



Eco-friendly Modified Biopolymers for Enhancing Oil Production: A Review

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Abstract

Biopolymers are gaining increased attention in the industry due to their unique characteristics, including being cost-effective, environmentally friendly, and biodegradable. It is also worth noting that natural polymers can be obtained in significant quantities from various renewable sources, whereas synthetic polymers are derived from non-renewable petroleum resources. Enhanced oil recovery (EOR) using biopolymers such as galactomannan, xanthan, welan gum, acacia gum, carboxy methyl cellulose, and corn starch is a developing trend and is projected to replace synthetic polymers (hydrophobically associated polyacrylamides) in the nearby future. The choice of polymers to be utilized in EOR technologies should be based on their cost and availability in addition to their functional properties. Biopolymers in enhanced oil recovery serve to enhance the mobility ratio by increasing the viscosity of displacing fluid and reducing permeability. Even though biopolymers have a tough structure and long polysaccharide chains that make them suitable for enduring severe reservoir conditions, they are highly susceptible to bacterial destruction. In this comprehensive review, we have illustrated the different techniques used to enhance the performance of biopolymers (xanthan gum, guar gum, and starch) in enhanced oil recovery and create new composites that can overcome the challenges faced by these biopolymers under reservoir conditions. We have found that the most famous and favorable techniques used in this approach are, grafting copolymerization, nanocomposites functionalization, amphiphilic style, and hydrogel formation. The review also discussed some other biopolymers (carboxy methyl cellulose, welan gum, and acacia gum) that can be utilized to improve oil recovery and evaluated how widely they have been applied in this field. In this review, we have addressed several important issues (knowledge gaps) that have not been covered in recent studies. We have also provided recommendations and prospects for the successful future implementation of these composites in the EOR field. In conclusion, we hope that this review will help in better understanding the use of these modified biopolymers for enhanced oil recovery (EOR).

Keywords Enhanced oil recovery · Biopolymer flooding · Xanthan gum · Galactomannan · Starch · Carboxy methyl cellulose · Welan gum and Acacia gum

Abbreviations

EOR	Enhanced oil recovery
HPAM	Hydrophobically associated polyacrylamide
XG	Xanthan gum
GG	Guar gum
NPs	Nanoparticles

ES	Equilibrium states
TiO ₂	Titanium dioxide
Ni NPs	Nickel nanoparticles
SiO ₂	Silicon dioxide
Al ₂ O ₃	Aluminum oxide
Fe (OH) ₃	Ferric oxyhydroxide
OOIP	Original oil in place
S _{or}	Residual oil saturation
SDBS	Sodium dodecylbenzene sulfonate
CTAB	Cetyl trimethyl ammonium bromide
MPS	3-(Methacryloyloxy)propyltrimethoxysilane
OTES	Octyltriethoxysilane
CMC	Critical micelle concentration
B-PPG	Branched-preformed particle gel
SDS	Sodium dodecyl sulfate

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WH	Biosurfactant
HMTA	Hexamethylenetetramine
HQ	Hydroquinone
AM	Acrylamide
AA	Acrylic acid
VAG	Viscosity-augmented guar
MMA	Methyl methacrylate
TEVS	Vinyl triethoxy silane
TMVS	Vinyl trimethyl silane
AMPS	2-Acrylamido-2-methylpropane sulfonic acid
PGG	Palmitate-guar gum
VMA	Vinyl metha acrylate
NVP	1-Vinyl-2-pyrrolidone
DMPVS	Dimethyl phenyl vinyl silane
MBAM	N, N'-Methylenebisacrylamide
CSNP	Crystalline starch nanoparticles
CSNF	Crystalline starch nanofluid
IFT	Interfacial tension
NaCl	Sodium chloride
CaCl ₂	Calcium chloride
NaOH	Sodium hydroxide
NCP	Quaternary ammonium cationic starch
MT	A montmorillonite-based reservoir
CMC	Carboxymethyl cellulose
WLG	Welan gum
GA	Gum Arabic
GNPs	Graphene nanoplatelets
AOS	Alpha-olefin sulfonate

Introduction

Biodegradable polymers known as natural materials are currently used in a range of industries, like tissue culture, biomedicine, farming, food, and smart fabrics [1, 2]. Biopolymers can be obtained from animal, plant, or natural sources and are considered a new generation of natural materials. Employing a biopolymer has the benefit of not being harmful and not having a considerable adverse effect on the environment [3–6]. It is also worth noting that natural polymers can be obtained in significant quantities from various renewable sources, whereas synthetic polymers are derived from non-renewable petroleum resources. Using biopolymers for enhanced oil recovery (EOR) is a growing trend and is projected to replace synthetic polymers (hydrophobically associated polyacrylamides) shortly. This is because it is important to innovate oil production in a cost-effective and environmentally friendly way. According to Ghomrassi-Barr and Aliouche [7] biopolymers could be a preferable choice over synthetic polymers (HPAMs) for enhanced oil recovery in high-temperature and salinity reservoirs [8].

Background of Biopolymers in EOR

Over the past five years, several studies have focused on utilizing biopolymer flooding for enhanced oil recovery in various countries, including China, the United States, and Iran. Figure 1a, b shows the findings of these studies where these statistical data were collected from Scopus Databank.

Even though biopolymers have distinctive helical structures and long rigid polysaccharide chains that make them

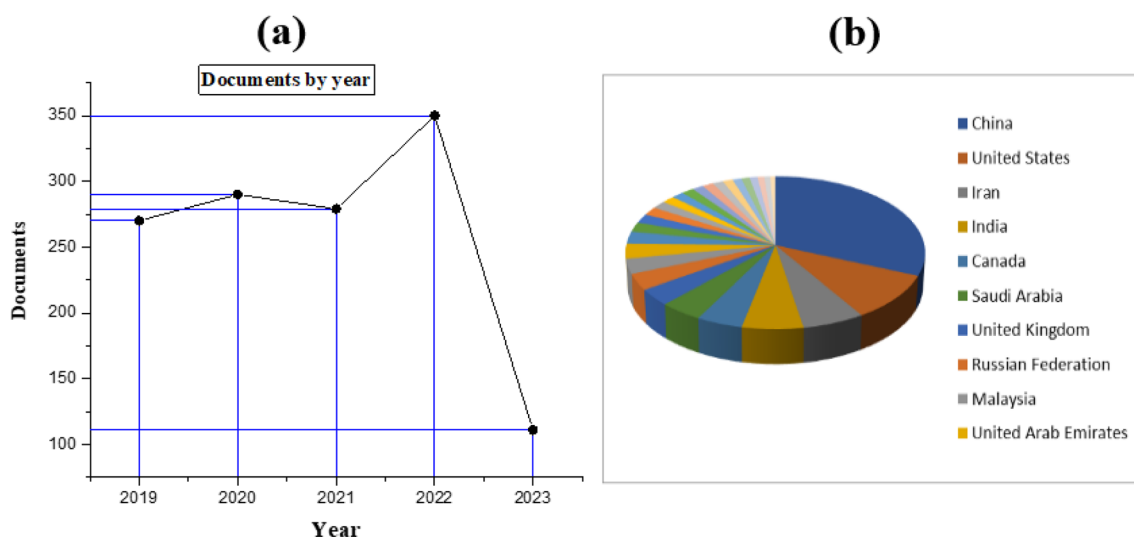


Fig. 1 **a** The number of biopolymer flooding research studies in EOR per year, and **b** The biopolymer flooding research studies in EOR in different countries. Statistical data over the past five years were collected from Scopus Databank, Elsevier

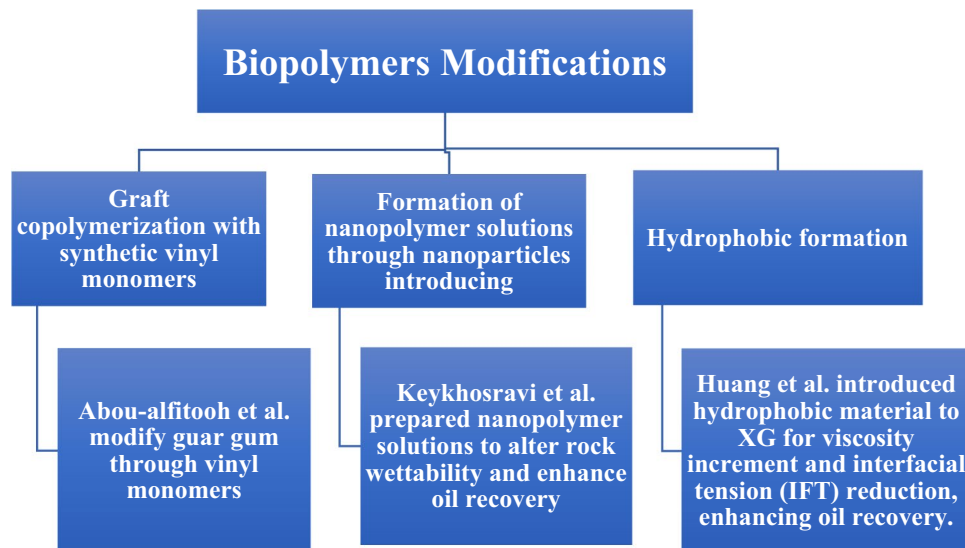
well-suited for severe reservoir conditions [9, 10], they are highly susceptible to bacterial degradation, uncontrolled hydration, and viscosity loss during storage. Researchers have recently studied different ways to modify the physical and chemical properties of biopolymers and make them more suitable for use in EOR in severe reservoir environments. There are various techniques available to modify biopolymers where several reactive parts on their structure surfaces allow for modifications as indicated in the following Fig. 2. One of their most famous is introducing synthetic vinyl monomers through graft copolymerization. This method is considered the most favorable because it allows the natural polymers to acquire desired properties and benefits from both synthetic and natural materials in the resulting composites.

The Scope and Novelty of This Review

Recently, there have been some reviews talking about applying biopolymers in EOR [14] for example, Pu et al. [2] summarized the available data for the different biopolymers in EOR and discussed the relationship from flask to field-scale applications in a summary way. However, they discussed only the properties of each approach with its limitations to apply in EOR. Also, Corredor et al. [15] discussed the most developments in polymer nanohybrids for oil recovery, and the different mechanisms to enhance oil recovery were highlighted. In their review, only one method to enhance the performance of the biopolymers has been discussed, and only xanthan gum has been mentioned. On the same approach, Kakati et al. [16] focused on nanoparticle-assisted polymer flooding for enhanced oil recovery with experimental and simulation studies. In another way, Afolabi et al. [17] stated one technique (hydrophobic formation) (polymeric surfactants) to enhance the performance of the polymers in

EOR and mentioned one biopolymer (cellulose). The synergy of polymer with surfactant and alkaline was also discussed by Firozjahi et al. [18] with experimental and numerical simulations in detail where two biopolymers (Xanthan gum and schizophyllan) have been found. Agi et al. [19] mentioned some natural polymers that can be applied for EOR and talked only about the mechanism of the polymer flow in the porous media and the rheological behaviors. Moreover, Gbadamosi et al. [20] focused on the mechanism of polymer flooding in EOR and the impact of reservoir conditions on them mentioning the properties of the two types of polymers (synthetic and natural polymers). Matovanni et al. [21] also discussed the application of some biopolymers in EOR and mentioned very briefly some techniques to enhance their properties. In this comprehensive review, an effort has been taken to illustrate the different techniques used to enhance the performance of biopolymers (Xanthan gum, guar gum, and starch) in enhanced oil recovery and create new composites that can overcome challenges faced by these biopolymers under reservoir conditions such as temperature, pressure, salinity, bacteria, chemicals, and mechanical effects. Numerous laboratory studies using these techniques are available. However, it is important to summarize them to enhance the future approach in biopolymer flooding for enhanced oil recovery (EOR). The most famous and favorable techniques used in this approach are, introducing synthetic vinyl monomers to natural polymers through graft copolymerization reactions, functionalizing nanocomposites with biopolymers to create nano-polymer solutions, modifying biodegradable polymers to have an amphiphilic style by introducing hydrophobic materials, and creating hydrogels. The review also discusses some other biopolymers (carboxy methyl cellulose, welan gum, and acacia gum) that can be utilized to improve oil recovery and evaluates how widely they have been applied in this

Fig. 2 Different techniques to modify biopolymers using several reactive parts on their structure surfaces [11–13]



field. In this review, we have addressed several important issues (knowledge gaps) that have not been covered in recent studies. These knowledge gaps can impact the efficiency of modified biopolymers. We have also provided recommendations and prospects for the successful future implementation of these composites in the EOR field. Figure 3 showcases the flow chart of the structure of the review.

Xanthan Gum Polysaccharide

Xanthan is a significant natural polysaccharide biopolymer [22]. For the first time, this polymer was detected in the 1950s by the Northern Regional Research Labs of the United States Agriculture Branch [23]. The microbiological process of *Xanthomonas campestris* produces a xanthan polymer, by fermenting fructose or glucose with the addition of protein and an inorganic supply of N_2 [24, 25]. Figure 4 illustrates its major backbone, which consists of glucose units connected at sites 1 & 4 and structured in a helical form with folding branches along the backbone. The structure of its

backbone is like that of cellulose [26]. The branched-chain is composed of alpha-D-mannose with an acetyl group, beta-D-mannose with a pyruvate group, and beta-D-glucuronic acid. Alternative glucose has glucuronic acid wedged between two mannose units to form a short, three-sugar branch. Consequently, a pentasaccharide is the main repeating structure. The mannose at the end of the branch has a pyruvate group, while the mannose next to the backbone has an acetyl group linked to C_6 [27–29]. Thus, the glucuronic and pyruvic acid groups are accountable for the extremely negative charge of this natural polymer. Significant commercial manufacturing of this polymer started in early 1964. Currently, the main xanthan manufacturers are Merck and Pfizer, Jungbunzlauer, Rhoˆne Poulenc, and Sanofi-Elf in the United States, Austria, and France, respectively [30]. The biopolymer molecule appears to possess two different forms, spirals, and random coils, according to the temperature at which it dissolves [31–33].

