microbial biotechnology

Minireview

Water-soluble polymers in agriculture: xanthan gum as eco-friendly alternative to synthetics

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Summary

Water-soluble polymers (WSPs) are a versatile group of chemicals used across industries for different purposes such as thickening, stabilizing, adhesion and gelation. Synthetic polymers have tailored characteristics and are chemically homogeneous, whereas plant-derived biopolymers vary more widely in their specifications and are chemically heterogeneous. Between both sources, microbial polysaccharides are an advantageous compromise. They combine naturalness with defined material properties, precisely controlled by optimizing strain selection, fermentation operational parameters and downstream processes. The relevance of such bio-based and biodegradable materials is rising due to increasing environmental awareness of consumers and a tightening regulatory framework, causing both solid and water-soluble synthetic polymers, also termed 'microplastics', to have come under scrutiny. Xanthan gum is the most important microbial polysaccharide in terms of production volume and diversity of applications, and available as different grades with specific properties. In this review, we will focus on the applicability of xanthan gum in agriculture (drift control, encapsulation and soil improvement), considering its potential to replace traditionally used synthetic WSPs. As a spray adjuvant, xanthan gum prevents the formation of driftable fine droplets and shows particular resistance to mechanical shear.

Xanthan gum as a component in encapsulated formulations modifies release properties or provides additional protection to encapsulated agents. In geotechnical engineering, soil amended with xanthan gum has proven to increase water retention, reduce water evaporation, percolation and soil erosion – topics of high relevance in the agriculture of the 21st century. Finally, hands-on formulation tips are provided to facilitate exploiting the full potential of xanthan gum in diverse agricultural applications and thus providing sustainable solutions.

Introduction

Efficiency in agriculture is continuously being improved by the implementation of new and high-performance materials. These are applied to beneficially modify the properties of soil, water, fertilizers and plant protection products.

One important class of chemical compounds are WSPs, which are widely used as thickeners, stabilizers and binders. Being of synthetic origin, their properties can be tailored and precisely controlled to obtain versatile functionalities and high reliability in performance. However, despite their high molecular weight, synthetic WSPs can break down over time into potentially toxic and carcinogenic monomers like in the case of polyacrylamides (Xiong et al., 2018). Their degradation is usually slow and has been estimated to be around 10% per year (Hennecke et al., 2018), which may result in deleterious effects on the environment. Due to a lack of analytical methods for the quantification of WSPs in environmental matrices, this impact is still under debate, but has been compared to issues caused by solid microplastics nowadays (Huppertsberg et al., 2020). In the case of synthetic WSPs, the research is still on the very beginning (Arp and Knutsen, 2019). Therefore, they have come under scrutiny by environmental protection agencies and regulatory bodies. Regulatory pressure peaked when the European Chemicals Agency (ECHA) published its proposal for a restriction of intentionally added microplastics in January 2019 (ECHA European Chemicals Agency, 2019), which in its initial version comprised not only

solids, but also synthetic WSPs in the definition of microplastics. Although in the latest version these are not comprised any more, researchers have further emphasized the importance of considering synthetic WSPs in the risk evaluation and regulating their release into the environment (Arp and Knutsen, 2019). With consumers becoming more and more aware of the broadened scope of microplastics, re-formulation efforts are intensifying to avoid the use of synthetic WSPs, especially in the cosmetics and home care segment. In the agricultural sector, manufacturers face additional regulatory changes. According to the new Regulation (EU) 2019/1009, non-nutrient polymers used in fertilizing products for the EU market will have to comply with biodegradability criteria (The European Parliament and the Council of the European Union, 2019). In practice, this means that non-biodegradable polymers used for controlled nutrient release or improved water retention will have to be replaced by biodegradable alternatives.

In view of recent findings on the presence of solid microplastic particles in drinking water (Pivokonsky *et al.*, 2018; Eerkes-Medrano *et al.*, 2019; Novotna *et al.*, 2019) and fresh produce (Oliveri Conti *et al.*, 2020), it is not unlikely that retailers will increasingly be confronted with end consumers calling for 'zero residue' products – also referring to microplastic residues. This may push for farming practices, in which only biodegradable, eco-friendly co-formulants, adjuvants, technological processing aids or soil amendments are used. Furthermore, the future might bring about stricter regulations on carbon emissions, thus favouring natural solutions over synthetic polymers of petrochemical origin.

These regulatory and market developments promote the search for biodegradable and environmentally friendly WSPs, which degrade into non-contaminating compounds. One alternative to synthetic polymers are natural polysaccharides. They can be subdivided into two main categories: the starch-based and non-starch polysaccharides. Non-starch polysaccharides can be obtained from plants (e.g. guar gum, locust bean gum, pectin), by microbial fermentation (e.g. xanthan gum and gellan gum), from animal origin (e.g. chitosan and gelatin) or from marine plants (e.g. alginate and carrageenan) (Nobre *et al.*, 2015). Plant-derived polysaccharides often struggle with fluctuating availability, yearly production and variations in their chemical characteristics. Their production is relatively cheap but season-dependent and taking place under uncontrolled environmental conditions (Giavasis, 2013). In contrast, polysaccharides derived from microbial fermentation are bio-synthesized under precisely controlled conditions, requiring limited space and production time. This results in stable chemical characteristics with narrow specifications and a high purity. It also ensures broad availability

in the market. Therefore, microbial polysaccharides unite the aspects of naturalness and compound quality in a unique manner.

Elaborating on the potential of one of the most prominent microbial polysaccharides, xanthan gum, to replace synthetic WSPs, we will look briefly into the function of microbial polysaccharides in nature, the transfer to industrial production and how the fermentation process can be fine-tuned to create products with distinct properties. We will discuss the use of xanthan gum in relevant technical applications and summarize further aspects influencing the performance of xanthan gum in a formulation.

Microbial polysaccharides: functionalities and their applicability in industry

In nature, microbial polysaccharides occur as essential components of biofilms. Biofilms are considered the main support of the oldest, most widely distributed and successful form of life on earth (Flemming, *et al.*, 2016b), and the predominant form of microorganisms lifestyle (Cavalcante *et al.*, 2017; Penesyan *et al.*, 2019). These biofilms are aggregates of microorganisms, in which cells are embedded within a self-produced matrix of extracellular polymeric substance (EPS) (Vert *et al.*, 2012; Flemming, *et al.*, 2016b). This matrix is mainly composed of polysaccharides, proteins, lipids and nucleic acids (Powell *et al.*, 2018), but the relative composition and molecular structure of components vary depending on the producing microorganism and environmental conditions. This fact can be exploited in industrial fermentation to obtain a range of microbial polysaccharides with different properties. Apart from xanthan gum, commercially relevant microbial exopolysaccharides include gellan gum produced by *Sphingomonas paucimobilis* (Giavasis *et al.*, 2000), pullulan synthesized by *Aureobasidium pullulans* (Cheng *et al.*, 2011) and welan gum obtained from *Alicaligenes* sp. (Kaur *et al.*, 2014).

