Review Paper

Synthetic polymers: A review of applications in drilling fluids

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ABSTRACT

With the growth of deep drilling and the complexity of the well profile, the requirements for a more complete and efficient exploitation of productive formations increase, which increases the risk of various complications. Currently, reagents based on modified natural polymers (which are naturally occurring compounds) and synthetic polymers (SPs) which are polymeric compounds created industrially, are widely used to prevent emerging complications in the drilling process. However, compared to modified natural polymers, SPs form a family of high-molecular-weight compounds that are fully synthesized by undergoing chemical polymerization reactions. SPs provide substantial flexibility in their design. Moreover, their size and chemical composition can be adjusted to provide properties for nearly all the functional objectives of drilling fluids. They can be classified based on chemical ingredients, type of reaction, and their responses to heating. However, some of SPs, due to their structural characteristics, have a high cost, a poor temperature and salt resistance in drilling fluids, and degradation begins when the temperature reaches 130 °C. These drawbacks prevent SP use in some medium and deep wells. Thus, this review addresses the historical development, the characteristics, manufacturing methods, classification, and the applications of SPs in drilling fluids. The contributions of SPs as additives to drilling fluids to enhance rheology, filtrate generation, carrying of cuttings, fluid lubricity, and clay/shale stability are explained in detail. The mechanisms, impacts, and advances achieved when SPs are added to drilling fluids are also described. The typical challenges encountered by SPs when deployed in drilling fluids and their advantages and drawbacks are also discussed. Economic issues also impact the applications of SPs in drilling fluids. Consequently, the cost of the most relevant SPs, and the monomers used in their synthesis, are assessed. Environmental impacts of SPs when deployed in drilling fluids, and their manufacturing processes are identified, together with advances in SP-treatment methods aimed at reducing those impacts. Recommendations for required future research addressing SP property and performance gaps are provided.

1. Introduction

The rapid development of well drilling technologies over the past fifty years largely facilitated by improvements in the quality of drilling fluids. To date, drilling fluids must perform a number of functions, namely: suspending and transporting drill cuttings, cooling the bit and drill string, maintaining wellbore stability, providing essential lubrication; cleaning the borehole; gaining information from the drilled formation; enhancing drilling rate; contributing to rock fragmentation at the bit face; providing effective penetration of productive layers; reducing corrosive activity, preventing blockages and other complications in the wellbore; and, avoiding negative formation-damage effects on the porosity and permeability properties of the reservoir (Fink, 2021; Li et al., 2015; Morariu et al., 2022; Yahya et al., 2022). More than two thousand years ago, in ancient China, wetting the bottom of a well with water was applied to remove cuttings (He, 2010; Wang et al., 2017). The term "drilling fluid" has evolved over time, along with the operationally synonymous reference to "drilling mud", "drilling fluid", with now largely redundant terms "clay mud" and "flushing

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mud" also used historically (Apaleke et al., 2012). In 1846, the French engineer Fauvel discovered a method for continuously removing cuttings from a well with a circulating stream of water (Grattan-Guinness, 2014). That concept involved pumping water into the wells through hollow pipes from ground level, and the water ultimately returning to the surface carrying drill cuttings with it. From that development drilling fluid deployment technology has not undergone significant changes (Hay, 2021; Riding, 2021). Chaudhary and Sharma (2019) received the first patents for drilling fluids (Gerali, 2018). Over recent decades drilling fluids have evolved to include water-based, oil-based, synthetic-based, gas-based and foam-based formulations (Aboulrous et al., 2022; Friedheim, 1997). As a new generation of drilling-fluid formulations, in the last two decades synthetic-based drilling fluids (SBDF) has greatly enhanced the performance of oil-based drilling fluid's (OBDF). Specifically, in terms of environmental impacts, because SBDF is less toxic, achieves fast penetration rates, results in less fluid-related nonproductive time, and degrades faster than diesel and mineral oils (Friedheim, 1997). Most of the base oils used in SBDFs are synthetic chemicals. Esters were the first type of base oil used in SBDFs followed by the SPs, such as poly alpha olefins (Fig. 1) (Celino et al., 2022; Li et al., 2016a, b, c). Although SBDF has many advantages, it also has several disadvantages. These include higher cost, slower biodegradability, complex formulation, and reduced stability in low temperature conditions, such as with ester-based fluids (Fink, 2021).