Xanthan gum is employed in a variety of studies and applications owing to its exceptional capabilities in thickening aqueous solutions, serving as a dispersion factor, and

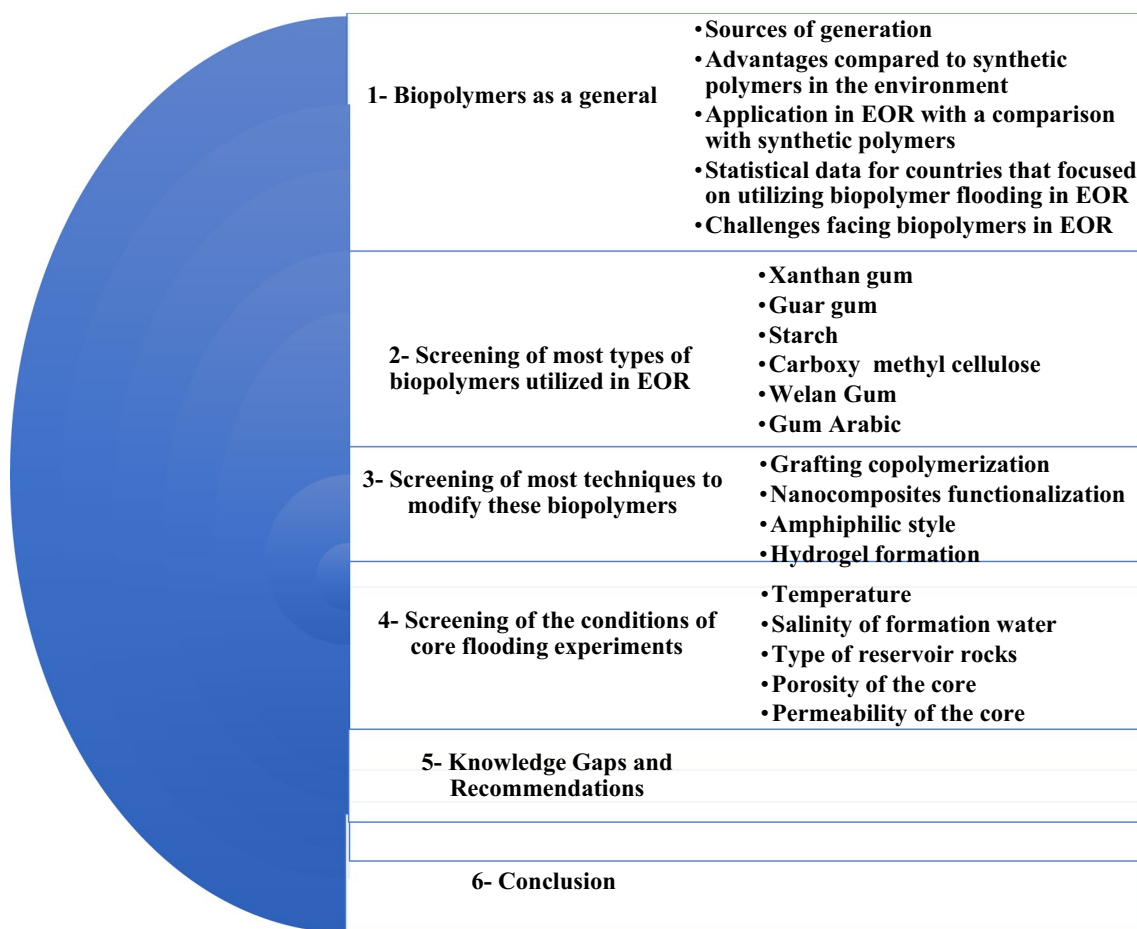
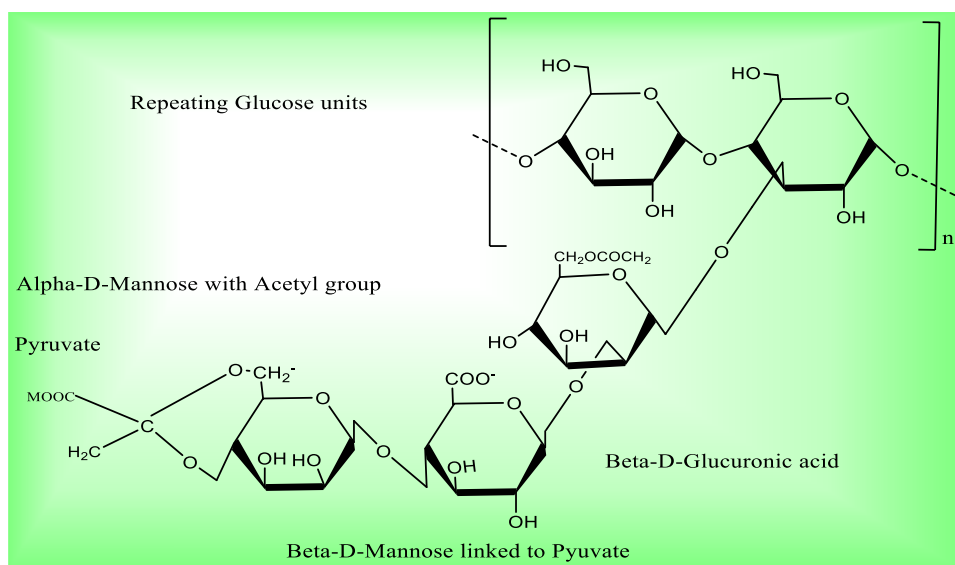


Fig. 3 The flow chart of the structure of the review

Fig. 4 Polymer's molecular structure (XG)

stabilizing blends and suspensions. Additionally, the number of publications on this intriguing material will increase dramatically [34, 35]. As a result of the extremely high viscosity of biopolymer solutions and solubility in water as well as its well-known unmatched pseudoplastic rheological properties, xanthan gum has an extensive range of important applications in petroleum engineering. It is commonly found in drilling fluids and enhanced oil recovery projects [36, 37]. This polymer has a high solubility in both hot and cold water due to the presence of anionic side chains that enhance hydration. Its molecular mass ranges between $(2\text{--}50) \times 10^6$ g/mol, which is extremely high [38]. Additionally, the biopolymer is compatible with most surface-active agents and other injection solution additives applied in improved oil extraction approaches because it exhibits pseudoplastic behavior and has excellent viscosifying characteristics, even in high-salinity reservoirs. Furthermore, it can considerably increase the injected brine's viscosity at extremely low quantities [39]. Compared to hydrolyzed polyacrylamides, xanthan is more tolerant to mechanical shearing, salt stress, and divalent ion concentration and also more stable over a wide pH range due to its stiff polymer structure [40–42]. The uses of this polymer and synthetic polymer (hydrolyzed polyacrylamide (HPAM)) as enhanced oil recovery candidates were compared [36] for heavy oil reservoirs under various salinity [43–47]. According to these findings, the solution's shear viscosity of xanthan gum was less susceptible than that of the HPAM solution to rising temperatures and salinity. As a result, in greater salinity reservoir conditions, a xanthan gum injection is superior to HPAM. Also, Ghomrassi-Barr and Aliouche [7] reported using this polymer as a candidate for the polymer-flooding to enhance oil recovery in a particular Devonian oil reservoir. They discovered that the polymer solutions maintained about 60% of their primary viscosity at

reservoir temperature (68 °C). Sveistrup et al. [48] evaluated the environmentally friendly xanthan and scleroglucan as agents for the enhanced oil recovery (EOR) technique. They discovered that scleroglucan and xanthan gum are suitable options for EOR polymer flooding because they exhibit good viscosifying properties along with shear and salt resistance. However, their reactions with surfactants are complex and reliant on the biopolymer's charge physical characteristics. Due to its natural origin, xanthan gum has also some disadvantages such as uncontrolled hydration, bacterial attack, and viscosity loss during storage where xanthan gum is biodegradable after two days [49–51].

Researchers have recently worked on modifying xanthan gum to improve its physicochemical and rheological properties and expand its applications to be suitable for use in EOR under severe reservoir conditions. It is simple to obtain a variety of methods for modifying the xanthan gum, like chemical action, hydrogel formation, and nanocomposite complexation due to the existence of several reactive parts on its structure surface as shown in Table 1. The blending of polymers and nanoparticles to form nano-polymer solutions has been considered by some researchers to boost the properties of natural polymers and hence raise oil production. For example, a nano-polymer suspension was prepared from TiO_2 nanoparticles with xanthan-gum polymer to enhance oil recovery by Keykhosravi et al. [12] and compared with native xanthan gum. They discovered that adding salt and raising the temperature of polymeric solutions reduced the shear viscosity while adding nanoparticles to the polymeric solutions might somewhat restore the viscosity. The inclusion of natural polymers in the nanocomposites maintained the distribution steadiness of NPs. Also, compared to nano-fluids, the suspensions of nano-polymer composites could increase the nanoparticles' capacity for modification of

Table 1 Different methods for modifying the xanthan gum to apply in EOR under severe conditions

Modification	Improvement	Oil recovery factor	Reservoir type	Reservoir conditions (T, Salinity, porosity & permeability)	References
Xanthan with nanoparticles (physical mixing)					
Xanthan-TiO ₂ NPs	Increase viscosity and improve wettability	19% and 25% of OOIP for native polymer and modified polymer, respectively	Carbonate	75 °C, 50,000 ppm, 19% & 77 mD	Keykhosravi et al. [12]
Xanthan-Ni NPs	Increase viscosity	4.48% and 5.98% of S _{or} for native polymer and modified polymer, respectively	Sandstone	25 °C, -, 40% & -	Rellegadla et al. [52]
Xanthan-SiO ₂ , Al ₂ O ₃ , Fe(OH) ₃ , and TiO ₂ NPs	Increase viscosity	0% & 0.3 wt. % salinity, the NPs increased oil extraction between 3% & 9% and 1% & 5%, respectively	Sandstone	25 °C, 3000 ppm, 0.35% & 6.25 D	Corredor et al. [54]
Modified xanthan using grafting reaction					
Xanthan- (Amide- and alkyl-modified SiO ₂ NPs) (AANPs)	Increase viscosity, temperature resistance, and salt tolerance	18.5% and 11.3% of OOIP for modified polymer and xanthan alone, respectively	Sandstone	75 °C, 10,000 ppm, 40% & 2 μm ²	Xu et al. [55]
Xanthan- (chloride-substituted octyl phenoxy polyoxyethylene) (COP20)	Improve thickening properties, and good surface and interfacial activities	Improve oil displacement efficiency	Sandstone	45 °C, 5177 ppm, 26% & 0.09 μm ²	Huang et al. [13]
Xanthan-g- long-chain alkyl groups	excellent thickening, and rheological properties at higher temperatures and salinity	25% and 18% of S _{or} for modified polymer and native polymer alone, respectively	Sandstone	65 °C, 7542 ppm	Fu et al. [56]
Xanthan-branched-preformed particle gel (B-PPG)	Improve thickening properties and salt tolerance	8.2% and 5.3% of OOIP for modified polymer and B-PPG alone, respectively	Sandstone	90 °C, 244,121 ppm, 41.4% & 2.62 μm ²	Xu et al. [57]
Xanthan-biosurfactant (water hyacinth)	Improve temperature resistance and salt tolerance also increase the viscosity	-	-	-	Machale et al. [58]
Xanthan-g- poly (Acrylamide) crosslinked with HMTA and HQ	Improve temperature resistance and salt tolerance also increase the viscosity	Under 50% of OOIP for PAM and over 50% of OOIP for grafted copolymer	Sandstone	100 °C, 20,000 ppm, 38.8% & 0.351 D	Boakye and Mahto [59]
Xanthan- Acrylic acid	Improve viscosity at high temperature	19% and 14% of S _{or} for modified polymer and native polymer alone, respectively	Sandstone	52 °C, 30,000 ppm, 19.58% & 102.66 mD	Said et al. [60]