Microorganisms produce polysaccharides for different purposes, many of which can be transferred to technological applications:

i. *Adhesive and structural properties*: One of the most important functions of microbial polysaccharides is to increase the adhesion capacity of microorganisms to each other and to surfaces (Smith *et al.*, 2016; Alaa, 2018). This adhesive characteristic also facilitates cell-to-cell interactions (Dos Santos *et al.*, 2018). In addition, polysaccharides provide a structure with viscoelastic properties to increase resistance of the biofilm to mechanical challenges (Peterson *et al.*, 2015). Taking advantage of this mechanism, increasing the viscosity of aqueous liquids is one of the most

relevant uses of purified microbial polysaccharides in technical applications. Furthermore, adhesion of particles to each other or to a target site is a central aim in different applications.

ii. *Protection from environment:* Biofilms help microorganisms to protect themselves in extreme environments (Yin *et al.*, 2019), against ultraviolet radiation (UV) (de Carvalho, 2017), extreme temperatures (Smith *et al.*, 2016; Kent *et al.*, 2018), pH variations (Narayanan *et al.*, 2016), salinity or drought stress (Alaa, 2018; Wang *et al.*, 2019) and limitation of nutrients (Gingichashvili *et al.*, 2020). In general, a biofilm can be described as a protective matrix in which both the polysaccharide-producing microorganisms and co-living cells are encapsulated. Looking at the industry, encapsulation is a relevant strategy in formulation of active agents to enhance their stability and ensure controlled release and improved efficacy. Additionally, the water retention capacity of polysaccharides can be utilized to support biological processes.

iii. *Nutrient availability:* Biofilms are a source of nutrients able to be used by the biofilm community (Flemming *et al.*, 2016a). They also facilitate the uptake and accumulation of nutrients from the environment (Kurniawan and Yamamoto, 2019). Latest studies described a channel structure in *E. coli* biofilms that allows for a distribution of nutrients through the biofilm (Rooney *et al.*, 2020). This channel structure could potentially be used as new route for plant nutrient availability and could have implications for the use of microbial polysaccharides in encapsulation.

Considering these functionalities, humans can imitate nature and use microbial polysaccharides with different purposes. We will depict the potential of xanthan gum in three relevant applications in agriculture:

Soil improvement: The water holding capacity and adhesiveness of xanthan gum open a wide field of uses in soil improvement, for example to ameliorate drought stress of plants and reduce erosion.

Drift control: The capacity of xanthan gum to modify the rheology of liquids and to increase adhesiveness is important in the effectiveness of foliar applications.

Encapsulation: In this formulation approach, which is highly relevant for the growing market of biostimulants and biocontrol agents, xanthan gum is a natural surrogate to protect microorganisms, thus potentially improving performance of the formulations.

Xanthan gum: Origin and structure

Isolated for the first time in 1959 (Jeanes *et al.*, 1961), xanthan gum is an EPS produced by different *Xanthomonas* spp. Even though mainly *X. campestris* strains are used in the production of xanthan gum, it can be also obtained from other *Xanthomonas* spp., like *X. citri* subsp. *citri* (Conforte *et al.*, 2019), *X. hortorum* or *X. axonopodis* (Demirci *et al.*, 2019).

Being a heteropolysaccharide, the primary structure consists of a cellulose-like backbone of β-1,4-linked glucose units, substituted alternately with a trisaccharide side chain (Jansson *et al.*, 1967). This side chain is composed of two mannose units separated by a glucuronic acid, where the internal mannose is mostly O-acetylated and the terminal mannose may be substituted by a pyruvic acid residue (Fig. 1). Due to the presence of glucuronic and pyruvic acid in the side chain, xanthan gum represents a highly charged polysaccharide with a very rigid polymer backbone. It has a high molecular weight of about 2×10^6 to 2×10^7 g mol^{-1} with a narrow distribution. Variations in fermentation conditions used in the production can influence the molecular weight of xanthan gum (Casas *et al.*, 2000). Via X-ray Powder Diffraction (XRD) measurements, the secondary structure of xanthan gum could be elucidated as a five-fold helical conformation, where the backbone is stabilized by the side chains (Moorhouse *et al.*, 1977).