Fig. 1 presents a classification of drilling fluids. It takes the nature and composition of both the dispersed phase and the dispersion medium into account (Al-Shargabi et al., 2022a; Deville, 2022; Friedheim, 1997; Li et al., 2016c).

Since the 1970s polymer solutions have been increasingly used as drilling fluid additives. This has become possible due to the development and production of macromolecular compounds by the chemical industry (Wang et al., 2019). Polymer drilling fluid is a solution of polymers in an aqueous dispersion medium with different structures such as linear, branched-chain, crosslinked or networked. They have mainly been exploited to drill abrasive rocks of high hardness. The main advantages of polymer drilling fluids

that distinguish them from others are hydrophilicity and pseudo-plasticity, providing them with the ability to change viscosity depending on the shear rate (Davoodi et al., 2019; Kariman Moghaddam et al., 2022).

The first deployment of polymer drilling fluid dates back to the 1950s (Sun et al., 2021). In addition to water, that formulation included: bentonite powder; copolymer of vinyl acetate and maleic acid; and soda ash (Austin, 1983). Initially, the composition of polymer drilling fluids was determined only by the need to maintain the stability of their functional properties and increase rate of penetration (ROP). Subsequently, more attention has been paid to their ability to maintain formation properties and/or avoid formation damage. However, traditional oil reservoirs are gradually being depleted and the share of developed harder-to-recover oil reserves is growing rapidly. Such dynamics involve a more complex range of sub-surface conditions now being associated with productive formations. As the depth of wells increases, the thermobaric conditions of drilling become tougher and a number of accompanying complicating factors arise. These factors require adjustments to be made to drilling fluids to suit the sub-surface conditions of specific reservoir targets (Ali et al., 2022; Kariman Moghaddam et al., 2022; Saboorian-Jooybari et al., 2016). Currently, drilling fluid formulation does not solely focus on increasing ROP, but also on wellbore stability, environmental compliance and the ability to maintain reservoir properties (Sun et al., 2021). Indeed, from a technological point of view synthetic polymers (SP) are now designed with all of these attributes in mind. SPs are obtained primarily from petroleum products. Unlike natural and modified natural polymers, SPs tend to be built from relatively small molecules. SPs provide almost unlimited flexibility in their design. Their size and chemical composition can be adjusted to provide properties for nearly all sub-surface functional objectives (Ali et al., 2022; Chu and Lin, 2019; Sepehri et al., 2018). SPs are synthesized under artificially created conditions from various monomers. For example, ethylene in its natural form is a colorless gas, however, following its polymerization, solid polyethylene granules are produced (Riley, 2012). The conditions of the polymerization processes can be adjusted to alter the characteristics of the resulting polymers (Li et al., 2021;
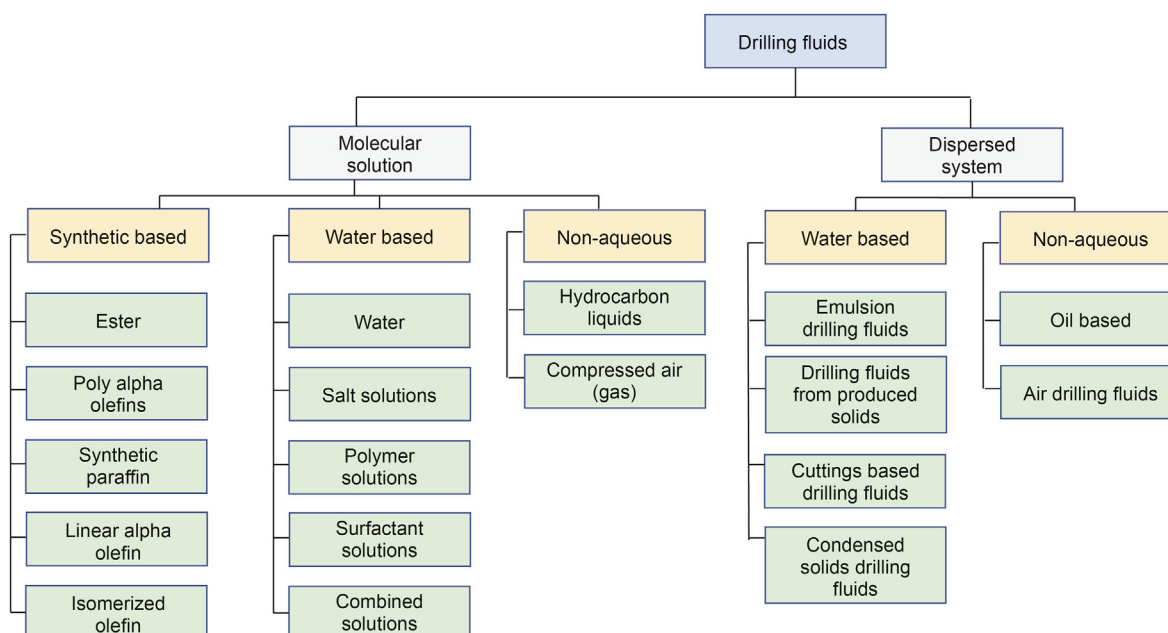