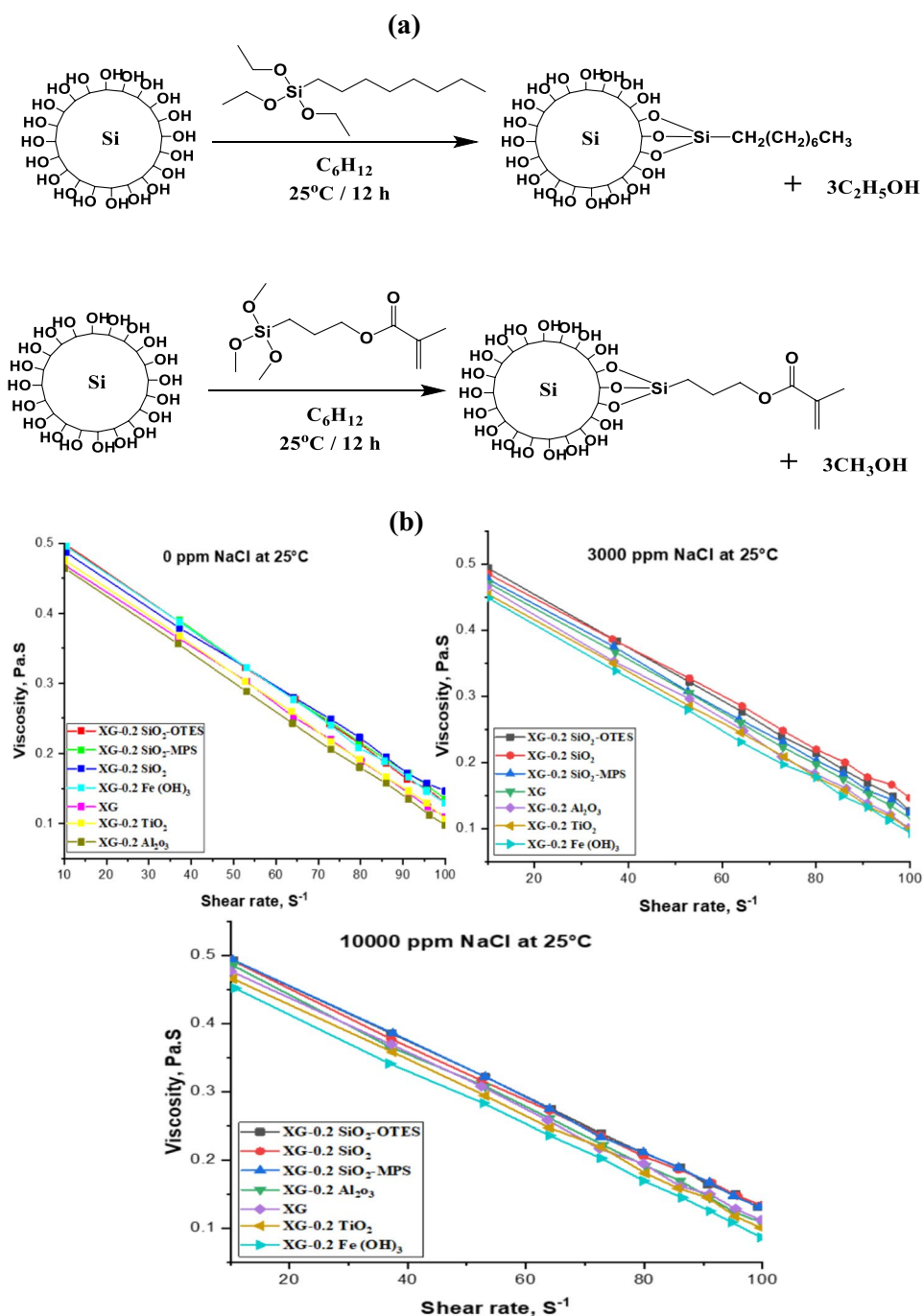
wetting and the faster equilibration obtained. According to the polymer flooding experiments results, the additional oil recovery values for the TiO_2 nanofluid and polymer solutions were 12% and 19% of original oil in place (OOIP), respectively while xanthan gum with TiO_2 produced 25% more oil. Also, Rellegadla et al. [52] used a combination of nickel nanoparticles and xanthan gum to progress the act of this biopolymer in the biopolymer flooding. It was discovered that a biopolymer-nickel nanoparticle blending has a greater viscosity of 55 dL/g contrasted to 49 dL/g for the native polymer solution by using Huggins and Kraemer models to calculate intrinsic viscosity. These models were chosen because their plots offered the best appropriate for a variety of biopolymer (XG)-dispersing medium solutions. Additionally, the xanthan-nickel nanoparticle mixture showed the highest recovery of residual oil saturation (S_{or}), at 5.9%, as opposed to 4.4% and 4.5% for the individual flooding of biopolymer and nanoparticles, separately. It was concluded from these findings that the innovative polymer flooding methodology assisted with nanoparticles can boost oil extraction beyond what is now possible. Hamedi-Shokrlu and Babadagli [53] tested xanthan gum and three various surface-active agents [sodium dodecylbenzene sulfonate (SDBS), cetyl trimethyl ammonium bromide (CTAB), and Tergitol Np-9] for stabilization of the nano nickel particles into porous media to enhance oil recovery. It was discovered that only the biopolymer could maintain the nanoparticles stable for the amount of time needed to transfer them into the oil reservoir. Corredor et al. [54] investigated the impact of titanium dioxide, aluminum oxide, in-situ produced $\text{Fe}(\text{OH})_3$, and surface-improved silicon dioxide nanoparticles (NPs) on the effectiveness of biopolymer solutions to enhance oil recovery. The surface of silicon dioxide nanoparticles was modified by reacting with 3—(methacryloyloxy) propyl trimethoxy silane (MPS) and octyl triethoxy silane (OTES) as shown in Fig. (5a). They discovered that the rheology behavior of the biopolymer solution was enhanced with the inclusion of both untouched and improved silicon dioxide nanoparticles at all brininess. However, the strong biopolymer adsorption on $\text{Fe}(\text{OH})_3$, aluminum oxide, and titanium dioxide. NP surfaces decreased the XG solution's rheology behavior (Fig. 5b). Furthermore, at (0–0.3) wt. % sodium chloride (salinity), the nanoparticles increased oil extraction between 3% & 9% and 1% & 5%, respectively. Except for $\text{Fe}(\text{OH})_3$ and titanium dioxide nanoparticles, the NPs decreased oil extraction by modified biopolymer solution by 5% to 12% at 1.0 wt. % NaCl as shown in Fig. 6. These NPs increased oil recovery by 2% to 3% due to reduced biopolymer adsorption brought on by the alkalinity of the iron hydroxide and titanium dioxide nano polymer sols.

Since alkylated biopolymers are commonly used as thickening and gelling agents in various industries. They

have an amphiphilic style due to the addition of hydrophobic materials to biopolymers. As a result, the hydrophobic modification of biodegradable polymers has attracted the attention of many researchers worldwide. Huang et al. [13] conducted a hydrophobic modification of XG to enhance its surface and interface activities. They grafted a chloride-substituted octyl phenoxy polyoxyethylene (COP20) onto the backbone of XG. The hydroxymethyl groups in the natural polymer's main chains acted as a nucleophile and interacted with COP20 to produce XGP20, as illustrated in Fig. 7a. This modified XG was then utilized in polymer flooding, as shown in Fig. 7b. From the experiment, it was found that XGP20 had better thickening properties and also displayed good surface and interfacial activity. This was attributed to the active chains that contained the hydrophobic octyl group and were inserted into the biopolymer. The interfacial tension in the saline solution was 0.46 mN/m, and the critical micelle concentration (CMC) was 300 ppm in water and 5000 ppm of sodium chloride at 30 °C. After performing several displacement processes, NMR imaging has shown that the modified biopolymer can boost the water sweep efficiency, resulting in enhanced oil recovery, as indicated in Fig. 7c. A new macro-improver, COP6 (chloride-substituted octyl phenoxy polyoxyethylene), was also created by Huang et al. [61]. They grafted it with xanthan gum to create XGP6, which was subsequently used in polymer flooding for strata with permeabilities of $(300 \times 10^{-3} - 50 \times 10^{-3}) \mu\text{m}^2$ and higher. Compared to native xanthan gum, XGP6 demonstrated simultaneous surface and interfacial activities as well as improved thickening behavior. Additionally, at a small NaCl concentration, this modified polymer exhibited salt-induced thickening behavior action. Its critical micelle content (CMC) in water at 30 °C was 0.2 g/L. It has been discovered that the anti-biodegradation ability of the XGP6 solution has improved. When compared to aqueous XG solutions under similar conditions, which tend to attack after five days if a bactericide is not present, the XGP6 bacterial solution was delayed until the fifteenth day.

A novel combination of two biopolymers diutan gum and xanthan with B-PPG (branched-preformed particle gel) as shown in Fig. 8a was studied by Xu et al. [57]. Through research, it was found that the combination of polysaccharides and B-PPG had a synergistic effect in thickening suspensions, as shown in Fig. 8b. Additionally, when natural polymer XG was blended with particle gel, it increased salt tolerance. Furthermore, the blending of natural polymer diutan gum with particle gel increased both salt tolerance and temperature. Also from flooding experiments results, it was found that at (T, 90 °C and salinity, 244,12 ppm) the oil extraction productivity was higher in the two blends (17.4% OOIP in the case of diutan/B-PPG composite and 8.2% OOIP in the case of xanthan/B-PPG composite) than gel alone (5.3% OOIP) as indicated in Fig. 8c.

Fig. 5 a Chemical grafting of SiO₂ NPs with MPS and OTES and **b** Viscosity of 4 g/l biopolymer solutions with 1 g/l SDS and SiO₂, SiO₂-OTES, SiO₂-MPS, Fe(OH)₃, Al₂O₃, and TiO₂. Derived with consent from ref.[54]. Publisher 2019, MDPI



Machale et al. [58] studied the effect of a new bio surface active agent that was prepared from water hyacinth on the rheological behavior of the biopolymer and matched with sodium dodecyl sulfate (SDS) (a commercially used surfactant) (Fig. 9). They found that there was barely a growth in the biopolymer solution's viscosity after the injection of synthetic surfactant (SDS) but biosurfactant (WH) significantly increased its viscosity. The aqueous XG-WH solution's remarkable increase in viscosity may be caused by the existence of fibers in the bio-surface active agent, where the XG

coils up on the surface of the WH fibers and forms a complicated association structure. At a shear rate of 10 s⁻¹, they investigated the outcomes of two parameters (salinity and temperature) on the rheological behavior of the polymer solutions. It was discovered that the temperature had a more pronounced effect on XG than the XG-SDS solution, which had a somewhat mild impact. Compared to that, the XG-WH system did not exhibit any noticeable temperature effect, and the viscosity of the XG-WH solution without salt was somewhat higher than that of the solution with salinity. They concluded that

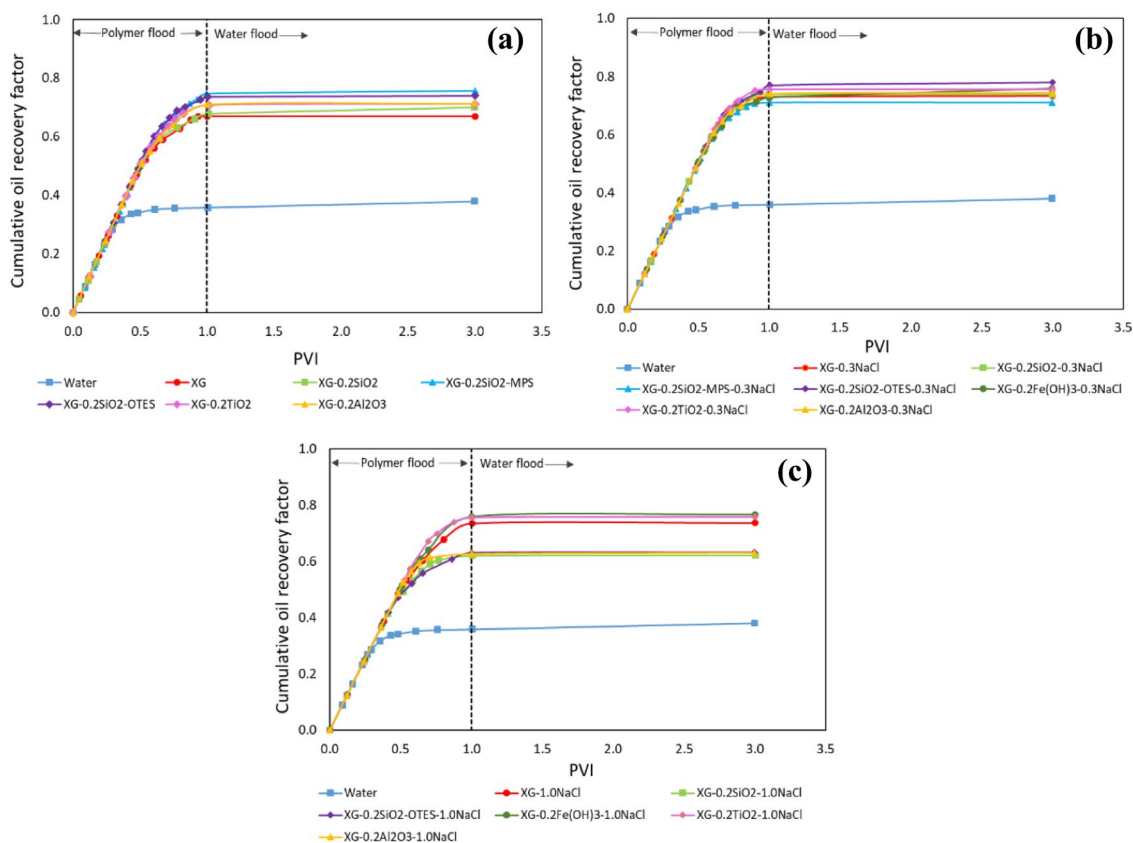


Fig. 6 Total recovery factor of 4 g/l biopolymer solutions with 1 g/l SDS and SiO_2 , SiO_2 -OTES, SiO_2 -MPS, $\text{Fe}(\text{OH})_3$, Al_2O_3 , and TiO_2 at a) 0 wt %, (b) 0.3 wt %, and (c) 1 wt % salinity at 25 °C. Derived with consent from ref.[54]. Publisher 2019, MDPI

the biosurfactant (WH) has temperature resistance and can be applied in severe reservoir conditions.

Boakye and Mahto, [59] grafted polyacrylamide on the biopolymer (XG) using a free radical copolymerization technique in the existence of potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$) as an initiator (Fig. 10a). After that, this modified composite was cross-linked with hexamethylenetetramine (HMTA) and hydroquinone (HQ) as shown in Fig. 10b. Based on the results, it was discovered that the crosslinked gel can be utilized for profile alteration tasks necessary to enhance oil recovery from mature oil fields with many reservoir heterogeneities, as shown in Fig. 10c. Additional modification for xanthan gum was made by Said et al. [60] by reacting it with acrylic acid to form xanthan acrylate. It was found that the new composite has a higher viscosity than native polymer and given oil recovery (19% of S_{or}) higher than xanthan gum alone (14% of S_{or}).