As a naturally occurring microbial polysaccharide, xanthan gum can be biodegraded into oligosaccharides, monosaccharides and ultimately water and carbon dioxide. The depolymerization of the polysaccharide is achieved by enzymatic attack, mainly xanthanase (endo-β-d-glucanase) (Cadmus *et al.*, 1982) and xanthan lyase (Sutherland, 1987) secreted by other microorganisms. Production of xanthan gum degrading enzymes has been observed, e.g. in *Bacillus* (Cadmus *et al.*, 1982), *Paenibacillus* (Ashraf *et al.*, 2018), *Enterobacter* (Chen *et al.*, 2014) and *Cellumonas* (Liu *et al.*, 2005). While it was found that for a complete depolymerization into monosaccharides, as many as five enzymes are required (Nankai *et al.*, 1999), even a partial reduction in polymerization can be sufficient to reduce viscosity and functionality of xanthan gum (Chen *et al.*, 2014). The speed of degradation depends on the presence of microorganisms producing relevant enzymes and environmental conditions (Hovland, 2015). For example, xanthan gum was shown to be degraded by bacteria of activated sludge within 7 days (Muchová *et al.*, 2009). Unpublished own data confirm this fast degradation, showing a degradation by 78% within 28 days measured by a manometric respiratory test according to OECD test guideline 301F. On the other hand, some authors observed a certain resistance of xanthan gum to microbial degradation in the range of several months (Cadmus *et al.*, 1982; Hovland, 2015). This is beneficial when a long-term effect of xanthan gum is desired, such as in soil application.
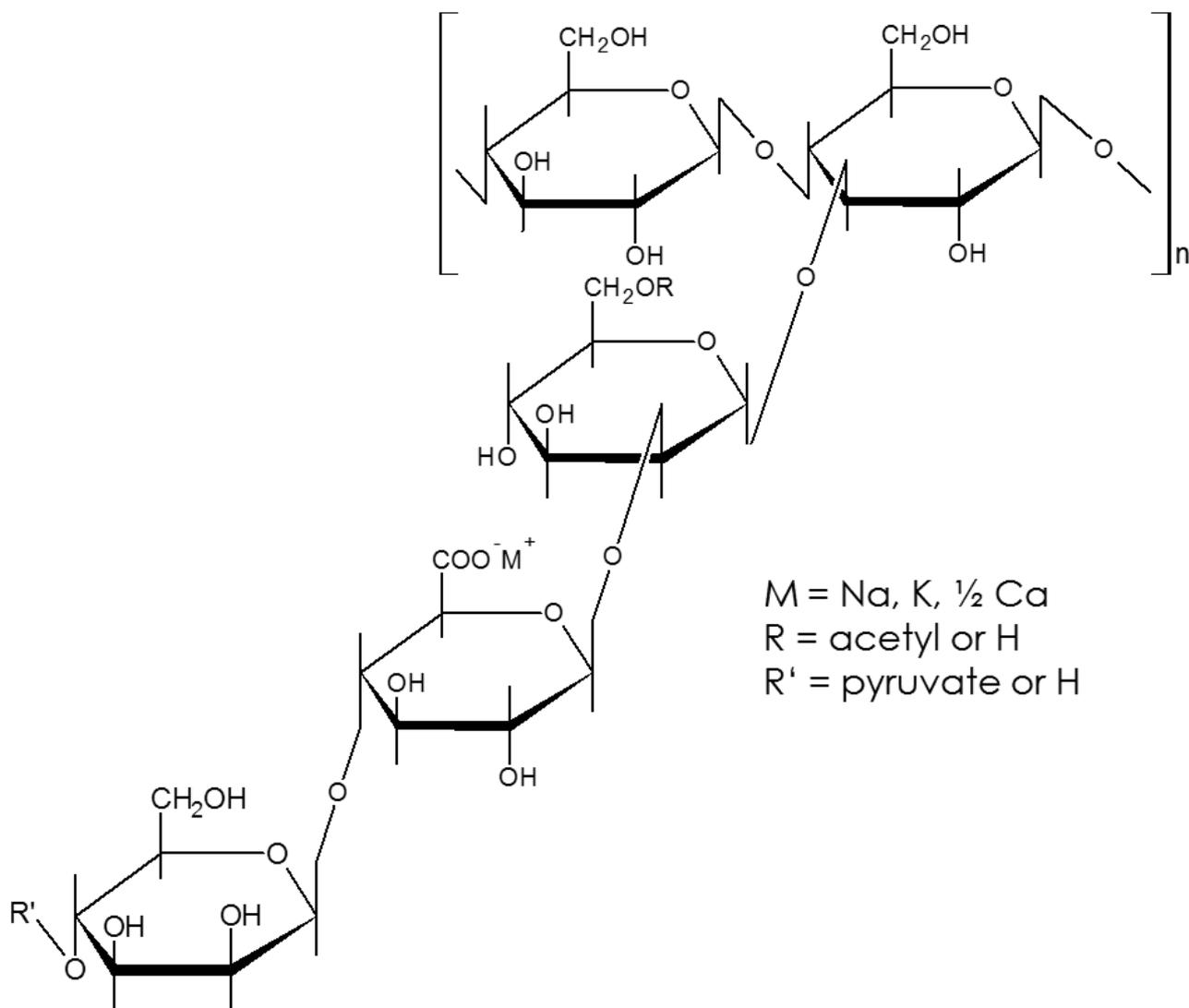
Fig. 1. Haworth formula of xanthan gum. The backbone consists of β-1,4-linked glucose units with a trisaccharide side chain whose terminal mannose unit is linked fifty–fifty to a pyruvate group and the non-terminal residue usually carries an acetyl group. Redrawn from (Sworn, 2009).

Xanthan gum: industrial production

Xanthan gum is one of the industrially most relevant microbial polysaccharides. Compared with other microbial polysaccharides, its price is competitive and it is therefore a viable option not only regarding performance but also from an economic point of view (Chang *et al.*, 2020). The main manufacturers of xanthan gum are Jungbunzlauer, ADM, Cargill, CP Kelco, Deosen Biochemicals, Fufeng Group, IFF (Dupont) and Meihua Group.

The production of xanthan gum can be separated into two main steps as shown in Fig. 2. The whole production starts with the fermentation step, where simple carbohydrate molecules are metabolized by *X. campestris* to synthesize xanthan gum. For this, *X. campestris* strain

is cultured in a well-aerated and well-agitated fermenter and is expanded by growth on solid surfaces or in liquid media to obtain the inoculum (Katzbauer, 1998; Garcia-Ochoa *et al.*, 2000). Apart from the precise medium composition, factors such as type of bioreactor used, mode of operation (batch or continuous), medium composition, and culture conditions (temperature, pH, dissolved oxygen concentration) have an influence on the growth of the microorganism and xanthan gum production. Culture environment and operational conditions also influence the molecular structure of xanthan gum. There is extensive literature on the production conditions, medium composition, used microorganism and how these can be improved (Garcia-Ochoa *et al.*, 2000; Rosalam and England, 2006; Rottava *et al.*, 2009; Palaniraj and Jayaraman, 2011; Lopes De Mônaco *et al.*, 2015; Habibi
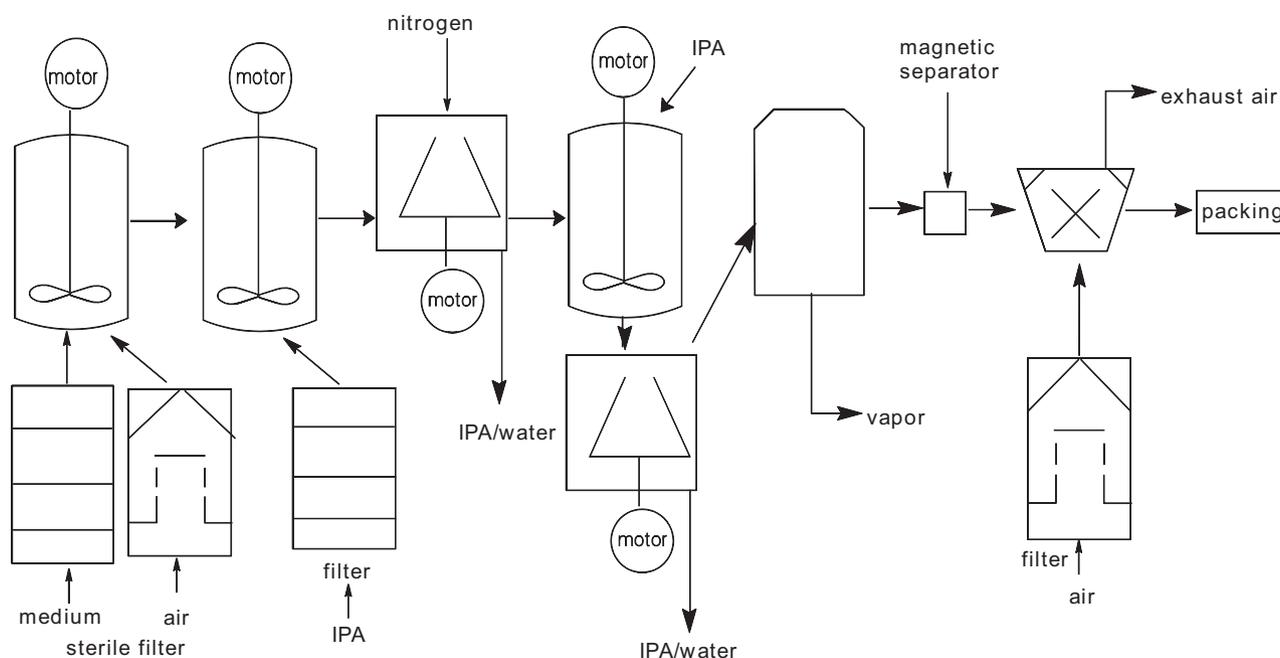
Fig. 2. Xanthan gum production steps: fermentation, pasteurization, precipitation with IPA (isopropanol), decantation, dehydration, drying, milling/sifting, packaging.