Fig. 1. Classification of drilling fluids.

Sepehri et al., 2018). For instance, it is possible to:

➢ introduce additional monomers in order to obtain co-polymers with improved properties (Davoodi et al., 2019);
➢ modify the properties of a polymer, for example, changing its resistance to shock or low temperatures (Sepehri et al., 2018);
➢ adjust viscosity and fluidity of a polymers softening and melting temperatures (Li et al., 2021);
➢ change its visual properties, such as color, transparency and other light-transmitting properties (Ali et al., 2022; Wang et al., 2019).

However, potentially negative environmental impacts are associated with some SPs. An important advantage of polymers, their durability, turns into a negative attribute if waste products are disposed of irresponsibly. Therefore, the key risk of the popularity of SPs on the planet can be considered the risk of substantial and long-lasting environmental pollution (Murtaza et al., 2021; Osipov et al., 2022).

To date, few publications have reviewed the roles of bio-polymers and SPs in drilling fluids (Abbas et al., 2021; Balaga and Kulkarni, 2022; Davoodi et al., 2022b; Koh et al., 2022). The following research gaps were identified in the aforementioned reviews:

• Evaluation of the polymer's role in drilling fluids, and their developments;
• Classification of SPs in terms of their chemical and physical features and well their functions in drilling fluids;
• Manufacturing methods, characterization, classification, and applications for synthesis of the SPs deployed in drilling fluids;
• Detailed applications of SP in drilling fluids;
• Considerations of the difficulties, economics, environmental concerns, and process safety issues regarding the use of different types of SP in drilling fluids.

Thus, this review highlights the characteristics, manufacturing processes, and classification of SPs, and their responsible petroleum-industry applications with a precise focus on drilling fluids. It differs from existing reviews by collectively addressing:

• Manufacturing processes, property characteristics and SP classes
• Oil and gas industry applications of SPs
• Detailed properties of polymer drilling fluids
• Economic and environmental impacts of SP drilling applications
• Clay swelling and fluid filtration mechanisms
• SPs specific contributions to drilling fluids to improve:
a) rheology and associated properties
b) fluid-loss behaviors
c) lubricity
d) lifting of cuttings and wellbore cleansing
e) stabilization of clay-rich/shaley formations

2. Evolution of polymer deployments in drilling fluids

2.1. Developmental advances of polymers in drilling fluids

Historically, the initial evolution of polymer drilling fluids was driven by the desire to increase ROP. Over time, with changing sub-surface conditions of prospective strata, due to increasing well depths, temperatures, pressures and the presence of unstable zones, drilling fluid designs have become more robust, resistant to extreme conditions and environmentally friendly. They have pro-gressively developed the ability to ensure stability of the rock for-mations penetrated and preserve their reservoir properties (Fig. 2) (Abbas et al., 2021). Currently, drilling fluid polymers can be clas-sified according to their chemical composition, their use in drilling fluids, and their origin. Chemically, they can be anionic, nonionic, and cationic (Beg et al., 2018; Davoodi et al., 2022b). Moreover, according to their structure, polymers are divided into linear, branched-chain and crosslinked or network (Steube et al., 2022). The linear molecule consists of a chain of monomers, these include natural rubber, elastomers, carboxymethyl cellulose, partially hy-drolyzed polyacrylamide, hydroxyethyl cellulose, and other poly-mers of high elasticity (Baba Hamed and Belhadri, 2009; Liu J. et al., 2020; Xia et al., 2020). A chain of branched-chain links has side branches, for example, amylopectin, starch, and xanthan gum (William et al., 2014). Cross-links exist between adjacent macro-molecules, insoluble and inelastic polymers, for example, epoxy resins in the curing stage, and cross-linked xanthan gum, a poly-saccharide secreted by the bacteria Xanthomonas campestris (Steube et al., 2022).