Guar Gum Polysaccharide

The biopolymer (GG) (an off-white powder) is a hydrophilic, nonionic, and heterogeneous natural polysaccharide [62]. It is produced from the guar seed endosperms

(*Cyamopsis tetragonoloba*) with molecular weight ranging from $(1-2 \times 10^6 \text{ g/mol})$ [63–65]. The structure of guar gum is given in Fig. 11 [11]. A study of the guar gum structure indicates it is a branched copolymer. Mannose units make up the polymer's backbone structure. A galactose branch is joined to every other mannose unit in the molecule. The natural polymer is referred to as a "polysaccharide" or, more specifically, a "galactomannan" since the two monomers, mannose and galactose, are simple sugars. The polymer is known as "nonionic" because no ions are found within its structure [66–68].

Due to its nonionic character, guar gum can be hydrated in many types of mixing waters and is highly compatible with sodium chloride and potassium chloride. Compatibility with salts of polyvalent metal ions such as calcium chloride, magnesium chloride, and aluminum chloride is dependent on salt concentration [69, 70]. Guar gum solutions are fairly stable until 175 °F but tend to degrade rapidly above this temperature. The degradation is the loss in viscosity due to cleavage of the acetal linkage that results in depolymerization [71]. Investigations were conducted to increase the thermal stability of guar and other polysaccharides.

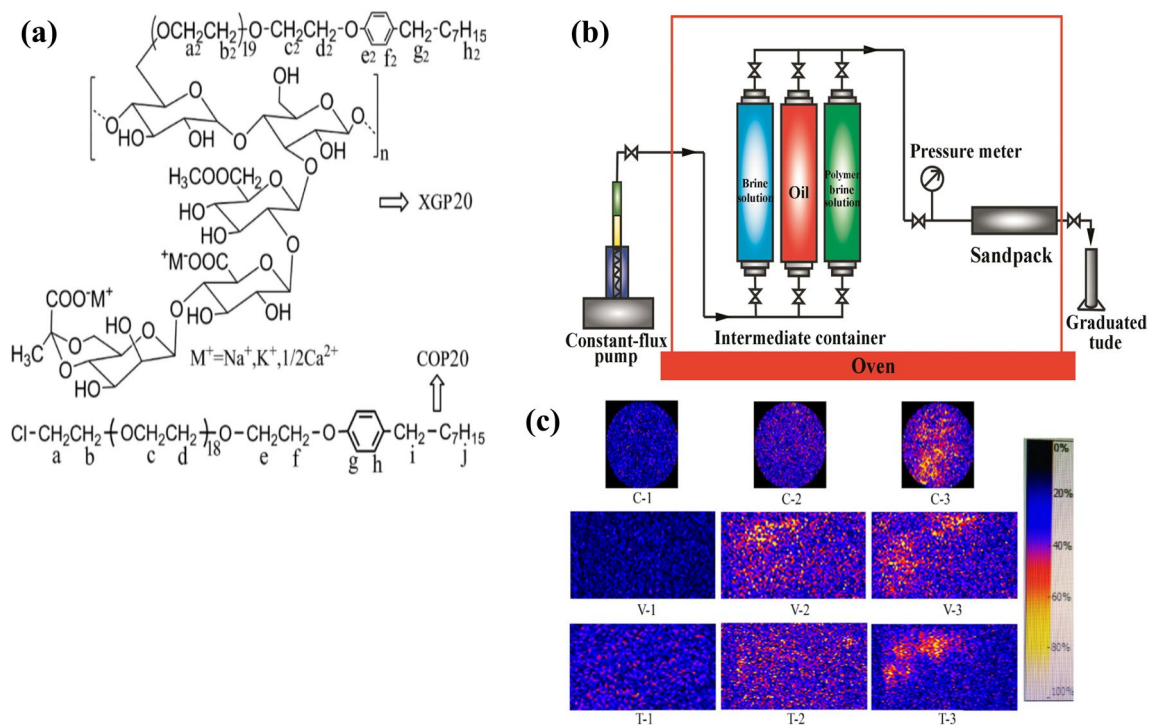


Fig. 7 **a** Molecular structures of COP20 and XGP20S, **b** The experimental equipment for the polymer flooding study, and **c** NMR spectroscopy of core on 3 parts after 3 separate displacing operations. **1:**

the first brine flooding; **2:** biopolymer flooding; **3:** the second brine flooding. **C** cross-part; **V** vertical part; **T** top part. Derived with consent from ref. [13]. Publisher 2020, Elsevier

The biopolymer is unchanging across a large pH range. However, the constancy of an acidic biopolymer solution over an extended period is poor. This is due to the acid-catalyzed cleavage of the acetal linkage between mannose units [72, 73]. The acetal linkage is indicated in Fig. 12a. The cleavage of the acetal linkage is indicated in Fig. 12b. The destruction of an acetal linkage breaks the polymer chain into two fragments. This process occurs randomly along the polymer chain [74, 75]. As the molecular mass of the biopolymer is decreased, the viscosity of the solution drops impulsively.

Guar gum is extremely susceptible to enzymatic attack. The presence of both cellulose-producing and hemicellulose-producing bacteria can cause polymer degradation [76, 77]. Guar gum solutions are very stable in the pH 4.5–10 range, highly viscous, resistant to oils, chemicals, and greases, have excellent water binding capacity, multiple hydroxyl groups for hydrogen bonding creation, and a high ability for chemical treatment and copolymerization [8, 78, 79]. So, this biopolymer (GG) is utilized in a variety of items, like diet, cosmetics, pharmacy, papermaking, textile products, and coloring owing to its exceptional capacity to change the rheology properties [80, 81]. In the petroleum industry, GG derivatives are used in drilling mud agents, drag-reducing agents, proppant fluids, thickening agents of fracturing fluid, and stimulation of hydrocarbon recovery [82, 83]. Guar gum

and its modified forms are currently undergoing field testing for EOR (Table 2) where Musa et al. [78] estimated the usability of the native biopolymer for reservoirs that have severe conditions (high temperature and high salinity) and proved its usage as a biodegradable polymer for EOR operations in sandstone reservoirs. The findings indicated that while the biopolymer exhibits shear-thinning behavior and is very vulnerable to microbial deterioration, GG also demonstrates excellent characteristics and stability under high temperatures and salinity. The flooding experiment showed an increase in the recovery factor by 6%. Rellegadla et al. [8] prepared a biopolymer solution termed viscosity-augmented guar (VAG) by heating the native biopolymer and exclusion of insoluble impurities. They then tested the VAG's ability to alter wettability and enhance oil recovery (Scheme 1). According to experimental findings, the oil-wet surface's contact angle decreased from 102 degrees after being treated with VAG to 81 degrees, indicating modification of the wettability to water-wet states. Additionally, compared to 2.9% by partially hydrolyzed polyacrylamide, the EOR capacity of viscosity-augmented guar demonstrated an extra oil extraction of 7.3% of the total oil in place.

Nowadays, researchers are interested in nanoparticle-assisted polymer flooding. Where, the nanoparticles improve the rheological characteristics and stability of polymers (their rheological, mechanical, thermal, and optical

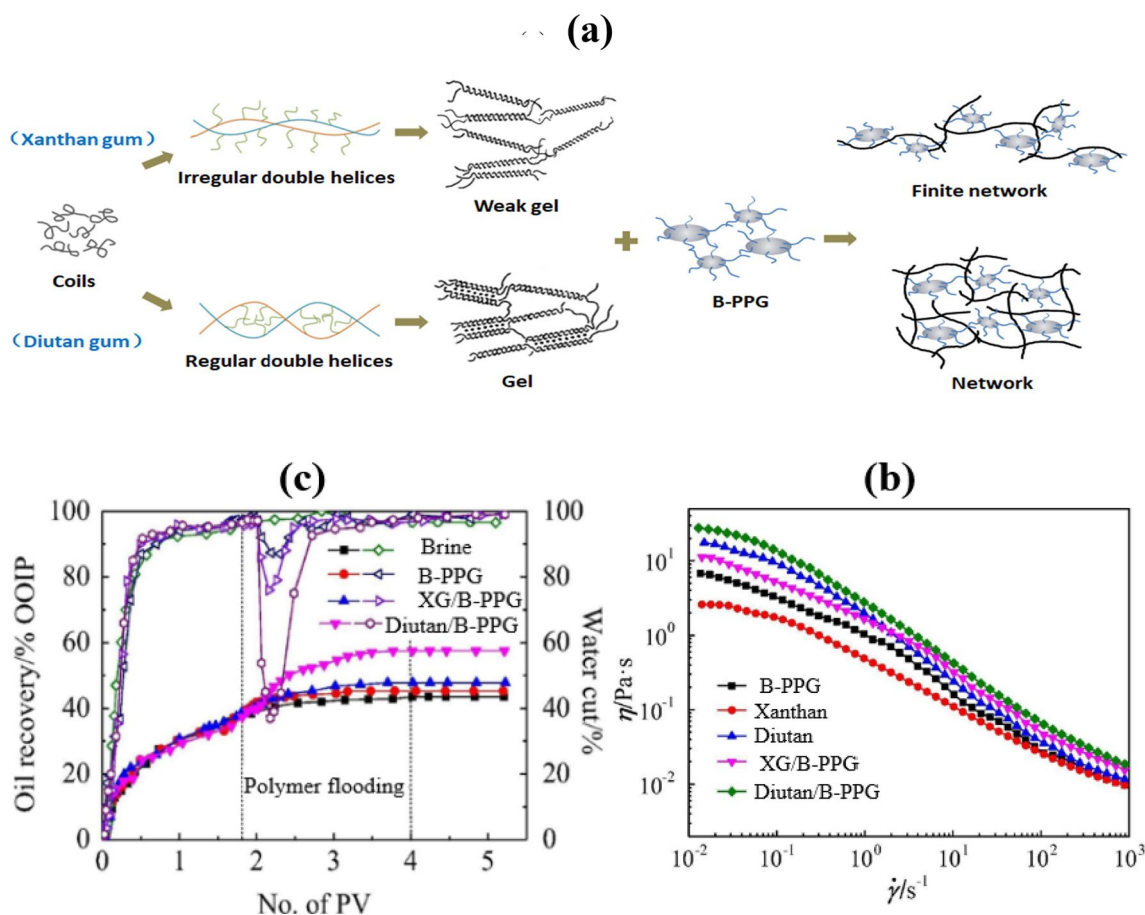


Fig. 8 **a** The schematic description for the interaction between two biopolymers and B-PPG, **b** The relationship between the viscosity (η) and the shear rate at 25 °C for Diutan, xanthan, B-PPG, diutan/B-PPG and anthan/B-PPG solutions, **c** oil recovery factor and water

cut for water, B-PPG and biopolymer/B-PPG composites flooding at 90 °C and 244, 12 ppm salinity. Derived with consent from ref.[57]. Publisher 2019, Elsevier

properties) and thereby lessen performance restrictions for polymer flooding in severe reservoir environments [86–90]. The effective improvement is related to stronger contacts among the particles of polymer and the nanoparticles, which are determined by the small size and stability of the distributed nanoparticles. Additionally, nanoparticles of small sizes are more stabilized and exhibit great surface/capacity ratios. Consequently, a greater variety of polymer chains may interact with the NPs. Furthermore, the polymer's reaction to shearing pressures and its relaxation period are influenced by the NP/polymer relative size. In this context, Bera et al. [84] investigated the guar gum's rheological characteristics containing silica nanoparticles and used it with and without silica nanoparticles as polymer-flooding agents. Also, they investigated how the wettability changed when guar gum and silica nanoparticles were present. Researchers found that the quantity of nanoparticles in the biopolymer solution causes a considerable increase in viscosity. Additionally, they discovered that a natural polymer (GG) that contains nanoparticles can effectively shift the contact angle from hydrophobic to

hydrophilic. Results of core flooding experiments revealed that guar gum with silica nanoparticles recovers 44.3% of OOP, which is higher than native guar (which recovers 27.2% of OOP) and silica NPs (which recovers 10.73% of OOP), improving the effectiveness of guar gum polymer as shown in Fig. 13. Due to their distinctive characteristics, which combine the benefits of inorganic NPs with organic polymers, these nanocomposites are of tremendous interest.