and Khosravi-Darani, 2017). The main parameters to adjust yield and molecular structure are related to nutrients content, temperature and production kinetics. *X. campestris* needs several micronutrients (e.g. sodium, potassium, iron and calcium salts) and macronutrients such as carbon (glucose or fructose) and nitrogen to produce xanthan gum. At the end of the fermentation, the broth is pasteurized to inactivate the microorganisms.

The second step in production is a comprehensive recovery process including precipitation, drying and milling. The xanthan gum is recovered by precipitation with water-miscible non-solvents such as isopropyl alcohol and further purified by pH adjustments (Garcia-Ochoa *et al.*, 2000). These recovery steps can vary depending on the desired purity and quality of the xanthan gum product, which in turn determines the end use, e.g. in oil, technical, food, personal care or pharma applications. For example, for xanthan gum to be applied as food additive, it should be free from viable cells of *X. campestris* and reagents used in the recovery process. For personal care or pharma applications, even stricter purity requirements are in place, because active enzymes still present after an inadequate recovery may influence the final application. Once the polysaccharide is obtained as a wet precipitate, it is dried in batch or continuous dryers, under vacuum or with forced circulation of an inert gas. Most commercial xanthan gum products have a final moisture content of about 10–15%.

After drying, the polysaccharide is milled to a predetermined mesh size and in some cases agglomerated to control dispersability and dissolution rates. Prior to packaging, xanthan gum routinely undergoes a quality control in which viscosity, microbial plate count and heavy metal residues are examined to comply with product specifications.

Further optimization of the xanthan gum production process is a subject of ongoing research. Apart from 'traditional' approaches such as optimizing growth conditions, the use of agro-industrial, organic by-products as a sustainable, alternative nutrient source is an interesting aspect (Murad *et al.*, 2019). In this sense, a variety of waste materials has been evaluated, for example shrimp shell (De Sousa Costa *et al.*, 2014), lignocellulosic waste such as coconut shell and cocoa husk (da Silva *et al.*, 2018) as well as chicken feather peptone and sugar beet molasses (Ozdal and Kurbanoglu, 2019). Nevertheless, the transfer of these approaches to industrial scale is limited, since the choice of the nutrient source is tightly coupled to considerations regarding supply security and continuously high raw material quality, absence of impurities and required upstream processes.

Regarding production optimization, it has also been found that xanthan gum molecular properties such the substitution pattern with acetyl and pyruvate groups and thus rheological behaviour can be fine-tuned on a genetic level (Gansbiller *et al.*, 2019). Strain genetic

engineering also proved feasible to increase whiteness of the xanthan gum product while using lower amounts of ethanol in the downstream processing (Dai *et al.*, 2019). However, on an industrial scale, this approach may be prohibitive due to regulatory compliance and product labelling. Therefore, several producers of xanthan gum, including Jungbunzlauer, guarantee a GMO-free production process.

Xanthan gum: general applications and properties

Dissolved in cold water, xanthan gum produces highly viscous solutions with a weak gel character. It has long been used as a thickener or suspending agent in food applications such as salad dressings, sauces, instant products, desserts, bakery, dairy products and fruit juices as well as in various low-calorie foods. In cosmetics, xanthan gum serves as stabilizer and thickener, for example in toothpastes, creams, lotions, gels and shampoos. It is also relevant for pharmaceutical applications, modifying drug release from delivery systems such as tablets, films, hydrogels and nanoformulations (Cortes *et al.*, 2020) and potential base material in tissue engineering (Petri, 2015; Kumar *et al.*, 2018). Typical industrial applications of xanthan gum are in cleaners, paints, ceramic glazes, inks, oil drilling fluids or agricultural flowables (Katzbauer, 1998). More specifically, the latter comprise suspension concentrates (SC) and flowable concentrates for seed treatment (FS) type of formulations, in which xanthan gum is widely used.

Due to its strong polyelectrolyte nature, xanthan gum solutions are highly viscous even at very low concentrations. Under shearing, xanthan gum solutions show a strong pseudoplastic behaviour, i.e. the viscosity decreases with increasing shear rate (Milas *et al.*, 1990). The viscosity depends on polymer concentration, temperature, salt and pH. The viscosity of xanthan gum solutions increases strongly with increasing concentration of the polymer. With increasing temperature, the viscosity declines caused by a conformational transition from a rigid helical to a flexible coil molecular structure (Norton *et al.*, 1984). The presence of salts in solution influences the xanthan gum viscosity. At low polysaccharide concentration (approximately < 0.3 wt%), the viscosity decreases when a small amount of salt (approximately < 0.1 wt%) is added, whereas at higher xanthan gum concentration or when a larger amount of salt is added, the viscosity increases (Zatz and Knapp, 1984). Xanthan gum as an anionic polysaccharide exhibits a certain sensitivity to pH changes since its charge density is changed and therefore the molecular associations between the single molecules are influenced (Pastor *et al.*, 1994).

Commercially, there are different xanthan gum grades available, offering different distinct properties (Table 1). They can be classified according to their purity, particle size and rheological performance. The purity of the available grades refers to microbiological plate count, residual isopropanol (IPA) and heavy metal contaminations, but does not impact flow and stabilization behaviour. The particle size or granulation of xanthan gum strongly influences the hydrating and dispersing performance. A fine granulation results in a fast hydration but with the compromise of a worse dispersibility due to a higher tendency to form lumps. Coarser granulations hydrate slower, but are easier to disperse. There is also an agglomerated xanthan gum available on the market allowing for an easy dispersion without the formation of lumps. This grade is especially suited if no or low performance mixers are used for hydration (Fig. 3).

