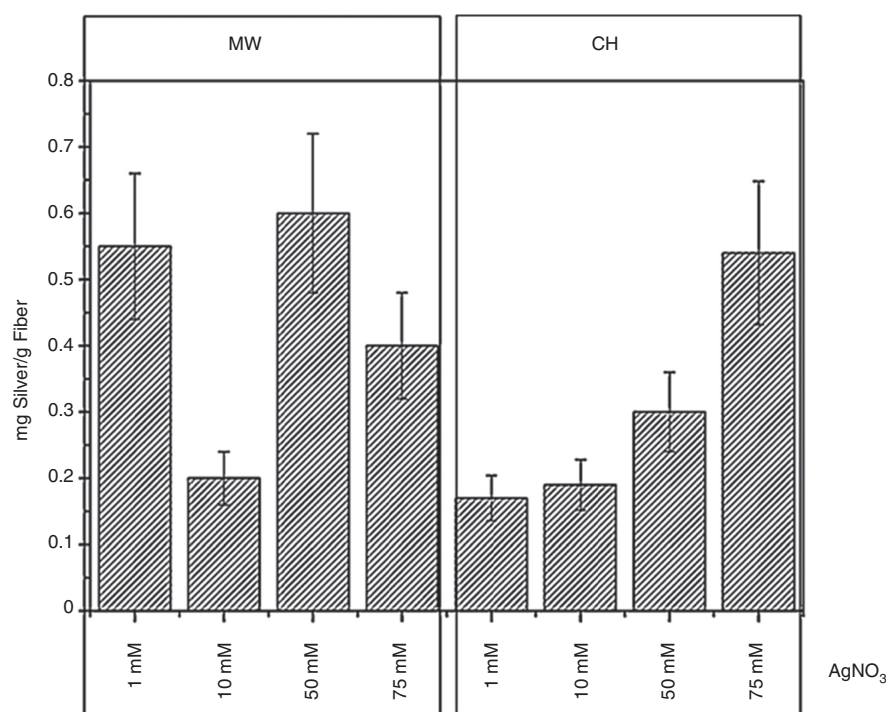
Fig. 4 Comparison of the silver content of the modified fibers in dependence of the initial AgNO$_3$ concentration obtained by microwave (MW, 80 °C, 5 min) and conventional heating (CH, 80 °C, 2 h) as determined by atomic absorption spectroscopy ([53], reproduced from Carbohydrate Polymers with permission from Elsevier).

Polysaccharides as valuable resources

During the last decades there has been increased interest in the development of friendly environmentally processes for the preparation of valuable chemicals from agricultural wastes. As the availability of the fossil fuel reserves will become limited, renewable naturally abundant resources are becoming a viable and an important alternative resource. Carbohydrates are the most abundant and inexpensive naturally occurring compounds. Lignocellulosic biomass, as an abundant renewable resource has the potential to become a sustainable supply for the production of chemical intermediates and fuels. Hemicellulose, constituted principally of xylans, polysaccharides consisting of D-xylose units is among the polysaccharide of major interest for such applications. Hydrolysis of xylans was considered to produce rare pentoses employing the catalytic effect of Mo(VI) ions and microwave irradiation as the thermal energy source [54]. This method led to a rapid release of D-xylose from xylans and its immediate transformation to rare aldose, D-lyxose. The combination of two steps makes the method possible to achieve reaction mixture of two valuable pentoses, D-xylose and D-lyxose (Scheme 2), which could be easily transformed to the corresponding alditols (D-xylitol and D-lyxitol) or furfural.

The results obtained by application of two heating techniques clearly show that the microwave irradiation caused the differences in the equilibration of the reaction mixtures and thus led to faster conversions and higher yields (Fig. 5).