In contrast, the characteristics of natural and synthetic polymers can be combined chemically to create novel components. These new components may have the benefit of combining biopolymers' common properties, such as higher thermal and shear stability, with those of synthetic polymers, including higher resistance to bacterial attack and useful properties as rheology modifiers. Accordingly, Abou-alfitoh et al. [11] improved the properties of native guar gum by grafting it with synthetic vinyl monomers (acrylamide, methyl methacrylate, and trimethoxy phenyl silane) through a free radical reaction. This modification was done to enhance the rheological and solution properties of the polymer. The analysis of rheology

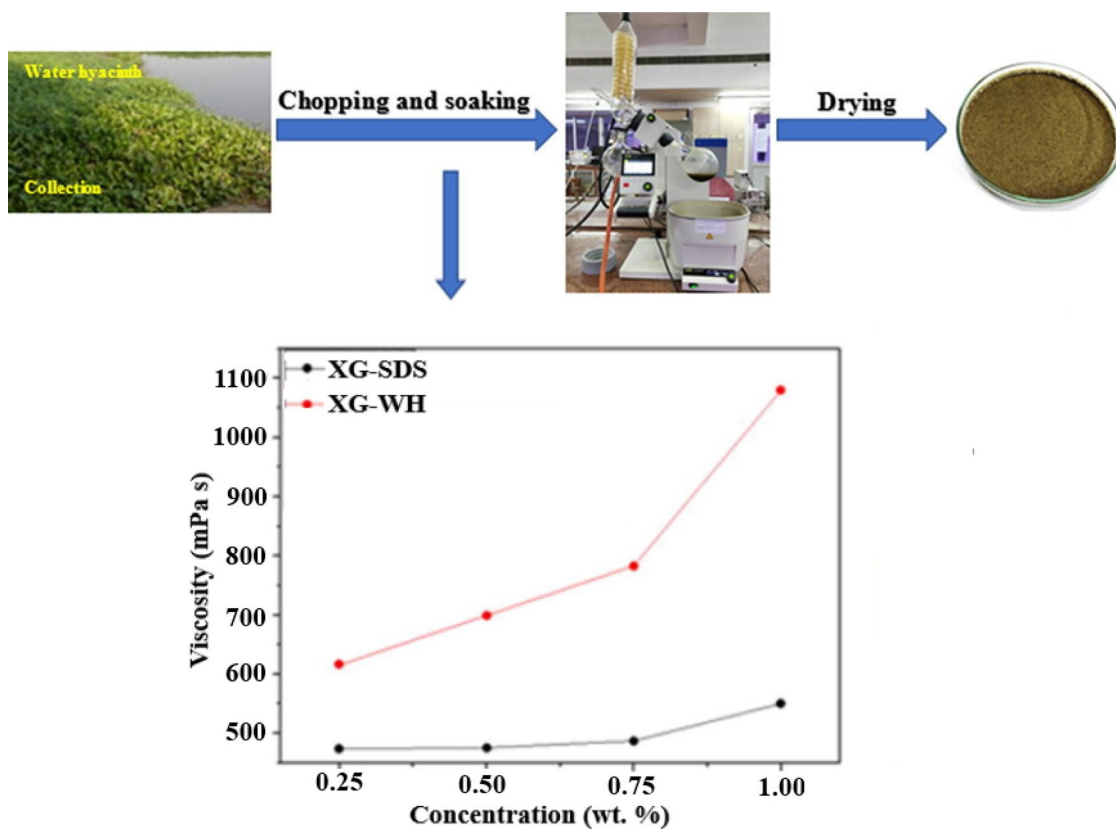


Fig. 9 The schematic representation for synthesizing a novel biosurfactant and its impact on xanthan gum viscosity compared to a commercially used surfactant (SDS). Derived with consent from ref.[58]. Publisher 2019, Elsevier

has confirmed that the existence of synthetic acrylamide (AM) and methylmethacrylate (MMA) polymers can increase the tolerance to temperature and salinity, as well as improve rheological behaviors. Additionally, the presence of trimethoxy phenyl silane (TEVS) polymer can enhance more and more guar properties. From flooding data, they discovered that the two modified forms (GG-g-AM-MMA and GG-g-AM-MMA-TEVS) are acceptable for enhancing oil recovery under severe conditions (Temperature, 90 °C, and Salinity, 80,000 ppm). The recovery factor was 47% S_{or} by applying GG-g-AM-MMA and 55% of S_{or} by applying GG-g-AM-MMA-TEVS while the polymer alone achieved 27% of S_{or} . Also, Elsaedi et al. [85] have developed two biodegradable biopolymers by cross-linking N, N'-methylene bisacrylamide with the biopolymer (GG) and two distinct co-synthetic polymers (AM and AMPS) using graft copolymerization reaction. The resulting biodegradable biopolymers, GG-g-poly(AM-AMPS) (GH) and GG-g-poly(AM-AMPS)/Biochar (GBH composite) were tested as potential applicants for enhanced oil recovery (EOR) in high salinity environments. Guar hydrogel (GH) and guar/biochar composite hydrogel (GHB) were shown to be efficient biopolymers for enhanced oil recovery in elevated salinity fields and demonstrated a considerable impact on postponing the water breakthrough during flooding trials. El-hoshoudy

et al. [62] examined the potentiality of palmitate-guar (PGG) and native biopolymer (GG) for increasing oil recovery. They discovered that the proposed native and modified biopolymers can be applied as candidates for enhanced oil recovery (EOR) and hydrophilicity modification in elevated salinity reservoirs. Also, Samanta et al. [91] reported natural surfactants and polymers could be applied to improve oil extraction. Galactomanan was applied as the biopolymer and the natural surfactant was extracted from the soapnut shell. By pumping an equal volume of biopolymer, surfactant-biopolymer, and alkaline-surfactant-biopolymer slug following water swamping, three levels of studies were conducted to evaluate enhanced oil recovery. Alkaline-surfactant-polymer flooding produced a significantly higher extra recovery (equivalent to 24% original oil in place) than the other two procedures over waterflooding (equivalent to 50% original oil in place).

Starch Polysaccharide

The most important carb in human food is starch, one of the more prevalent glucose natural polymers found in plants [92]. Commercially, it is obtained from a variety of sources, including corn, potato, rice, wheat, grains, legumes, tubers,

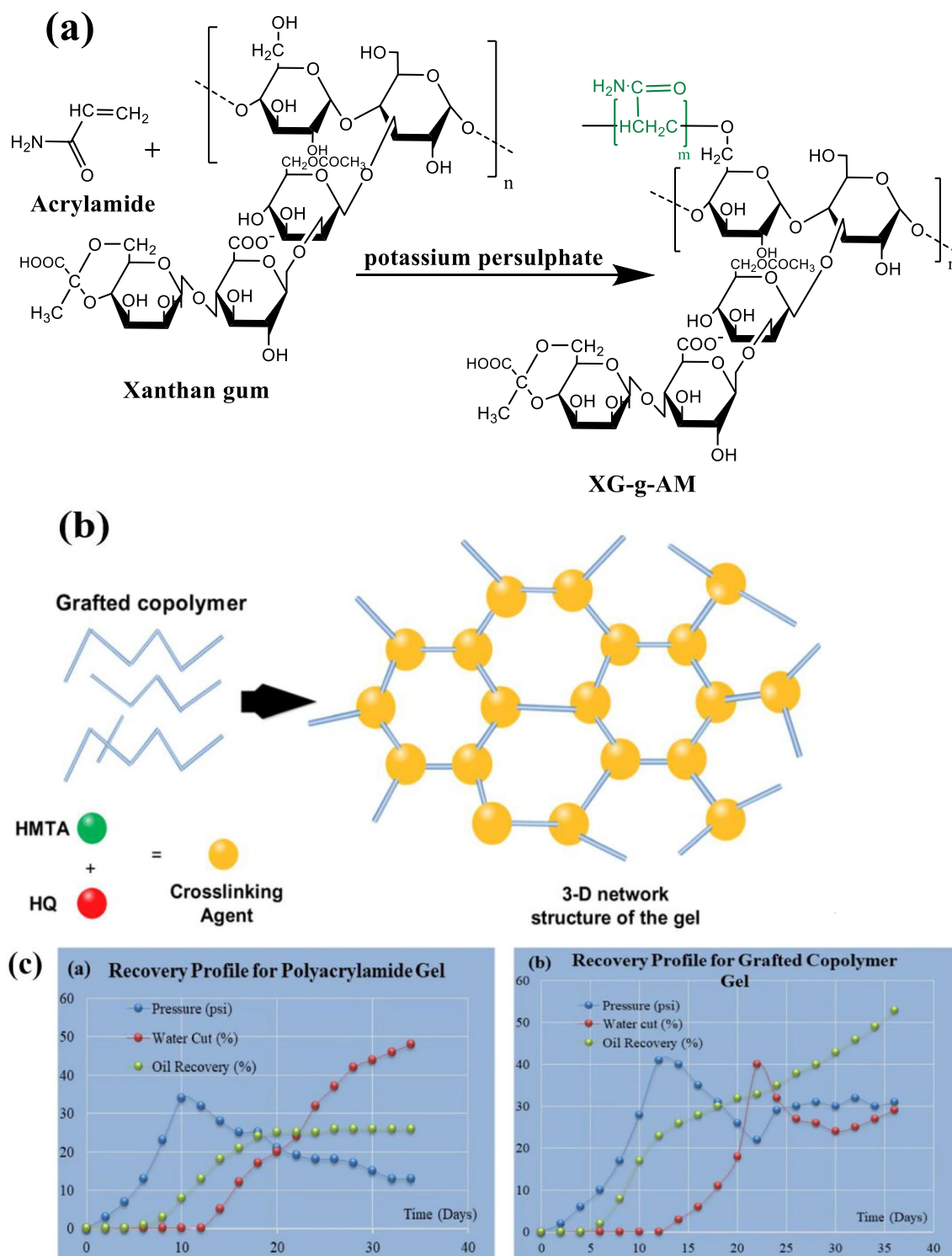


Fig. 10 **a** The grafted copolymer's creation procedure, **b** Schematic illustration of the modified copolymer gel structure, and **c** The recovery profile for profile modification with **a** Synthetic polymer gel and

b Modified biopolymer gel. Derived with consent from ref.[59]. Publisher 2021, Springer

etc. [93]. Starch is a biopolymer created chemically by joining glucose molecules together with glycosidic linkages [94–96]. The amount of amylopectin and amylose in the

biopolymer grains is based on the nature of connections connecting these units of glucose. Amylose is a linear polymer with long-chain from α -D-glucose rings attached

Fig. 11 Molecular structure of guar gum. Derived with consent from ref. [11]. Publisher 2021, Elsevier

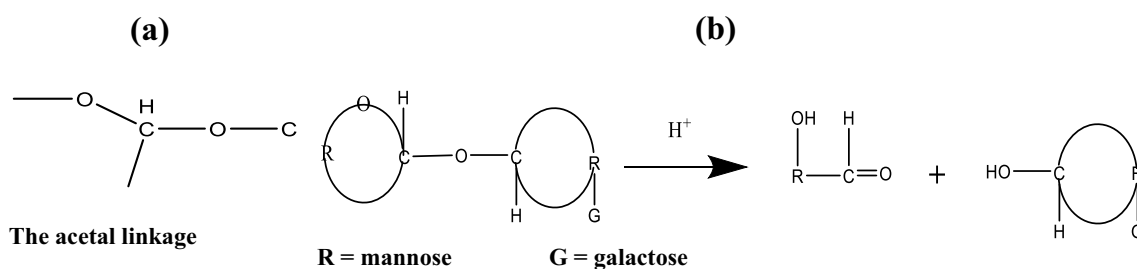
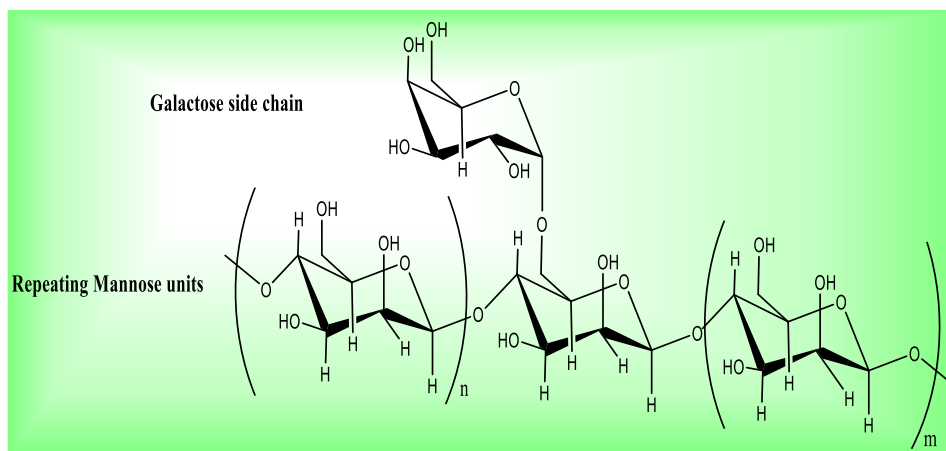
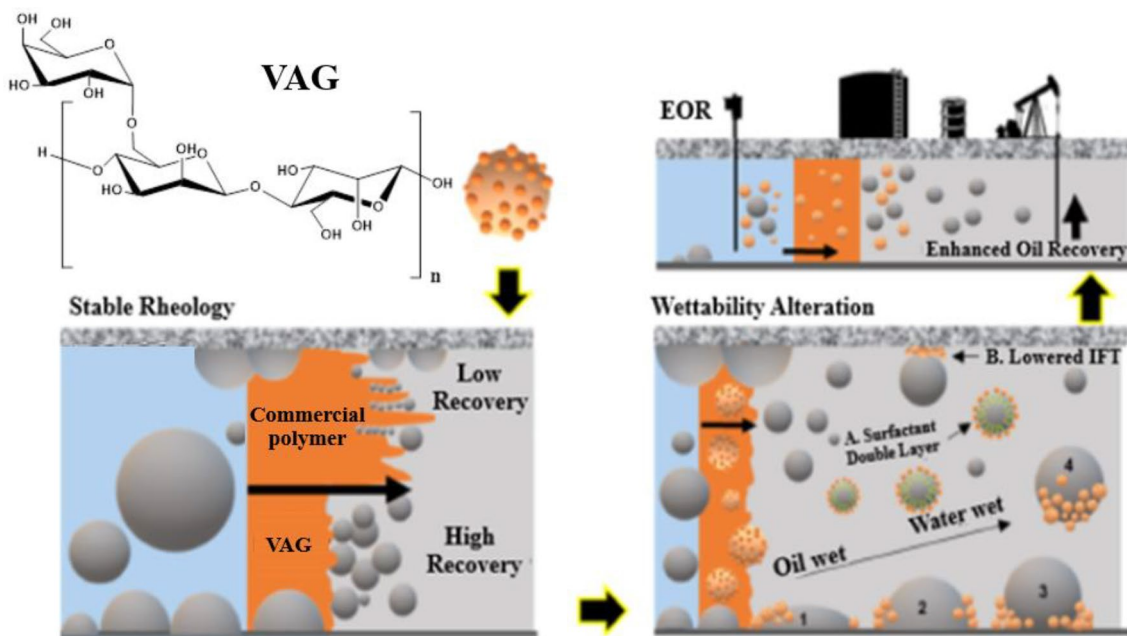