Different rheological properties may be important for applications containing high amounts of salts, with highly acidic conditions or where specific smooth flow properties are desired in the end product. Here, the commercial market offers different possibilities including, e.g. particularly salt-tolerant xanthan gum or xanthan gum exhibiting

Table 1. Compilation of possible modifications of xanthan gum, resulting properties and their relevance for agricultural applications (own data).

Property	Description	Modifications	Relevance for application
Reduced pseudoplasticity	• Lower viscosity at low shear	Fermentation conditions	• Smooth flow, better pourability of agrochemical formulations • Better sprayability at low pressure • Easier soil infiltration
Salt tolerance	• Extra high viscosity in the low shear range also in presence of salts • Fast hydration also in presence of salts	Fermentation conditions	• Formulation of fertilizers • Agrochemical formulations
Acid stable	• Maintenance of viscosity in low pH solutions	Fermentation conditions	• High stability of low pH disinfectants
Dust free	• Absence of fine dusts	Oil coating	• Better handling in manufacturing process
Clear solution	• Transparent appearance of xanthan gum solution	Additional clarification	• Formulation aesthetics
Easily dispersible	• Easy dispersion and reduction of lumping also under slow agitation	Agglomeration	• Lump-free hydration, e.g. when adding as dry product in the spray tank

a reduced pseudoplastic flow behaviour (Fig. 4). Salt-tolerant xanthan gum has been developed for use with high concentrations of salt (up to 20% NaCl) maintaining an excellent viscosity forming potential. A typical technical application example is the formulation of fire retardants, where high concentrations of ammonium phosphates are present in combination with colouring particles of iron oxide, which need stabilization. In the food industry, salt-tolerant xanthan gum is used in sauces and dressings with high salt content.

Besides the rheological properties, the transparency of the xanthan gum solution or the dusting of the xanthan gum powder can be adjusted by different special grades. Clear solution xanthan gum, e.g. shows the same functional rheological properties as standard xanthan gum but allows the preparation of transparent solutions. Transparency is obtained by an additional treatment to remove cell residues. Dust free xanthan gum has been developed to avoid dusting during handling in industrial processes. The product is treated with 1% of an edible oil to bind the smallest particles and thus eliminate dust formation.

The availability of such different xanthan gum grades gives formulators the opportunity to select the material to best match the specific application requirements.

Soil improvement with xanthan gum

Soil improvement or soil conditioning describes a wide range of activities to modify soil characteristics according to specific needs. In general, this term has been used mostly in the context of soil physical properties in geotechnical engineering (Mirzababaei *et al.*, 2017;

Armistead *et al.*, 2020; Chen *et al.*, 2020), but also in agriculture (Majeed *et al.*, 2018), forestry (Stöcker *et al.*, 2020) and other fields. Therefore, soil improvement is not restricted to a specific industry and could be defined as the modification of any soil property by any method. In this sense, soil modifications can be of physical, chemical or biological nature (Molnár *et al.*, 2016; Cheng *et al.*, 2017; Oliveira *et al.*, 2017; de Melo *et al.*, 2019; Jiang *et al.*, 2020).

Due to their diversity and versatility, polymers are a group of widely used materials for soil improvement purposes. Specifically, in agriculture, the use of polymers is self-evident, since their mode of action resembles the functions of the microbial polysaccharides produced by the soil microbiota. Simulating those functions, polymers are applied to the soil mainly in order to: (i) modify water retention capacity (superabsorbents) (Vundavalli *et al.*, 2015), (ii) improve soil structure or physical characteristics (Yang and Antonietti, 2020), (iii) as a controlled release system for fertilizers or phytochemicals (Guilherme *et al.*, 2015; Tran *et al.*, 2018), (iv) in soil remediation for removal of heavy metals (Guo *et al.*, 2020) and oil contamination (Cao *et al.*, 2016; Jung and Hu, 2017) or (v) as a biocide (Chauhan, 2019).

We will focus on the use of polymers and specifically xanthan gum to improve water retention and plant development. In face of an increasing need to use scarce water sources more efficiently, the number of research publications and the commercialization of polymers for soil improvement has grown in the last years (Milani *et al.*, 2017), underlining the relevance of this topic.

Superabsorbent polymers (SAPs) or hydrogels are cross-linked hydrophilic polymers able to absorb
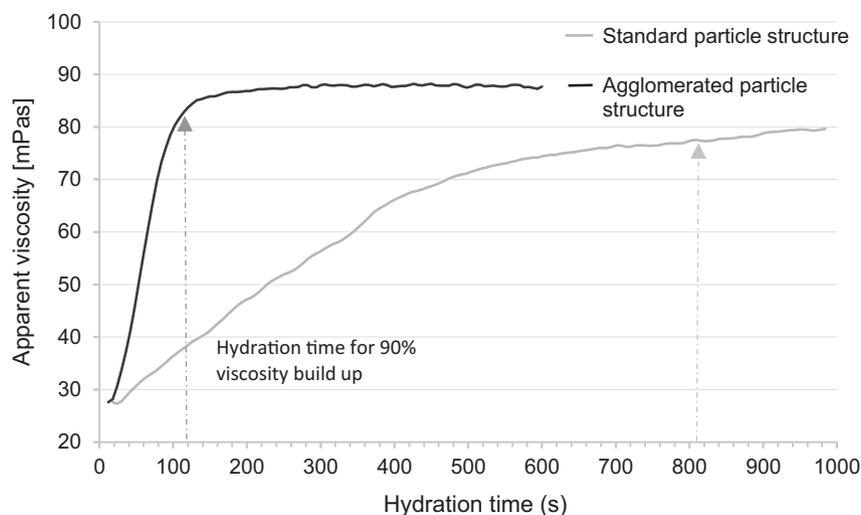
Fig. 3. Model curves of viscosity build-up of xanthan gum of two different particle structures, added to distilled H_2O at 0.3% [w/v]. The agglomerated grade reaches 90% of the maximum viscosity after approx. 115 s. The standard grade reaches 90% of the maximum viscosity after approx. 810 s.
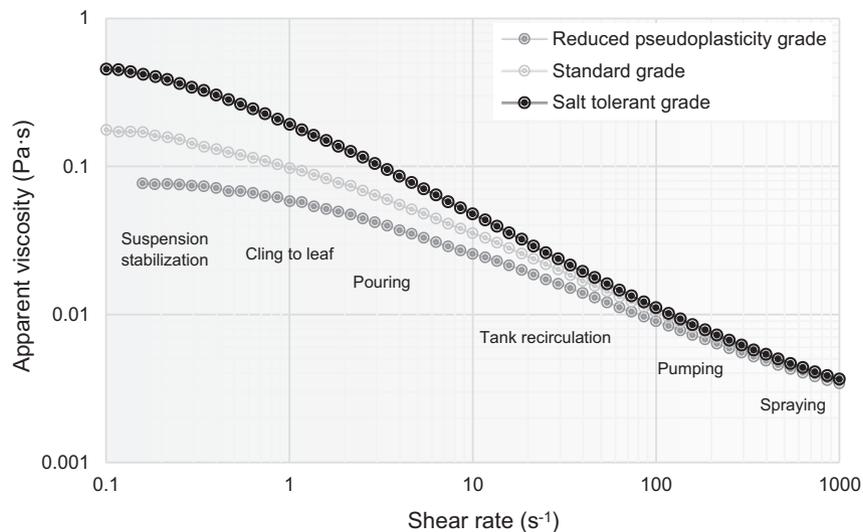
Fig. 4. Model flow curves of solutions of 0.1% [w/v] different xanthan gum grades in standard tap water (1 g l^{-1} NaCl, 0.15 g l^{-1} CaCl$_2$·2H$_2$O). Typical application-related shear rates are denoted. Differences in apparent viscosity are particularly pronounced in the low shear regime with implications for grade selection depending on desired behaviour.