There are different types of natural, modified-natural polymers, and SP which are utilized in drilling fluids. The most readily available natural polymers (biopolymers) include: starch (Al-Hameedi et al., 2019), xanthan gum (Akpan et al., 2020), quebracho (Bergman and Fisher, 2002), guar gum (Ogunkunle et al., 2022), scleroglucan (Chang et al., 2020), welan gum (Chang et al., 2020; Li W. et al., 2020; Xu et al., 2013a, b), lignosulfonates (Browning, 1955; Neshat and Shadizadeh, 2016), and locust bean gum (Hall et al., 2018; Ibrahim et al., 2019). The most applicable modified-natural polymers include: carboxy methyl starch (CMS) with salt resistance up to 0.7×10^4 mg/L and temperature tolerance up to 100–120 °C (Davoodi et al., 2022b; El-Hamshary et al., 2014; Xu et al., 2017a, b), carboxymethyl cellulose with salt resistance up to 0.5×10^4 mg/L (part per million of degree of substitution) and temperature tolerance up to 149 °C (CMC) (Fagundes et al., 2018; Ibrahim et al., 2017), polyanionic cellulose (PAC) with salt resistance up to 0.5×10^4 mg/L (part per million of degree of substitution) and temperature tolerance up to 149 °C (Fagundes et al., 2018; Jia et al., 2022), hydroxyethylcellulose with salt resistance up to 2.5×10^4 mg/L and temperature tolerance up to 150 °C (HEC) (Ouaer and Gareche, 2018; Sun and Bai, 2023; Wang H. et al., 2022; Wypych, 2022), and styrene copolymer with temperature tolerance up to 190–195 °C (Luo et al., 2018; Mohamadian et al., 2019). Even so, each modified-natural polymer has its own specific perfor-mance limits in the presence of salt or at high temperatures. These limits may rely on factors such as the degree of substitution of the modified-natural polymer, as was shown with CMC and PAC, the specific monomers employed or the type of chemical modification to enhance the performance of the modified-natural polymer (Davoodi et al., 2022b; Gautam et al., 2022).

However, every polymer has its advantages and disadvantages when deployed in drilling fluids. For instance, one of the most commonly utilized polymers for filtrate control is the starch but its poor thermal stability and low biodegradability limiting its appli-cation in drilling fluids. Consequently, CMS was developed to enhance its application however, compared to polyanionic cellu-lose, CMS polymer has a poorer filtering performance in high-permeability rocks. Polyanionic cellulose can be utilized to raise and stabilize viscosity in the return flow to improve wellbore cleaning and decrease pressure loss (El-Hamshary et al., 2014; Jia et al., 2022).