Fig. 12 **a** The acetal linkage, and **b** Polymer degradation by acid-catalyzed hydrolysis of the acetal linkage

Table 2 Guar gum and its modified composites in enhanced oil recovery

Modification	Improvement	Oil Recovery Factor	Reservoir type	Reservoir conditions (T, Salinity, porosity & permeability)	References
Native guar gum	–	6% of S_{or} for native polymer	Sandstone	90 °C, 50,000 ppm, 20% & 1200 mD	Musa et al. [78]
viscosity-augmented guar (VAG)	Enhance wettability to intermediate water-wet	7.31% of OOIP	Carbonate	65 °C, 5367 ppm, 34.95% & -	Rellegadla et al. [8]
Guar- SiO ₂ NPs	Increase viscosity, and enhance wettability to water-wet	44.3% and 27.2% of OOIP for modified polymer and guar alone, respectively	Sandstone	50 °C, 2000 ppm, 17% & 205 mD	Bera et al. [84]
GG-g-AM-MMA and GG-g-AM- MMA-TEVS	Improve temperature resistance and salt tolerance also increase the viscosity	47.7% and 55.5% of S_{or} for two modified composites, respectively	Sandstone	90 °C, 80,000 ppm, 26.3% & 68.5 mD	Abou-alfitooh et al. [11]
GG-g-poly(AM-AMPS) and GG-g-poly(AM-AMPS) /Biochar	Enhance rheological properties of native polymer	13.69% and 8.95% of OOIP for the first one at (5.0 g/L) and the second one at (2.0 g/L), respectively	Sandstone	25 °C, 35,000 ppm, 30.35% & 721.85 mD	Elsaeed et al. [85]
palmitate-guar gum	Modifying wettability to water-wet	17% and 12% of OOIP for modified polymer and guar alone, respectively	Sandstone	70 °C, 75,000 ppm, 26.464% & 551 mD	El-hoshoudy et al. [62]



Scheme 1: Diagram of the VAG polymer application in EOR from the carbonate reservoir. Reproduced with permission from ref. [8]. Copyright 2021, ACS

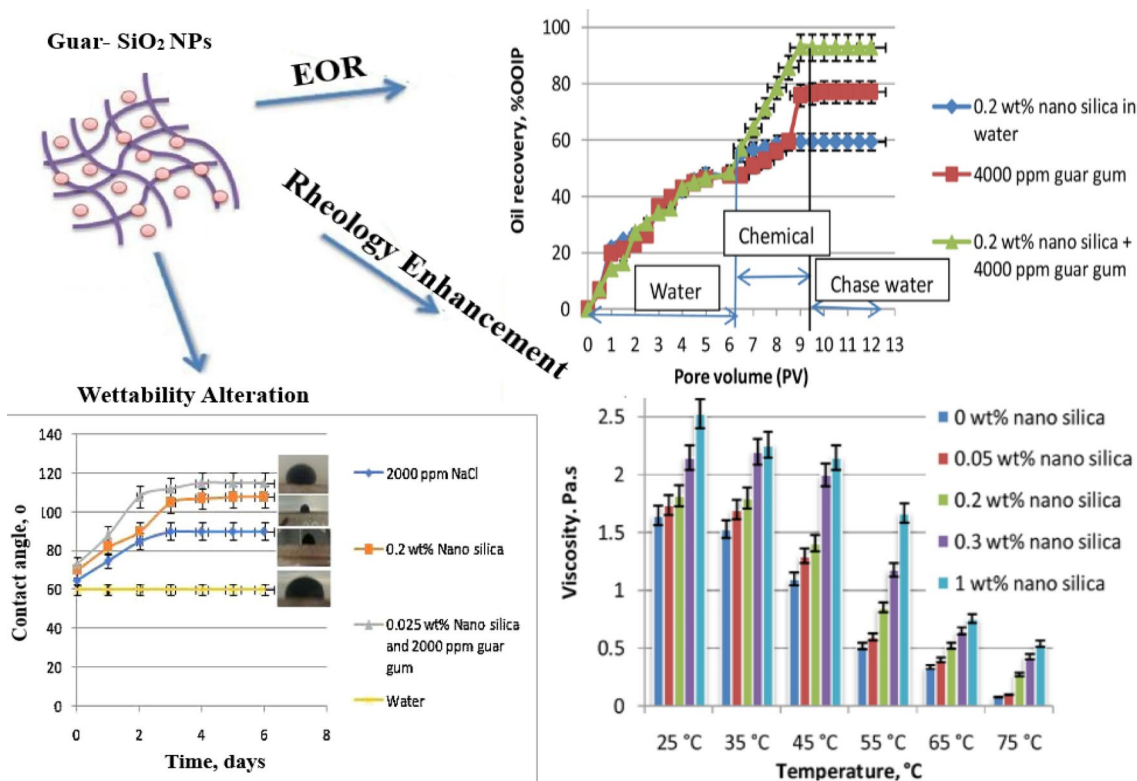


Fig. 13 Silica nanoparticles' impact on biopolymer (GG) in terms of rheological properties, wettability alteration, and oil recovery factor. Derived with consent from ref. [84]. Publisher 2020, Elsevier

by α -(1 \rightarrow 4) glycosidic connection as denoted in Fig. 14A. Amylopectin is a highly branched polymer of α -D-glucose rings with multiple small chains that are attached through α -(1 \rightarrow 6) glycosidic connection to the backbone of the macromolecule as illustrated in Fig. 14B. The amylopectin and amylose percent of starch determines its chemical and physical characteristics. While amylopectin is water soluble and improves the starch's adhesive capabilities, Amylose is not soluble in water and increases the ability of biopolymer to gelatinize [97]. Starch is a very versatile raw material in different applications such as the food industry, coatings, glues, oil drilling fluid additives, drug transporters, biofuels, etc. [98]. Studies conducted in the field of enhanced oil recovery have demonstrated that adding starch to waterflood sites results in a 6%–8% increase in cumulative oil production more than synthetic polymer (commercial polyacrylamide) flooding [99].

Considering its availability, stability, and environmental sustainability, it would be advantageous to improve this biopolymer for use in EOR applications. This is because the effectiveness of native starch is negatively affected by

harsh conditions such as high pressure, temperature, and salt in a hydrocarbon reservoir. There is much literature that describes the application of starch derivatives such as pre-gelatinized starches, etherified starches, grafted starches copolymers [100], and crosslinked and blended starches [101] in improved oil extraction techniques (Table 3). In contrast to native starch, crosslinked starch produced by grafting vinyl monomers onto starch displays reduced microbial attack, enhanced rheological behavior of the solution, and rising thermal stability [102]. In this regard, El-hoshoudy [94], made modifications to starch by introducing a double bond (vinyl type) on the biopolymer structure using Fang et al. [103] method to obtain acryloylated starch. He then used this acryloylated starch to undergo a grafting reaction with two different monomers (acrylamide and acrylic acid monomers). This process was performed through an emulsion copolymerization reaction with the presence of vinyl trimethyl silane (Fig. 15a). He found that the presence of two different synthetic polymers enhances the water absorption capacity of the biopolymer. Additionally, the inclusion of SiO₂ particles strengthens

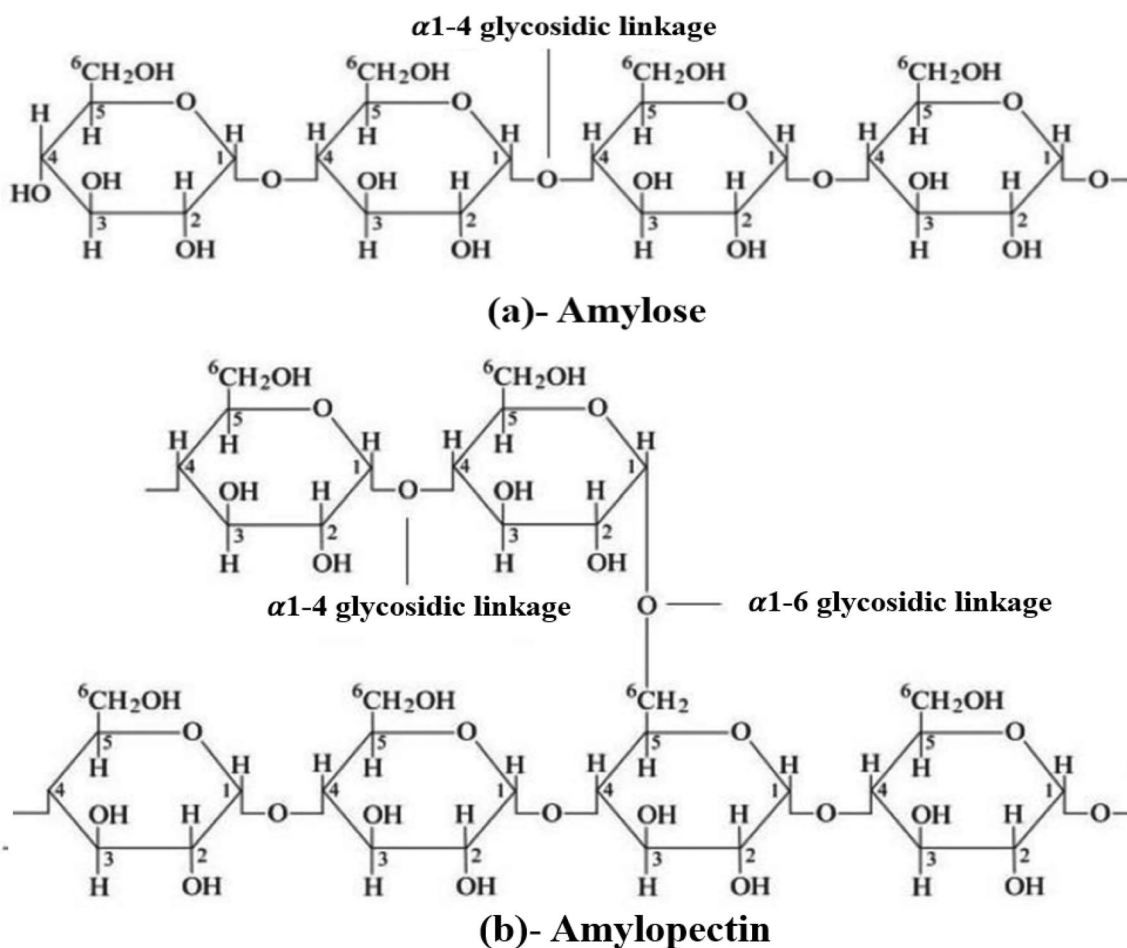


Fig. 14 Molecular structure of starch (A amylose fraction and B amylopectin fraction)

Table 3 Different starch derivatives in enhanced oil recovery applications

Modification	Improvement	Oil recovery factor	Reservoir type	Reservoir conditions (T, Salinity, porosity & permeability)	References
Acryloylated starch-g-poly (AM-AA)/ TMVS	Enhance the water absorption capacity of polymer and increase salt tolerant	46% of S_{or}	Sandstone	70 °C, 80,000 ppm, 21.9% & 45.39 mD	El-hoshoudy [94]
Acryloylated starch-g-poly (AM-VMA-NVP)/ DMPVS	Enhance thermal stability and salt tolerance (severe reservoir conditions)	49% of S_{or}	Sandstone	80 °C, 80,000 ppm, 21.9% & 45 mD	El-hoshoudy and Desouky [96]
Sulfonic starch-g-MBAM&TEVS	Enhance wettability to hydrophilicity	39% of S_{or}	Sandstone	50 °C, 100,000 ppm, 22% & 45.4 mD	El-hoshoudy et al. [95]
crystalline starch nanoparticles (CSNP)	Decrease IFT and enhance the wettability of the rocks to hydrophilicity	23% of OOIP	Sandstone	120 °C, 22,000 ppm, 15.3% & 167.43 mD	Agi et al. [104]
Quaternary ammonium cationic starch	Improve wettability to hydrophilicity and salt tolerance	18% of OOIP	Sandstone	70 °C, 5727 ppm, 25% & 1.46 μm^2	Fu et al. [105]
Quaternary ammonium cationic starch	Modifying the wettability of core to hydrophilicity	14.9% of OOIP	Sandstone	70 °C, 6000 ppm, 25% & 1.627 μm^2	Qiao et al. [106]

the polymer and increases its resistance to salt. When he applied the modified biopolymer composite in polymer flooding using a linear sandstone model (to simulate the reservoir) the result indicated a recovery factor of 46% S_{or} . This modified composite is successful for biopolymer flooding operations in harsh reservoir environments. El-hoshoudy and Desouky, [96] also grafted acryloylated starch with three different synthetic polymers (Acrylamide, vinylmethacrylate, and 1-vinyl-2-pyrrolidone) in the existence of dimethyl phenyl vinylsilane through a grafting copolymerization reaction (Fig. 15b). Based on the results of the polymer flooding tests, it was found that the generated composite can endure harsh conditions of high salinity and temperature in the reservoir. Additionally, it has the potential to increase oil extraction by up to 49% of the remaining oil saturation. This makes it a promising candidate for biopolymer flooding applications.