significant quantities of water of up to 1000 times their dry weight (Li *et al.*, 2014; Lejcuś *et al.*, 2018). By binding a large amount of water in the soil and making it available to the plants for longer periods, crop yields can be improved, especially in arid regions (Hou *et al.*, 2018; Satriani *et al.*, 2018; Jahan and Nassiri Mahallati, 2020).

At the moment, the most relevant SAPs for soil application are potassium polyacrylates, but also other polyacrylates and polyacrylamides as well as their cross-linked derivatives. Non-soluble, cross-linked SAPs are incorporated into the soil either in a powder form by homogeneously mixing during ploughing, or already hydrated, using specific machinery allowing its injection at high pressure into the soil. The use of synthetic SAPs is common despite their slow degradation and the potential release of toxic compounds. For example, polyacrylamide can degrade into acrylamide monomers over time, which are known as toxins and potential carcinogens (Xiong *et al.*, 2018).

The increasing awareness about these drawbacks of synthetic SAPs has triggered a demand for biopolymers to be used as readily biodegradable, environmental-friendly SAPs. In this sense, different biopolymers such as cellulose, starch, guar gum, alginate and chitosan as well as composites have been investigated. Some examples are biodegradable and biocompatible SAP made from two cellulose derivatives, sodium carboxymethyl cellulose (CMCNa) and hydroxyethyl cellulose (HEC), using citric acid as cross-linking agent (Montesano *et al.*, 2015; Thombare *et al.*, 2018; Saruchi *et al.*, 2019).

Xanthan gum has an extraordinary water binding capacity in comparison with other microbial polysaccharides (Wallingford and Labuza, 1983; Sánchez *et al.*, 1995) and it is thus a suitable candidate to be used as SAP. Its suitability as soil improver has been demonstrated in geotechnical engineering, improving soil mechanical properties (Dehghan *et al.*, 2019) such as soil strengthening and stabilization (Chang *et al.*, 2015a; Latifi *et al.*, 2017; Dehghan *et al.*, 2019). Results with xanthan gum are remarkable in many cases when compared to other polysaccharides (Soldo *et al.*, 2020). In engineering, xanthan gum application rates lay normally between 0.5 and 4%. Nevertheless, positive effects can already be observed when using concentrations of xanthan gum as low as 0.1% (Chen *et al.*, 2019).

The improved water retention can be ascribed to the formation of a crystallized top soil layer promoted by the microbial polysaccharide after drying, which maintains moisture in the inner bulk soil (Chen *et al.*, 2019). These results were particularly pronounced in sandy soils, where the initial water content after saturation doubled when as little as 0.5% of xanthan gum was added, delaying also water drainage (Tran *et al.*, 2018). Moreover, positive results were observed in other substrates. Xanthan gum at a concentration of 0.5% outperformed starch in terms of water retention and plant survival under drought stress, using Korean standard poor graded sand (Tran *et al.*, 2019). Also, on silty soils and garden substrates, xanthan gum has proven a suitable amendment in order to increase water retention, seed germination and plant growth (Abobatta, 2018; Chang *et al.*, 2020). Another beneficial effect is the reduction of soil erosion on different soils (Chang *et al.*, 2015b).

From a practical point of view, xanthan gum has the advantage of being able to be applied as a water-based solution. Xanthan gum is not only compatible with diverse irrigation methods like drop by drop or sprinklers, but also is an effective drag reducer, decreasing frictions in the flow of the irrigation water (Han and Choi, 2017). This implies a potential double function of xanthan gum in irrigation.

In the case of application of SAPs as a dry powder, their hydration capacity and hydration speed are affected by the depth they are delivered to, i.e. the soil load they bear. Increasing loads simulating different depths resulted in a significant reduction in the capacity of the SAPs to absorb water (Lejcuś *et al.*, 2018). This makes xanthan gum a more efficient and thus potentially less costly solution.

One of the main problems regarding studies on xanthan gum in soil amendment is that frequently, a similar concentration range is used for agriculture-related applications as for geotechnical engineering. This could result in some phenomena like cemented soil, in which plant growth or seed germination can be negatively affected (Tran *et al.*, 2019). Also, the use of high concentrations of xanthan gum can cause clogging of soil pores, resulting in a slow infiltration of the xanthan gum (Chang *et al.*, 2020). These properties are desired in soil engineering, but not in agriculture, so the approach for both applications needs to be different (Rahbari *et al.*, 2016).

While xanthan gum has proven to confer beneficial effects by its own, latest studies have investigated the possibility to cross-link it with other compounds, resulting in similar characteristics as synthetic SAPs. Composite materials have shown potential to be used to control the release of fertilizers (Singh and Dhaliwal, 2020), to improve the development of *Camelina sativa* L. under drought stress conditions (Lim *et al.*, 2018) or to enhance water retention capacity (Feng *et al.*, 2014).

The increasing impact of climate change, as well as the limited availability of water and good quality soils, will make soil improvement techniques more and more important in the future. Xanthan gum as an eco-friendly and sustainable polymer is one of the most promising materials to be used in agriculture, both conventional and organic.