On the other hand, xanthan gum is a common biopolymer which is widely utilized in drilling fluids to provide viscosity, solid suspension, and fluid-loss control. However, it has a low tolerance
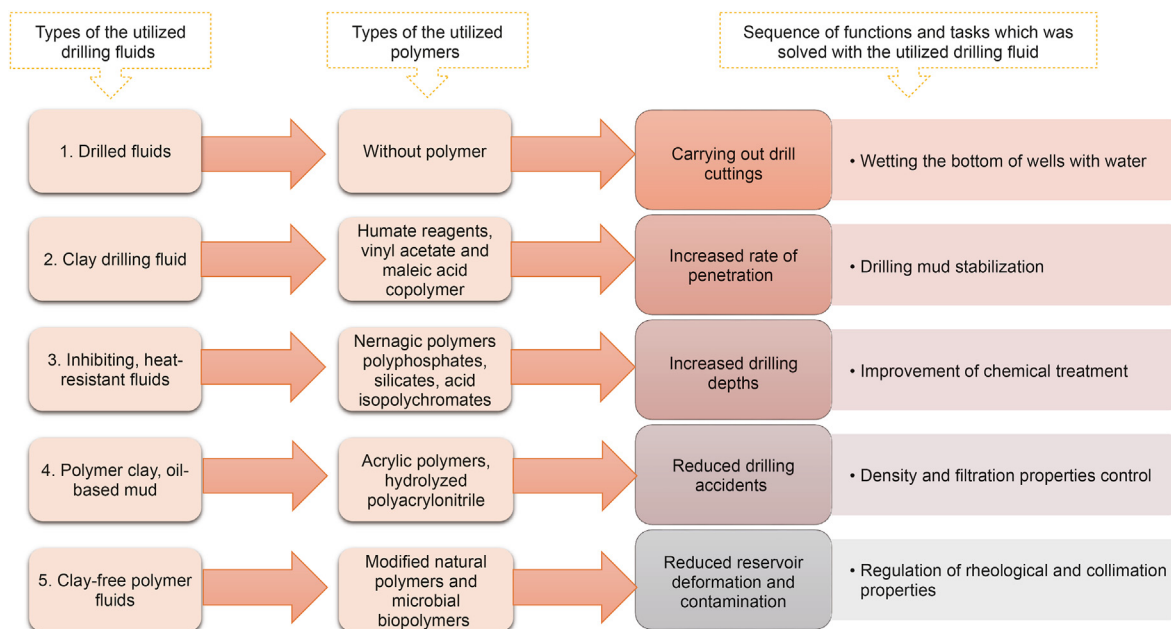
Fig. 2. Functional evolution of polymer drilling fluids and their compositions.

to high temperature and tends to degrade temperature above 120 °C (Akpan et al., 2020). Hydroxyethylcellulose does perform well at high temperature and can be utilized as a thickening agent in various types of drilling fluids required for operations such as drilling, cementing and hydraulic fracturing. It provides the necessary stability and fluidity to the drilling fluid (Ouaer and Gareche, 2018).

Some polymers are expensive to produce or in limited supply such as quebracho, which was frequently used until the 1950s, when lignosulfonate became commercially accessible and provided the same function as quebracho at a lower cost (Bergman and Fisher, 2002; Ghazali et al., 2018). All natural and modified-natural polymers have their advantages and drawbacks which have led to attempts to further modify them to enhance their performance by utilizing suitable monomers in the synthesis of new SPs (Davoodi et al., 2022b).

To ensure the effective performance of polymers in drilling fluids, rheological and solution characteristics need to be evaluated at simulated conditions as a function of polymer content, salinity, temperature, and shear properties (El-hoshoudy et al., 2017). In the last three decades, the evolution of polymer drilling fluid compositions has moved from a stability focus to ensuring effective performance in harsh conditions such as high-pressure and high-temperature (HPHT) and salt contamination (Davoodi et al., 2022b; Deville, 2022). At moderate bottom-hole temperatures, thermal motion of polymer molecules becomes considerable, and temperature increases the distance between molecules. Friction and a weak intermolecular force are the reason for this behavior. At higher temperatures, water molecules can also move more freely with a slight resistance to flow. When the temperature decreases, the intermolecular distance shrinks and the intermolecular force grows. More molecular entanglements are produced as a result of the molecular chain's decreased activity and twisting (Bland et al., 2006; Davoodi et al., 2022b; Deville, 2022).

At low temperatures, polymer solutions have a high viscosity because many free-water molecules are trapped in the polymer structures. Pressure increases cause the density of the drilling fluid to rise, which lowers the drilling ROP. However, pressure tends to improve the viscosity of the drilling fluid filtrate and reduce seepage losses, but it has minimal impact on the filtration rate (Fig. 3(a)) (Davoodi et al., 2022b). The addition of salts to polymers dramatically alters drilling fluid viscosity, with the reliance of the drilling fluid effective viscosity on the shear rate reducing. In this situation, the drilling fluid's effective viscosity approaches the greatest "Newtonian" viscosity in conditions of low shear rates (i.e., near to zero shear rate). When the shear rate increases, the effective viscosity of the drilling fluid drops, nearing the lowest effective viscosity value, also known as the lowest Newtonian viscosity (Fig. 3(b)) (Davoodi et al., 2022b; Oncsik et al., 2015).