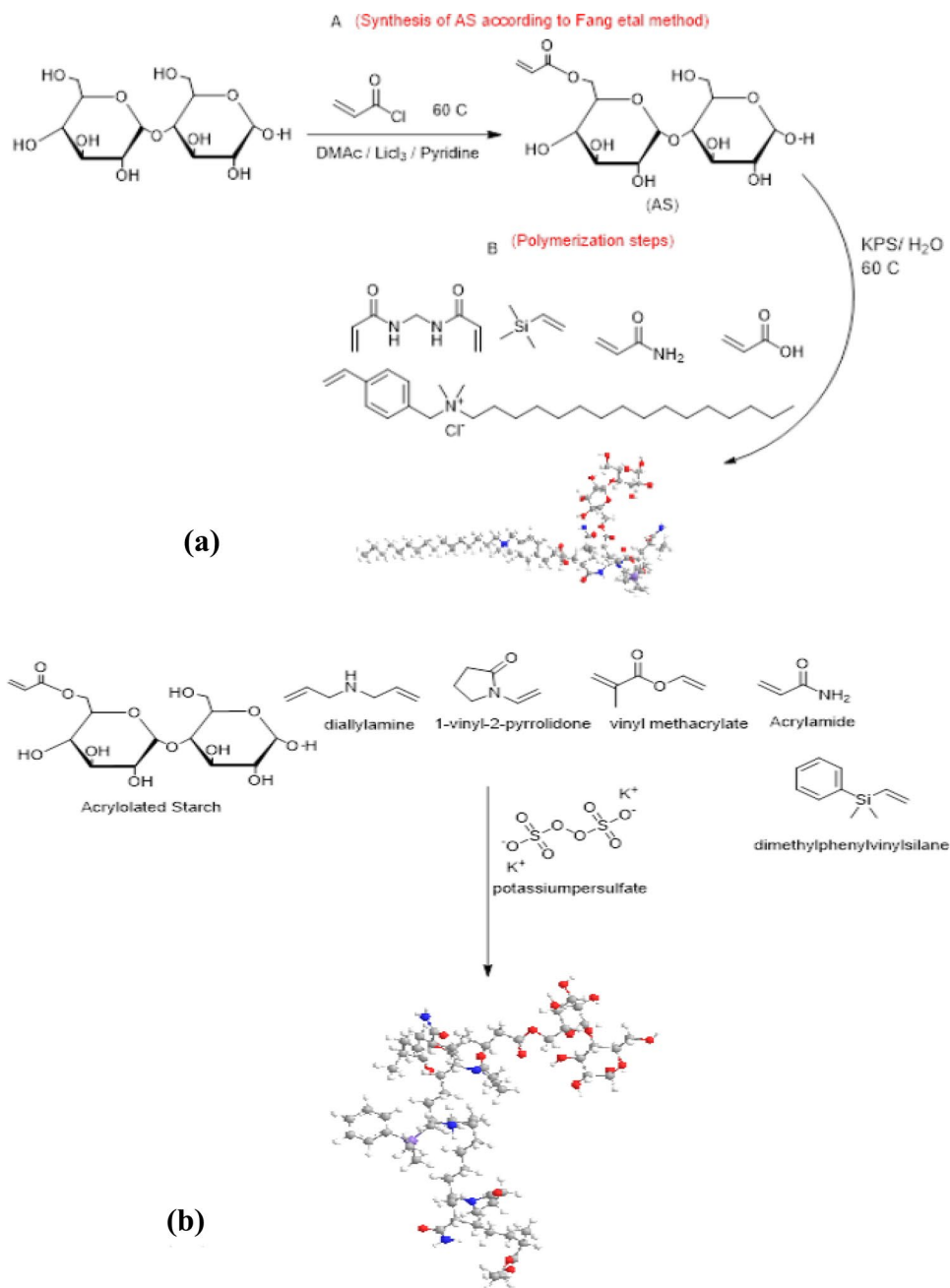
In another protocol, El-hoshoudy et al. [95] modified starch by functionalization of it with sulfur derivatives where starch was functionalized with thiourea. Through an eco-friendly oxidation method, it was converted to a sulfonic acid derivative. Next, a quaternized bipolymer sulfonic acid derivative was created and polymerized with nanoparticles (SiO_2 NPs) using a redox initiation mechanism at 40 °C as shown in Fig. 16. They stated that the created composite is an inexpensive, available, and eco-friendly candidate for the petroleum industry. Additionally, they said that electrostatic forces between the negatively charged sand surface and the cationic N^+ -group on the polymer stimulate the produced

composite to cling to the pore surface. The recovery factor of oil by using this modified composite reached 39%.

One of the most important problems facing water flooding is the wettability of reservoir soil where in hydrophobic reservoirs water cannot be soaked up on the rock surface resulting in low oil extraction [107, 108]. The alteration in the contact angle (hydrophilicity) of rock by making it more hydrophilic (water-wet) would enable the removal of the oil coating to the rock and would also let water seep into the rock's surface increasing the flow restriction of subsequent water pumps. Reduced water channeling would progress the efficiency of the oil movement as an outcome. Based on this, many researchers [109, 110] have used nanofluids to solve this problem where it was discovered that nanofluids could drastically alter the surface of rocks. Because of the chemistry of the solid surface in connection with the type of nanoparticles, nanofluid is effective at changing wettability [111].

Agi et al. [104] synthesized crystalline starch nanoparticles (CSNP) as a natural nanofluid by using ascorbic acid assisted with ultrasonic and nanoprecipitation. They examined the interfacial characteristics of this nanofluid (CSNF) at different concentrations, electrolyte concentrations (NaCl), and temperatures. The results showed that the surface tension reduced with the rise in the intensity of the nanofluid, the concentration of salt, and temperatures. They also screened how well the nanofluid affected the wettability of sandstone using the contact angle approach. According to this method, a rock is water-wet if its contact angle is below 70 degrees, intermediately wet if it is between 70 and

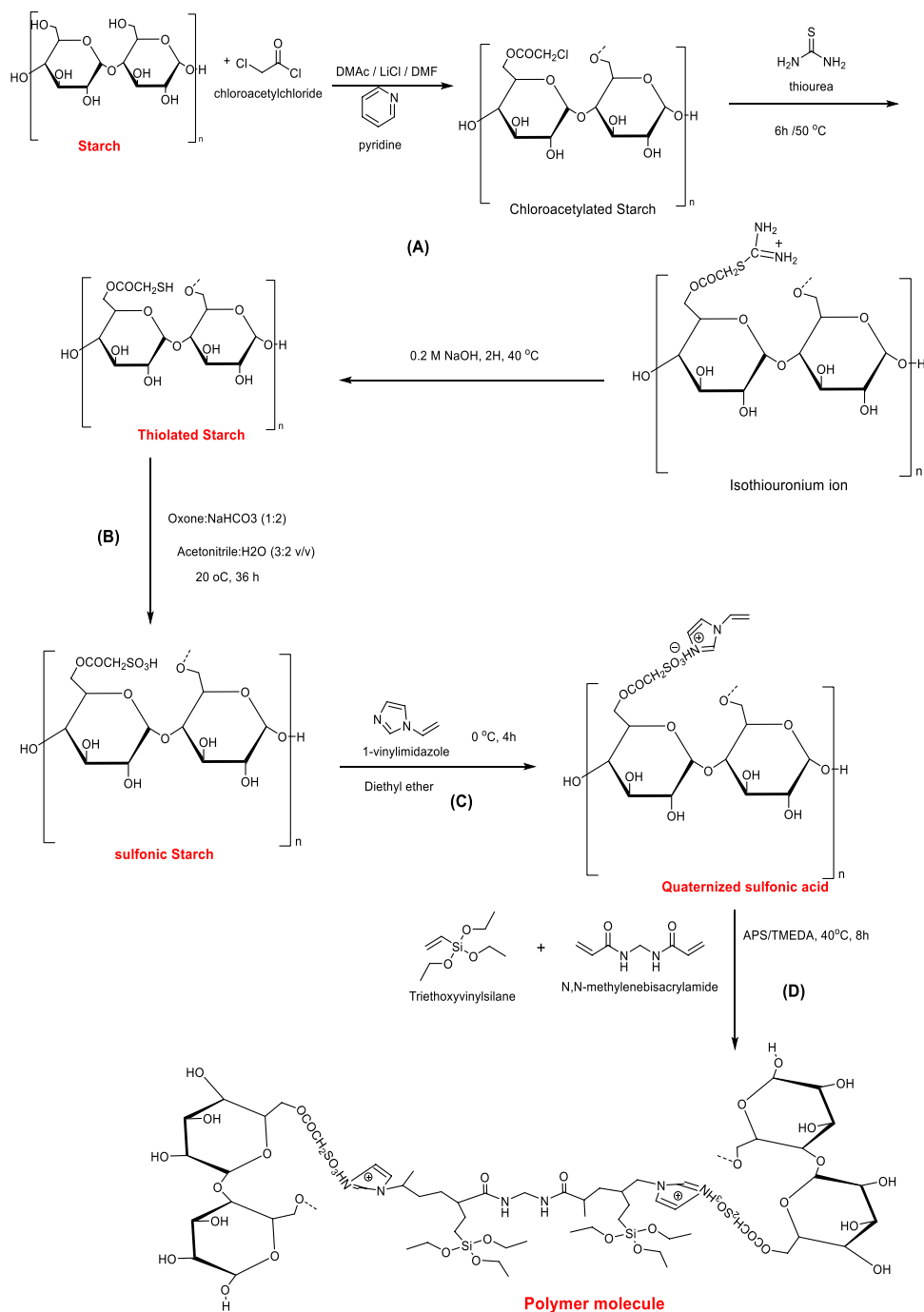
Fig. 15 Grafting copolymerization reaction of acryloylated starch with different vinyl monomers. **a** Derived with consent from ref. [94]. Publisher 2019, Elsevier. **b** Derived with consent from ref. [96]. Publisher 2018, Elsevier



110 degrees, or oil-wet if it is over 110 degrees. As the concentration of the nanofluid rose, it was discovered that the contact angle diminished. This suggests that the absorption of nanofluid particles into the rock core's matrix resulted in a shift from a hydrophobic state to a hydrophilic state, causing the cores to become wet. They conducted core flooding experiments at the reservoir conditions (T, 120 °C and P, 3000 psi) using this modified composite (CSNF) and commercial xanthan gum. When utilizing CSNF, oil recovery was seen to rise by 23% OOIP as opposed to the initial 11% when using native biopolymer (XG). These results confirm the importance of wettability in recovering remaining oil.

It was found also that cationic and anionic starch derivatives can influence the wettability of the reservoir rocks and make them more hydrophilic [102, 105, 112–115] depending on the type of rock and its isoelectric point (IEP) [116]. Where IEP is described as the pH at which a rock matrix bears no electrical charge. The electrical charge of a rock surface is positive below this point and negative above it. Limestone reservoirs have an isoelectric point of 8.2 [117] while sandstone reservoirs have an isoelectric point of 4.7 [118]. In sandstone reservoirs, if the pH is more than 4.7, negative charges form on the rock, so cationic starch derivatives can be applied because

Fig. 16 Steps of starch modification reactions. Derived with consent from ref. [95]. Publisher 2018, Elsevier



of electrostatic intermolecular forces among the modified polymer and the rock's surface, and the surface becomes more hydrophilic. On the same approach if the pH of limestone reservoirs is less than 8.2 (positive charges on the surface) it is preferable to use anionic starch derivatives for the same reason mentioned earlier. Within this context, Fu et al. [105] created a water-soluble cationic starch by reacting a biopolymer with (2-chloroethyl) trimethylammonium chloride (CCC) in the presence of NaOH as a catalyst using a solution method. The researchers then

examined the adsorption ability of this modified biopolymer (known as a cationic biopolymer) on the oil core matrix. They studied how the adsorption ability varied with changes in pH, which could affect the hydrophilicity and ionic conductivity of sand particles. Ultimately, this could contribute to enhance oil recovery. Based on their static adsorption tests, it was discovered that the cationic biopolymer had a saturation adsorption capacity of approximately 1.3 mg/g, surpassing that of the HPAM solution (0.35 mg/g). Researchers found that the modified

biopolymer's ability to adsorb was significantly higher at high pH levels, especially around pH values of 6 and 9. Conversely, the synthetic polymer HPAM's adsorption efficiency decreased with higher pH values due to electrostatic repulsion forces between HPAM molecules and the surface of the oil rock. Additionally, results from sand-pack core-flood testing showed that pumping modified biopolymer into the well after traditional water flooding can greatly improve the extraction of oil (up to 18% of OOIP) and dramatically lower the water cut. Qiao et al. [106] modified maize starch to cationic starch (Quats biopolymer (NCP)) by reaction with (2,3 epoxypropyl) trimethylammonium chloride using a facile solid-state method. They tested the efficiency of this modified starch in enhancing the hydrophilicity of a montmorillonite-based reservoir (MT) by measuring the contact angle of NCP-MT. They also compared the results with those of HPAM-MT, using Washburn's equation. The findings of this test showed that the treatment with synthetic polymer (HPAM) slightly increased the rock's hydrophobic properties due to its generally poor hydrophilic properties. On the other hand, the adsorption of cationic biopolymer increased the rock's surface hydrophilicity and increased its water-wettability.