Drift control – potential replacement of synthetic polymers by xanthan gum

The delivery of pesticides as liquids to the plant foliage constitutes a highly relevant pathway of pesticide treatments. Across all techniques of spray delivery, unwanted drift compromises on safety and efficacy, causing losses of up to 10% (De Ruiter *et al.*, 2003). Drift control measures include the incorporation of drift control adjuvants (DCAs) into the spray liquid. These aim to reduce the fraction of droplets with a diameter < 100–200 μm, generally referred to as driftable fines (Hilz and Vermeer, 2013). Frequently, WSPs of high molecular weight ranging around 10^6 g mol^{-1} are used, such as polyacrylamide (PAM), polyethyleneoxide (PEO), polyvinylppyrrolidon (PVP) and polysaccharides (Spanoghe *et al.*, 2007; Lewis *et al.*, 2016). Even highly diluted, typically to 100–1000 ppm (Lewis *et al.*, 2016), these polymers are effective in delaying the break-up of the spray sheet and reducing the formation of satellite droplets (Harrison *et al.*, 1999). Polymer rigidity strongly influences extensional viscosity in response to the strain the liquid experiences when ejected through a nozzle. Comparing 50 ppm solutions of PAM as a flexible polymer and xanthan gum as a rigid representative, Harrison *et al.* (1999) found a significant difference in the Trouton ratio of both materials. PAM reached a Trouton ratio (η_e/η_s) of more than 20, while xanthan gum reached a value of 8. This indicates that even though rigid xanthan gum does induce a delay in the break-up of the spray sheet, flexible polyacrylamide does so more efficiently.

In practice, however, integrity of the molecular structure and thus functionality of polymers is often an issue. DCAs experience continuous shear forces of between 50 s^{-1} during recirculation in the spray tank, reaching up to 10^5 s^{-1} at the nozzle outlet (De Ruiter *et al.*, 2003), resulting in breakage of molecules into smaller fractions (Lewis *et al.*, 2016). For example, using a 400 ppm solution of non-ionic PEO, the volumetric percentage of droplets < 200 μm (% $V < 200$ μm) grew from 5.1% before recirculation to 17.3% after recirculation. In contrast, xanthan gum only experienced a minor increase in % $V < 200$ μm from 7.5 to 11.0 (Zhu *et al.*, 1997). Thus, xanthan gum shows a significantly higher resistance to mechanical stress and therefore better performance in drop size enhancement than many synthetic WSPs.

The molecular integrity and quick re-build of viscosity of xanthan gum further benefit the deposition of droplets on the target surface, improving cling to leaf and reducing run-off. Wang *et al.* (2018) demonstrated that the maximum retention [ml cm^{-3}] of an aqueous surfactant solution on a 45° inclined maize leaf could be doubled by adding xanthan gum in concentrations as low as 0.05%. They also showed that the addition of xanthan gum significantly decreased the dynamic spreading [mm^2 s^{-1}]. This implies the formation of more slowly evaporating 'hot spots' of AI (active ingredient), allowing for a higher concentration and longer contact time on the target surface (Flemmens *et al.*, 2018).

DCAs conferring a good droplet retention and moisture maintenance are also relevant in spray application of biocontrol agents. Biocompatibility of DCAs is a crucial requirement in this application (Peng *et al.*, 2000).

Particularly, xanthan gum may take on the function of providing a protective, surrogate biofilm to live organisms. As shown for the spray application of entomopathogenic nematodes, both PVA and xanthan gum were compatible with nematode viability. In addition, xanthan gum at 0.3% had the benefit of retarding settlement (Beck *et al.*, 2013). Another study investigated the effect of xanthan gum, PAM and other adjuvants on the performance of fungal bioherbicides. In the model system *Pyricularia setariae* spores against green foxtail, xanthan gum showed the best compatibility among all tested adjuvants, improving spore germination from 75% in the control to 83%. In contrast, PAM decreased sporulation to 61%, resulting in a significant efficacy loss (Byer *et al.*, 2006).

Clearly, there are pros and cons of replacing synthetic WSPs by xanthan gum in drift control. Looking particularly at extensional viscosity, PAMs seem to be superior to xanthan gum. However, molecular stability under high mechanical stress conditions and full biocompatibility make xanthan gum a viable alternative not only for spray treatments with biologicals.

Encapsulation and controlled release formulations with xanthan gum

In an effort to improve safety and efficacy of agrochemicals, controlled release systems (CRS) are rising in popularity. In a CRS, AIs are immobilized in carriers to ensure the timely release on the target site, reduce loss into the environment and avoid exposure of the end-user (Singh *et al.*, 2020). CRS may also refer to enhanced efficiency fertilizers (EEF), in which plant nutrients are formulated using coating or immobilization techniques (França *et al.*, 2019). Generally, the term CRS comprises manifold techniques and materials, which have been reviewed elsewhere (Campos *et al.*, 2015; Sinha *et al.*, 2019; Singh *et al.*, 2020).

Encapsulation is one of the most relevant techniques in CRS, with a broad application potential for polymers. Polymers from synthetic origin (polyamides, polyesters, polyvinylalcohol, polyurethane, polylactic acid etc.) and biopolymers (chitosan, sodium alginate, cyclodextrin, starch and cellulose) have been used (Sinha *et al.*, 2019; Singh *et al.*, 2020).

Generally being considered a non-gelling polymer by itself, xanthan gum is rather underrepresented in studies investigating bio-based encapsulation materials for CRS in agriculture. To the best of our knowledge, there are no studies comparing the use of synthetic, film-forming polymers with xanthan gum directly. Nevertheless, taking inspiration from other application fields such as biotechnology, food and pharma, there are several encapsulation approaches in which xanthan gum in combination with other materials has proven beneficial.

Matrix encapsulation based on xanthan gum in combination with other components is applicable for a variety of compounds such as secondary metabolites (Da Rosa *et al.*, 2014; Ravichandran *et al.*, 2014), enzymes (Liu *et al.*, 2011) and microorganisms (Jiménez-Pranteda *et al.*, 2012). Frequently, the basic principle is to add the AI to the xanthan gum hydrogel and subject the blend to drying by lyophilization or spray drying. 'Co-carriers', for example other hydrocolloids like alginate or chitosan, inorganic fillers such as clay (Liu *et al.*, 2011) or carbohydrates such as maltodextrin (Ravichandran *et al.*, 2014) may be incorporated. By help of these additives, properties such as capsule structure, encapsulation efficiency and release patterns can be shaped. Matrix encapsulation was also achieved by dripping blends of xanthan gum and gellan gum into a recovery bath of $CaCl_2$. At a ratio of 1:0.75 (xanthan: gellan gum), encapsulation of *Lactobacilli* resulted in an increased resistance of the probiotic microorganisms to simulated bile conditions (Jiménez-Pranteda *et al.*, 2012).