Owing to differences in the mode of energy transfer different ratios of stereoisomers as a function of time was observed. The reaction equilibrium was shifted in both cases to the aldose with the lower value of conformational instabilities, thus a larger amount of D-xylose was present. A high input of energy allows the reaction to overcome the energy barrier for products formation very fast (2–3 min) compared to conventional conditions (20–25 h). Moreover this catalyst was also efficient in the transformation of mixed sources of pentoses to furfural (Scheme 3) where three simultaneous steps (hydrolysis, epimerization and dehydration reaction) are combined in a one-pot reaction.
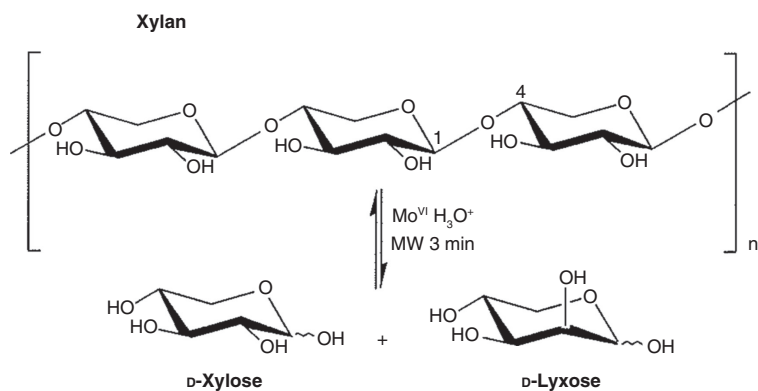
Scheme 2 Reaction scheme of xylan hydrolysis and simultaneous epimerization reaction of obtained D-xylose to D-lyxoze in microwave field ([54], reproduced from Carbohydrate Polymers with permission from Elsevier).
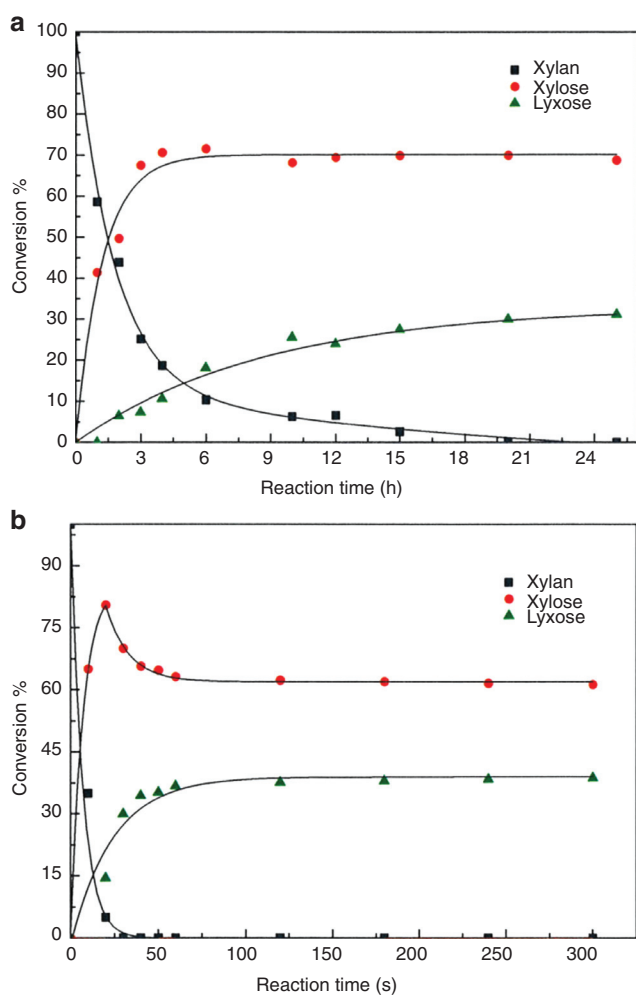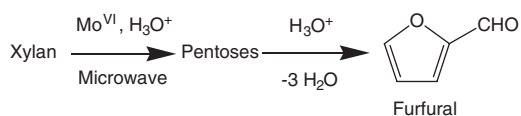

Fig. 5 Conversion of beechwood xylan (■), to D-xylose (●) and D-lyxoze (▲) as a function of time under conventional, oil-bath heating (a) or in microwave field (b) ([54], reproduced from Carbohydrate Polymers with permission from Elsevier).

Scheme 3 Microwave-assisted transformation of xylan to furfural.

Dramatically shorter reaction times (about two orders) and higher yields of products as compared to conventional methods make this method attractive and applicable also on a semi-preparative scale. Furfural can be considered as a synthon for furanic polymers, among them one finds high-modulus polyamides, insulating polyurethane foams, conjugated polymers for electronic and photonic applications... [55, 56].