The behaviour of polymers and their solutions is not only determined by temperature or salt concentration, but also by the stress and shear rate at which the solution flows. Although polymer synthesis technology has progressively improved, it still has issues that require attention. Polymer-based drilling fluids typically exhibit a non-Newtonian flow behavior, which means that their viscosity changes with the fluid's shear rate. At low shear rates, the polymer chains are relaxed and entangled, resulting in high viscosity. However, at high shear rates, such as those encountered close to the drill bit, the polymer chains are stretched and aligned in the flow direction, resulting in lower viscosity (Davoodi et al., 2022b). These characteristics impede the further application and improvement of polymer synthesis technologies. The severe shearing action of polymer solution is one of the key difficulties impacting their practical applications.

Under high mechanical-shear conditions, the solution performance is greatly diminished, resulting in a major disparity between the subterranean performance of the polymer and its performance in ground-level preparation systems (Jiao et al., 2023). To deal with the unavoidable mechanical shear impact in polymer applications and increase polymer solution performance, the creation of shear-resistant polymers is a major research area in polymer synthesis (Gaillard et al., 2017; Jiao et al., 2023). The tolerance to shear of polymers used in drilling fluids depends on several factors, including the type and molecular weight of the polymer, the concentration of the polymer in the fluid, and the conditions of the drilling operation. To improve the tolerance to shear, some
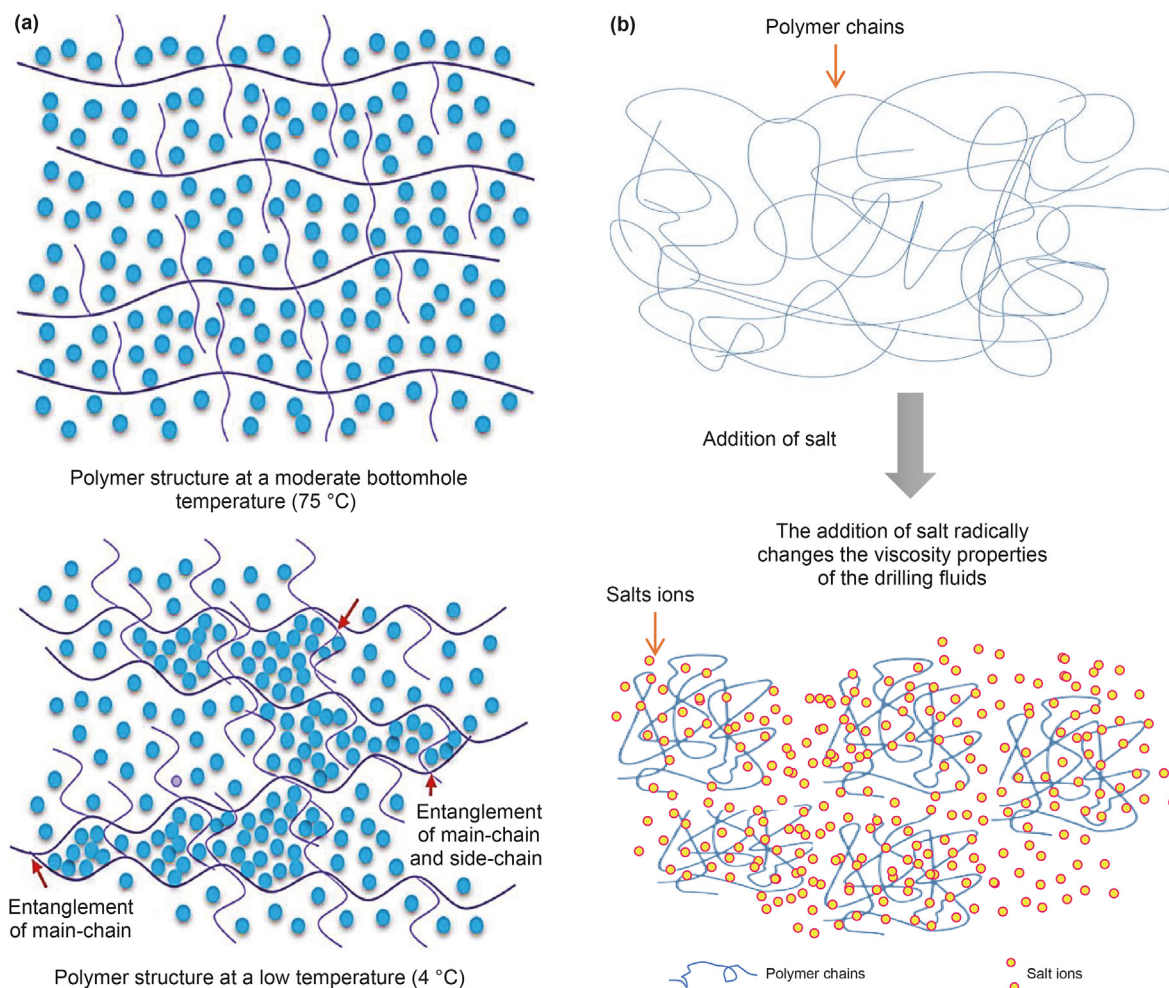
Fig. 3. The effect of temperature and salt on polymer structure: (**a**) Temperature effects on polymer structures. (**b**) The molecular chain structures modifies the behavior of polymeric solutions in the presence of salts. Reproduced from Elsevier (Davoodi et al., 2022b).