Another possibility is the preparation of core-shell capsules with solid or liquid core and one or several outer layers. This is possible by exploiting the electrostatic interaction between anionic xanthan gum and cationic chitosan. For example, Shu *et al.* (2018a,2018b) dispersed *Bifidobacterium bifidum* in xanthan gum hydrogel and extruded the blend into a chitosan solution to obtain capsules, which improved the survival of *B. bifidum* in milk. By alternating between xanthan gum solution and chitosan solution, the amount of coating layers can be modified. The beneficial effect of an additional layer was shown for *Lactobacillus acidophilus* in xanthan-chitosan capsules, resulting in a better control of the release as well as improved viability during storage in a dairy beverage and exposure to simulated gastric juice (Shu *et al.*, 2018a,2018b).

Core-shell capsules also can be produced using alginate as shell material and xanthan gum to adjust viscosity of the liquid core and thus stabilize encapsulated agents. This approach was pursued to encapsulate *Lactococcus lactis* and thus increase its viability and antimicrobial activity against food-spoilage bacteria *Listeria monocytogenes* (Bekhit *et al.*, 2016).

One of the less investigated approaches is the direct cross-linking of xanthan gum. This can be achieved by exposure to trivalent ions. For example, Pacheco-Aguirre *et al.* (2016) demonstrated the encapsulation of the biocontrol agent *Bacillus subtilis* in xanthan gum by extrusion into a $FeCl_3$ bath. In this form, the biocontrol of the plant-pathogenic nematode *Meleidogyne incognita* tended to be more efficient than when inoculating plants with non-encapsulated biocontrol agent.

Even though limited data are available on encapsulation of AIs for agriculture, the examples illustrate the

possibilities to use xanthan gum in encapsulated formulations, giving rise to potential new approaches.

Formulating with xanthan gum: practical tips and compatibilities

Xanthan gum hydrates both in hot and cold water. Working in an aqueous system, a proper incorporation of xanthan gum into the water phase is essential to achieve optimum performance. One of the main issues that may be observed is the formation of difficult to dissolve lumps. These lumps are caused by adding xanthan gum to the hydration medium all at once, too fast or by using improper techniques, impeding the complete hydration and thus its effective use. With the right approach, the formation of these lumps can be prevented.

The first requirement is a uniform dispersion of xanthan gum particles. Under fast agitation of the hydration medium, for example by a propeller stirrer, the bulk xanthan gum is ideally added to the upper part of the vortex where mixing velocity is highest. This is especially relevant for fine-particle-sized xanthan gum, which is difficult to disperse with low shear equipment. If the particles are not uniformly dispersed, they may stick together and the fast hydration of the outer surface can form a gel layer, preventing the entry of water. The resulting swollen lumps are also known as 'fish eyes', which can only be dissolved with high shear mixing equipment and/or prolonged mixing time (Sandford *et al.*, 1981). In many applications, this is not an option, so alternative approaches can be pursued:

i. *Preparation of a dry blend:* Depending on additional ingredients present in the formulation, the preparation of a dry blend may be feasible. For this, the particle sizes of the individual components should be similar to avoid separation. Suitable components are for example sugars, salts, starches and clays (Sworn, 2009). In this approach, a fine particle size xanthan gum is typically used, and the focus is on ensuring a homogeneous distribution and spatial separation of the single xanthan gum particles, which facilitates hydration upon addition of water.

ii. *Slurry in non-aqueous liquids:* Similarly to a dry matrix, a liquid medium can serve for homogeneous distribution of xanthan gum particles. For this, it is important to choose non-hydrating liquids. These could be (partly) water-miscible liquids like glycerol, ethanol, propylenglycol, ethyl lactate or triethyl citrate as well as oils. For oils, a ratio of xanthan gum to liquid of 1:5 to 1:10 is recommended, whereas for water-miscible liquids, the recommendation is 1:2 to 1:10. The slurry can be mixed with water under agitation for the hydration of xanthan gum.

iii. *Preparation of a stock paste:* If additional components are not acceptable in the formulation, an aqueous stock solution of xanthan gum can be prepared. Stock pastes of up to 6% are feasible and can be preserved and stored long-term until later dilution with water (Sworn, 2009). Obviously, this implies that high shear equipment has to be available during preparation of the stock solution.

iv. *Use of an easily dispersible xanthan gum grade:* The most efficient way of ensuring fast hydration with low shear equipment and no need to modify components of the formulation is the use of a commercially available, 'easily dispersible' xanthan gum grade. These specifically processed grades are agglomerates with porous structure, which allows for a fast entry of water and prevention of fish-eye formation.

Xanthan gum effectively thickens water-based solutions even at low concentrations. To give a starting point, typical usage concentrations are between 0.2% and 1.0% in relation to the aqueous phase for the stabilization of suspensions, depending on particle characteristics. When aiming for sprayable solutions, a concentration around 0.08–0.10% is recommended, depending on nozzle type and operational parameters.

Particularly regarding the transfer of laboratory-based research to application, it should be noted that viscosity build of xanthan gum differs in distilled water and when salts are present, such as in tap water.

In full formulations, possible interactions with xanthan gum and other components need to be considered. For example, typical anti-freeze agents such as glycerol, ethylene glycol and propylene glycol are compatible with xanthan gum in concentrations up to 50%. Ethanol can be incorporated up to approximately 40% before precipitation of xanthan gum occurs. Xanthan gum is largely compatible with non-ionic and anionic surfactants used in typical concentrations (approximately 15% active substance). However, due to its anionic nature, xanthan gum can interfere with cationic surfactants and amphoteric surfactants below their isoelectric point, where positive charge dominates.

The cellulose backbone of xanthan gum is well protected against enzymatic attack by its trisaccharide side chains and therefore shows better stability in presence of pectinases or amylases than other biopolymers. Nevertheless, for long-term storage of xanthan gum solutions, a preservative system is usually required, which may be based, e.g. on isothiazolinones or less sensitizing or toxic alternatives such as benzoates and sorbates.

Considering these aspects is important to ensure successful use of xanthan gum.

Conclusion

In this review, we elaborated on the use of WSPs in different agricultural applications, focussing on eco-friendly alternatives to synthetic materials. The process of biological synthesis by microbes, i.e. fermentation, delivers biodegradable polymers with narrow specifications and of high purity. Xanthan gum is one of the most prominent and commercially relevant examples for a microbial biopolymer. While xanthan gum is established in agriculture for formulation of suspension concentrates, there are still innovative applications to be explored. Among others, these comprise the use as spray adjuvant (drift control), co-formulant in encapsulation and as soil improver, where classically synthetic WSPs are employed. Changes in regulatory frameworks, an increasing environmental awareness and a promising performance of xanthan gum underline the feasibility of this direction of research. Choosing the most suitable xanthan gum grade in terms of rheological behaviour and downstream modifications requires material-specific knowledge and is crucial for successful application.

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Conflict of interest

All authors are employees of Jungbunzlauer Ladenburg GmbH or were so in the past.

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