Conclusion

Use of microwave irradiation was extended to polysaccharide chemical or enzymatic modification and widened their interest. Microwave heating is described as more homogeneous, selective and efficient as compared to conventional heating resulting in faster reactions with fewer or no side products, without affecting the original structure and physico-chemical characteristics of the polysaccharide. Microwave heating is not only an alternative for conventional thermal heating for such modifications, but it also offers an alternative environment friendly, cleaner, greener approach resulting in greater control and higher reproducibility in final product. Indeed, the use of water based solvents, dry media conditions but also low energy... present advancements in terms of safety, cost. Overall, it may be concluded that the current advancements in the area of polysaccharide modification under microwave irradiation have generated awareness on obtaining higher performance materials through such processes.

The combination of natural polymers and eco-friendly process based on microwave irradiation can be seen as an interesting breakthrough in the field of macromolecular "green chemistry".

References

[1] R. L. Davidson, *Handbook of Water Soluble Gums and Resins*. McGraw–Hill, New York (1980).

[2] J. N. BeMiller, R. L. Whistler (Eds.), *Industrial Gums: Polysaccharides and their Derivatives*, 3rd ed. Academic Press, New York (1992).

[3] P. T. Anastas, J. C. Warner. *Green Chemistry: Theory and Practice*. Oxford University Press, New York (1998).

[4] H. L. Chia, J. Jacob, F. Y. C. Boey. *J. Polym. Sci., Part A: Polym. Chem.* **34**, 2087 (1996).

[5] C. O. Kappe. *Angew. Chem. Int. Ed.* **43**, 6250 (2004).

[6] V. Singh, P. Kumar, R. Sanghi. *Progress in Polymer Science* **37**, 340 (2012).

[7] G. Sen, R. Kumar, G. Ghosh, S. Pal. *Carbohydr. Polym.* **77**, 822 (2009).

[8] S. Ghosh, G. Sen, U. Jha, S. Pal. *Bioresour. Technol.* **101**, 9638 (2010).

[9] V. Polshettiwar, R. S. Varma. *Chem. Soc. Rev.* **37**, 1546 (2008).

[10] R. P. Singh, B. R. Nayak, D. R. Biswal, T. Tripathy, K. Banik. *Mater. Res. Innovations* **7**, 331 (2003).

[11] R. P. Singh, S. Pal, S. Krishnamoorthy, P. Adhikary, S. K. Ali. *Pure Appl. Chem.* **81**, 525 (2009).

[12] R. Rahul, U. Jha, G. Sen, S. Mishra. *Carbohydr. Polym.* **99**, 11 (2014).

[13] H. M. Kang, Y. L. Cai, P. S. Liu. *Carbohydr. Res.* **11**, 2851 (2006).

[14] J. P. Wang, Y. Z. Chen, S. J. Zhang, H. Q. Yu. *Bioresour. Technol.* **99**, 3397 (2008).

[15] A. Vahdat, H. Bahrami, N. Ansari, F. Ziaie. *Radiat. Phys. Chem.* **76**, 787 (2007).

[16] W. Brostow, S. Pal, R. P. Singh. *Materials Letters* **61**, 4381 (2007).

[17] T. K. Healy, V. K. La Mer. *J. Colloid Sci.* **19**, 323 (1964).

[18] V. Singh, A. K. Sharma, P. Kumari, S. Tiwari. *Ind. Eng. Chem. Res.* **47**, 5267 (2008).

[19] M. Yigitoglu, G. Aydin, N. Isiklau. *Polym. Bull.* **71**, 385 (2014).

[20] Z-M. Liu, Z-K. Xu, J-Q. Wang, J. Wu, J-J. Fu. *Eur. Polym. J.* **40**, 2077 (2004).

[21] S. Jin, M. Liu, S. Chen, C. Gao. *Eur. Polym. J.* **44**, 2162 (2008).

[22] N. A. Peppas. *Pharm. Acta Helv.* **60**, 110 (1985).

[23] K. C. Gupta, F. H. Jabrail. *Carbohydrate Research* **342**, 2244 (2007).

[24] M. Mucha, K. Wankowicz, J. Balcerzak. J. *e-Polymers* **16**, 1 (2007).

[25] B. Wang, J. Zhang, G. Cheng, S. Dong. *Analytica Chimica Acta* **407**, 111 (2000).