Besides improving the wettability of the reservoir rocks and enhancing their hydrophilicity, it has been discovered that flooding the modified cationic starch composite solutions after polymer HPAM flooding can seal off the high permeability zone in the reservoir by creating a crosslinking gel system with the remaining polymer present in the areas with high permeability [119]. This leads to the fluid being pushed to mid-low permeability zones to enhance sweep efficiency [106]. Long-term flooding of oil fields with water typically causes a noticeable rise in the heterogeneity of oil reservoirs as well as the presence of large pores that correspond to a more permeable zone. As a result, HPAM channeling occurs in this zone of high permeability, and excessive amounts of premature polymer are produced from flooding reservoirs, which has an impact on the displacement of the oil phase [120–123].

Carboxy Methyl Cellulose (CMC) Polysaccharide

Carboxy methyl cellulose (CMC) is an anionic biopolymer, derived from insoluble cellulose and chloroacetic acid in the presence of an alkaline. The repeating unit of CMC is anhydro glucose, which is similar to that of starch [124, 125]. The structure of CMC varies depending on the degree of substitution of the OH groups on the anhydro glucose unit as shown in Fig. 17 [126]. The physical properties of CMC depend on the two factors related to its structure. The first factor is the degree of substitution (DS) of the OH groups on its unit where cellulose itself is water insoluble but sodium CMC (OH groups are substituted by Na^+) dissolves rapidly in cold water. The second one is the carboxy- methyl substituents distribution where the distribution of these substituents considerably affects the viscosity of CMC solutions. CMC is less tolerant to thermal degradation and oxidative decomposition so these limitations make it less applied in the pilot test of EOR [2].

Welan Gum (WLG) Polysaccharide

This natural polymer is an anionic highly water-soluble natural polymer manufactured by the fermentation of sugar using bacteria (*Alcaligenes*). The welan gum molecule structure consists of repeating tetrasaccharide units as the backbone with a single L-mannose or L rhamnose as the side chain (Fig. 18). Welan gum (WLG) is a promising biopolymer in enhanced oil recovery because this polymer has excellent rheological properties at high temperatures even in the presence of salinity [127]. In this regard, Gao [128] investigated WLG as a candidate for polymer flooding to enhance oil recovery. He used a sandstone core for flooding tests with a porosity of 20% and permeability of 90 mD also used a brine with a total salinity of 300,000 ppm (150,000 ppm NaCl and 150,000 ppm CaCl_2) and the temperature that he used was 85 °C. The results showed that WLG has salt tolerance

Fig. 17 Molecular structure of carboxy methyl cellulose (CMC)

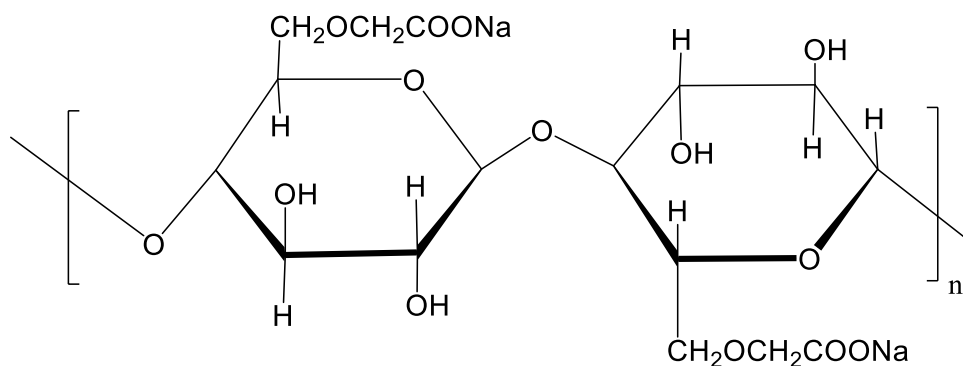
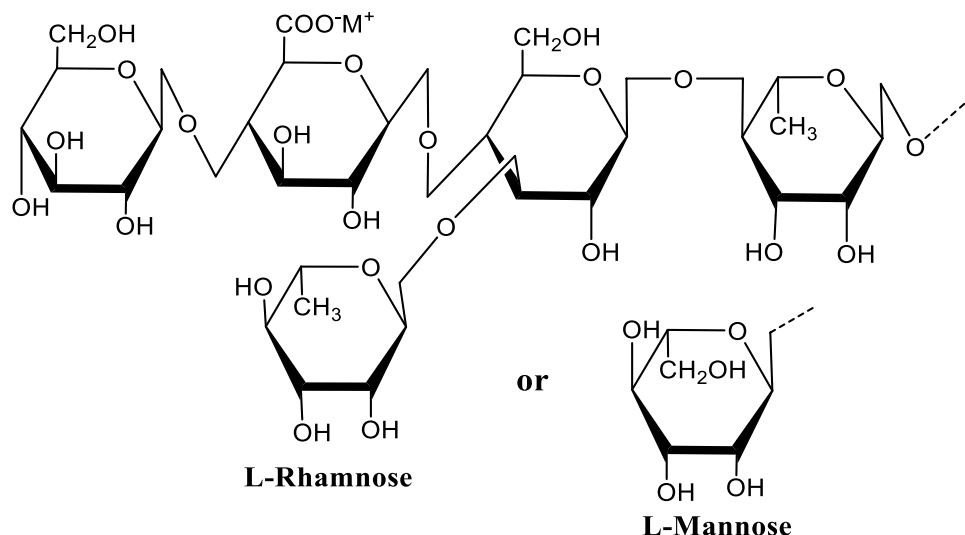


Fig. 18 Molecular structure of biopolymer welan gum (WLG)

and thermal stability also, the results from sandstone core flooding experiments indicated that this polymer can reduce the time to reach residual oil saturation. Xu et al. [129] also made a comparison between the displacement efficiency of welan gum and xanthan gum on enhanced heavy oil recovery (with a viscosity of 458 cP at a temperature, of 50 °C). The sand was used to simulate the rock of the reservoir in this study with a porosity of about 38% and the absolute permeability varied between 1.3–1.7 μm at a temperature of 50 °C also the salinity of the formation water used in this study was 9374 ppm. The results of oil recovery indicated that welan gum is more efficient (75.5% of OOIP) than xanthan gum (68.2% of OOIP) where waterflooding produced only 50.1% of OOIP. Recently, some studies have been made to modify welan gum to enhance its physical properties such as reducing its dissolution time, improving its viscosity and thickening, and making it more resistant to bacterial attack to be suitable for application in EOR under severe conditions [130–136].

Gum Arabic (GA) Polysaccharide

Gum Arabic or Acacia gum (the oldest and most well-known gum) is a versatile natural gum produced from the Acacia Senegal tree and used commercially for over 5000 years [137, 138]. Compared to other natural gums, this gum is considered somewhat complicated where the molecular structure of this polymer is highly branched, with high molecular weight (in the range of 2.5×10^5 – 10×10^5 g/mol) [139], and complex salts of polysaccharides (calcium, potassium, and magnesium) [140]. The backbone of the molecular structure is composed of 1,3-linked β -D-galactopyranosyl units whereas the branched chains consist of various combinations of arabinofuranose, galactopyranose, rhamnopyranose,

and uronic acid [141]. Acacia gum does not interact with a chemical compound and is easily soluble in water with colors varying from brown to white [142]. GA exhibits non-Newtonian behavior (shear thinning effect), especially at high concentrations, and has high thermal stability [143, 144]. The unique biochemical structure and properties of this polymer make it useful for various applications, such as thickening, emulsifying, and stabilizing. Recently, acacia gum was used with nanoparticles (nano-polymeric solutions) like graphene nanoplatelets (GNPs) [145], alumina nanoparticles [146], silica nanoparticles, and copper nanoparticles [147] in EOR. It was found that mixing NPs with acacia gum enhanced the stability of NPs and improved the rheological and thermal properties of the natural polymer under severe conditions of the core flooding (high temperature and high salinity) hence increasing oil recovery. The presence of nanoparticles in this polymer enhances its viscosity due to the electrostatic interactions between the nanoparticles and the polymer [148]. Also, this natural polymer is used with different surfactants (surfactant polymer flooding) for example, sodium dodecyl sulfate (SDS) [149], and alpha-olefin sulfonate (AOS) [150] in EOR. The function of surfactant is to reduce the interfacial tension (IFT) and capillary pressure while the function of polymer is to reduce the mobility ratio by increasing the viscosity of water.

Knowledge Gaps and Future Prospect of Biopolymers Flooding

After analyzing the review, we have found that new composites produced from modified native biopolymers using various techniques can overcome the severe conditions of reservoirs, resulting in a higher oil recovery factor compared to the biopolymers themselves. Also, we have identified several

important issues that have not been addressed in recent studies on biopolymer floodings in enhanced oil recovery (EOR) which can impact their efficiency. We recommend that these issues be addressed in future research. Some of the key issues are included as follows.

a. The Impact of Petroleum Reservoir Pressure on Biopolymer Core Flooding

Most published studies did not report the effect of reservoir pressure during the flooding runs on the lab scale where the overburden pressure of reservoirs produces new porosity and permeability which are the critical factors in polymer flooding. So, these flooding simulations did not represent the true field conditions, in the review, the authors recommend considering this effect in future research.

b. The Bacterial Effects on Biopolymer Core Flooding

Most studies focus on the chemical and thermal effects on reservoir media while overlooking the microbial and bacterial impact. However, microbial flora can significantly alter the petrophysical properties of reservoir media due to biological activity and bacterial metabolism. This alteration can include changes in rock wettability and pH of the medium. Additionally, some bacteria, such as acid-producing bacteria, can synthesize surfactants in-situ during their metabolism. Other bacteria, like sulfate-reducing bacteria (SRB), can increase or reduce the sulfur content in the producing oil.

c. The Simulation of Biopolymer Flow on Porous Media

Some literature discussed biopolymer simulation on a lab scale as a flooding agent, neglecting physical and viscoelastic properties of the polymer including storage modulus (G'), loss modulus (G''), and loss factor as a simulator input. Moreover, the conducted simulation did not discuss in detail the nature of porous media including pore throat size and shape, and pore size distribution and dimensions.

d. The Thickness of the Adsorbed Layer and Its Impact on Permeability Reduction in Porous Media Due to the Debris Effect

The adsorbed layer results in certain disorders related to permeability reduction and oil flow blockage. The screening of adsorbed layer thickness mitigates such disorders and allows the designing of appropriate slug polymer size and concentration which in turn saves cost and helps in designing an appropriate polymer flooding model.

e. Ensuring Compatibility with Other Injectants, Such as Surfactants and Alkalis

Most studies investigate the effectiveness of their flooding agent neglecting its compatibility with other reagents in the reservoir. This may lead to certain drawbacks such as scale formation and salts precipitation. So, investigating the compatibility and synergetic effect between flooded agents is of great importance for proper reservoir operation.

f. Applying Different Types of Cores

Most studies used sandstone cores to apply polymer flooding either on a lab scale or a simulation- scale, but few reports used carbonated cores. Extensive experimental and simulated core-flooding studies are necessary to be applied to understand the applicability of these new modified biopolymer composites for mineralogical rocks beyond sandstone (e.g., limestone and dolomite reservoirs).

g. Assessing the Economic Aspects of These Biopolymers

Economic and feasibility studies during chemical flooding are crucial factors in estimating the effectiveness of the process. On a financial scale, the management takes the action to proceed or not.

h. Applying of These Natural Polymers in Real Oil Field Tests (Pilot Field Tests)

Although most literature discusses polymer flooding either on a lab scale or a simulation- scale, few reports discuss actual field or pilot scale. Designing a pilot scale before the field trial helps in process management and the determination of advantages and drawbacks before the commencement of actual operation expenditure.

Conclusion

As crude oil will continue to be the primary source of energy to support the progress of humanity, creating an effective and environmentally friendly technique for extracting crude oil is continuously a huge aim for engineers and researchers. Regarding that, the application of biopolymers in polymer flooding processes is helpful as it can enhance the effectiveness of oil extraction at a lower cost compared with synthetic polymers. The operation procedure and reservoir environments such as salinity, temperature, pH, and the existence of bacteria, have a significant impact on the effectiveness of biopolymers' performance. To deliver successful biopolymer flooding

processes, the treatment of biopolymers is very important to produce new composites that can adapt to severe reservoir conditions and attack bacteria. This comprehensive review covers a wide range of methods that used recently for producing new compounds using xanthan, guar, and starch natural polymers that can be tailored to geological conditions and operational processes. Here are some techniques that have been used:

- A. Introducing synthetic vinyl monomers to natural polymers through graft copolymerization reactions.
- B. Functionalizing nanocomposites with biopolymers to create nano-polymer solutions.
- C. Modifying biodegradable polymers to have an amphiphilic style by introducing hydrophobic materials.
- D. Creating hydrogels.

Additionally, the review explores other biopolymers such as carboxy methyl cellulose, welan gum, and acacia gum, which have the potential to enhance oil recovery. The evaluation also encompasses the extent to which these biopolymers have been utilized in this field. In the current review, several important issues and recommendations that can impact the efficiency of the modified biopolymers have been addressed for the successful future implementation of these composites in enhanced oil recovery. Some of the key issues include:

- 1) The impact of petroleum reservoir pressure on biopolymer core flooding.
- 2) The bacterial effects on biopolymer core flooding.
- 3) The simulation of biopolymer flow on porous media.
- 4) The thickness of the adsorbed layer and its impact on permeability reduction in porous media due to the debris effect.
- 5) Ensuring compatibility with other injectants, such as surfactants and alkalis.
- 6) Applying different types of cores.
- 7) Assessing the economic aspects of these biopolymers.
- 8) Applying of these natural polymers in real oil field tests (pilot field tests).

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Declarations

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