polymers are designed with a higher molecular weight, which enhances their resistance to breakage and shear-induced degradation. Additionally, some polymers are formulated with stabilizing agents that help maintain their rheological properties under high shear rates (Davoodi et al., 2022b; Gaillard et al., 2017; Jiao et al., 2023). All these problems have led to researchers and oil and gas companies continued efforts to develop and synthesize polymers able to perform well in harsh subsurface conditions (Davoodi et al., 2022b).

Section 3 explains the manufacturing methods typically used to develop new SPs and their advantages and disadvantages. Section 4 explains the recent advances of SPs as deployed in different types of drilling fluids. It also highlights the ways in which SPs may be utilized to overcome harsh sub-surface conditions.

2.2. Nanopolymer contributions to drilling fluids

A nanocomposite is a multiphase material where, one of the phases has one, two, or three dimensions less than 100 nm, or the phases of the composite have nanoscale spaces between them (Al-Shargabi et al., 2022a). Because the composite size is much smaller than that of general macroscopic composite materials, this material provides a new opportunities for the preparation of high-performance new materials. The structure of polymers can be designed and adjusted according to the performance requirements.

Composites at the nanoscale make it possible to form polymer-based nanocomposites (Rajak et al., 2022). Because of their specific structure, shape and orientation, nanoparticles (NPs) substantially impact the properties of nanofluids, including physicochemical, hydrodynamic, thermal and electrical properties (Al-Shargabi et al., 2022a, b; Davoodi et al., 2022a). Polymer nanocomposites have excellent dimensional stability and adsorption properties, as well as good thermal stability and cutting properties. They have become a key research topic in the field of functional materials (Al-Shargabi et al., 2022a; Rajak et al., 2022). There are many nanopolymers (nanocomposites) available for use in drilling fluids. In particular, they help reduce drilling fluid filtration loss, minimize differential pipe sticking, enable safer drilling at HPHT conditions and improve shale stability (Al-Shargabi et al., 2022a; Saleh and Ibrahim, 2021).

Nanocomposites for use in drilling fluids can be created as single spheres making them more effective than NPs (Jia et al., 2022). The most commonly used nanocomposites (nanopolymers) in drilling fluids are polyacrylamide-grafted-polyethylene-glycol-silica and the nanopolymer has a micro-spherical morphology with a particle size of 200 nm (Jia et al., 2022), hydrophobic polymer-modified nanosilica and the nanopolymer has a micro-spherical morphology with a particle size of 200 nm (Saleh et al., 2022), polyacrylamide-nanoclay and the nanopolymer has a micro-spherical morphology with a particle size of 100 nm (Jain and