[26] R. Hejazi, M. Amiji. *Int. J. Pharm.* **272**, 99 (2004).

[27] L. Illum. *Pharma. Res.* **15**, 1326 (1998).

[28] S. Shiraishi, T. Imai, M. Otagiri. *J. Controlled Release* **25**, 217 (1993).

[29] K. C. Gupta, M. N. V. Ravikumar. *Biomaterials*, **21**, 1115 (2000).

[30] G. Crini. *Bioresource Technology* **9**, 1061 (2006).

[31] P. Baroni, R. S. Vieira, E. Meneghetti, M. G. C. da Silva, M. M. Beppu. *J. Hazard. Mater.* **152**, 1155 (2008).

[32] I. Arvanitoyannis, A. Nakayama, S. Aiba. *Carbohydr. Polym.* **37**, 371 (1998).

[33] I. Arvanitoyannis. *J. Macromol. Sci.* **C39**, 205 (1999).

[34] C. Tual, E. Espuche, M. Escoubes, A. Domard, *J. Polym. Sci. Pol. Phys.* **38**, 1521 (2000).

[35] M. M. Beppu, R. S. Vieira, C. G. Aimoli, C. C. Santana. *J. Membrane Sci.* **301**, 126 (2007).

[36] W. Won, X. Feng, D. Lawless. *J. Membrane Sci.* **209**, 493 (2002).

[37] Y. Tsai, S. Chen, H. W. Liaw. *Sensor. Actuat. B-Chem.* **125**, 474 (2007).

[38] Z. Wu, W. Feng, Y. Feng, Q. Liu, X. Xu, T. Sekino, A. Fujii, M. Ozaki. *Carbon* **45**, 1212 (2007).

[39] L. Coche-Guerente, J. Desbrieres, J. Fatisson, P. Labbe, M. C. Rodriguez, G. Rivas. *Electrochimica Acta* **50**, 2865 (2005).

[40] M. Peter. *J. Macromol. Sci., Pure Appl. Chem.* **A32**, 629 (1995).

[41] J. Desbrieres. *Polymer* **45**, 3285 (2004).

[42] V. G. Babak, M. Rinaudo, J. Desbrieres, G. A. Vikhoreva, M. C. Michalski. *Mendeleev Commun.* 149 (1997).

[43] J. E. Glass. *Advances in Chemistry Series*, vol. 248. American Chemical Society, Washington, DC (1996).

[44] O. Carrier, R. Covis, E. Marie, A. Durand. *Carbohydr. Polym.* **84**, 599 (2011).

[45] M. Yalpani, L. D. Hall. *Macromolecules* **17**, 272 (1984).

[46] C. Petit, S. Reynaud, J. Desbrieres. *Carbohydr. Polym.* (2014), http://doc.doi.org/10.1016/j.carbpol.2014.04.083.

[47] M. Lukasiewicz, S. Kowalski. *Starch* **64**, 188 (2012).

[48] N. N. Ghandi, N. S. Patel, S. B. Sawant, J. B. Joshi, P. P. Wangikar, D. Mukesh. *Catal. Rev. Sci. Eng.* **42**, 439 (2000).

[49] M. N. Gupta, I. Roy. *Eur. J. Biochem.* **271**, 2575 (2004).

[50] J. H. Johnston, T. Nilsson. *J. Mater. Sci.* **47**, 1103 (2012).

[51] R. Dastjerdi, M. Montazer. *Colloids and Surf. B: Biointerfaces* **79**, 5 (2010).

[52] J. A. Dahl, B. L. S. Maddux, J. E. Hutchinson. *Chemical Rev.* **107**, 2228 (2007).

[53] D. Breitwieser, M. M. Moghaddam, S. Spirk, M. Baghbanzadeh, T. Pirec, H. Fasl, V. Ribitsch, C. O. Kappe. *Carbohydr. Polym.* **94**, 677 (2013).

[54] Z. Hricoviniova. *Carbohydr. Polym.* **98**, 1416 (2013).

[55] A. Gandini, M. N. Belgacem. *Prog. Polym. Sci.* **22**, 1203 (1997).

[56] A. Gandini, M. N. Belgacem. *Actualites Chimiques* 56 (2002).