Mahto, 2015), polystyrene-methyl methacrylate-acrylic acid with nanoclay and the nanopolymer has a unique particle size of 1–2 nm and a density of 300–370 kg/m^3 and specific surface area of 220–270 m^2/g (Mohamadian et al., 2019), SP with carbon nanotubes/ZnO NPs (Ali Khan et al., 2018), styrene butadiene resin/nano-SiO$_2$ the nanopolymer has a unique round particle size of 70 nm (Li X. et al., 2020), and lignosulfonate/acrylamide graft co-polymers (Abdollahi et al., 2018). As an example, a nanopolymer was developed and synthesized through microemulsions utilizing butyl acrylate (BA), acrylic acid (AA), and styrene in water-based fluid (WBDF) for use as a shale inhibitor (Xu et al., 2018). The nanopolymer has a distributed size of 30–135 nm with a narrow particle size distribution and the median particle size was 62 nm. The results demonstrated that the shale samples absorbed water much less in the nanopolymer solution than in deionized water. The absorption mass reduced from 7.51% to 2.59% at a concentration of 2.0% of nanopolymer. The key factors that enabled the nanopolymer to substantially reduce the capillary effect include its nanoscale size, which acts to increase the contact angle of the shale samples, and lower the surface tension of the fluids tested (Xu et al., 2018).

In OBDF, a nanopolymer was developed based on a surface-modified nanoscale polystyrene (nanopolystyrene) for use as a plugging agent. The results revealed that after aging, the modified nanopolystyrene at a concentration of 2% was able to reduce fluid loss to 3.8 mL (Geng et al., 2021). In comparison to the base fluid without nanopolystyrene, the filtration loss of the permeability plugging equipment was reduced by 67%. In a pressure transmission test, the downstream pressure remained constant after 60 h with no discernible change, demonstrating an excellent plugging action (Geng et al., 2021). The mentioned tests confirm that nanopolymers can be effective with their main applications in drilling fluids being to enhance rheological properties (Oseh et al., 2019), control filtration loss (Blkoor et al., 2022), and act as shale formation stabilizers (Saleh and Ibrahim, 2021).

A novel nanopolymer was developed and named polyethylene-nanosilica composite modified by sodium dodecyl sulfate to test its impact of fluid filtration loss and rheological properties (Blkoor et al., 2022). The nanopolymer has a narrow range of sizes, from 82 to 410 nm, and a specific surface area of 41.4 m^2/g. The results showed that at 25.6 and 121.1 °C, the addition of the nanopolymer substantially increased the AV of the basic drilling fluid (CD0). The nanopolymer particles were capable of interacting within the clay pore structures and impart linkage with bentonite clay, resulting in increased viscosity (Blkoor et al., 2022). In terms of filtration loss control, the ability of the nanopolymer to offer efficient pore-sealing integrity across the drilled formations resulted in a decrease in the filtration loss volume and filter cake thickness at both API and HPHT conditions. The ideal nanopolymer concentration was shown to be 1.5 g. At that concentration it produced a thin, low-permeability filter cake on the surface of the borehole wall (Blkoor et al., 2022).

A grafted nanopolymer was developed and obtained from a less hydrophobic acrylic acid-acrylamide-activated carbon-amyl ester (less hydrophobic AA-AAm-C-Amyl) and a more hydrophobic acrylic acid-acrylamide-octadecene-activated carbon-amyl ester (more hydrophobic AA-AAm-OD-C-Amyl) as shale inhibitor (Saleh and Ibrahim, 2021). Fig. 4 presents the results revealing that the two nanopolymer composites efficiently stabilized the wellbore, with anti-swelling ratios of 93.7% and 95.2%, and shale recovery capacities of 95.2% for the more hydrophobic nanopolymer and 97% for less hydrophobic nanopolymer. The water-soluble acrylic acid grafted activated carbon (C-g-AA-NH$_2$) efficiently decreased shale hydration and displayed exceptional inhibitive capabilities to sodium bentonite (Na-Bt) clay, which has a similar character to

smectite components commonly present in shale formations (Saleh and Ibrahim, 2021).

These results suggest that nanopolymers can be utilized in drilling fluids as useful additives for enhancing the rheological properties, control of filtration loss, and for stabilizing shale formations, even at HPHT and salt contamination (Al-Shargabi et al., 2022a). However, numerous types of nanopolymers are commercially available, their varying quality, processing conditions, and other factors make it hard to have generally unified techniques for the manufacture of nanopolymer materials for use in drilling fluids in accordance with API recommendations and processes. As a result, a nanopolymer optimization study is necessary. This is required to assess and determine the financial implications of their use in drilling fluids (Oseh et al., 2023).

Table 1 describes some recent successful applications of nanopolymers as drilling-fluid additives. Table 1 shows that polyanionic cellulose with acrylamide quaternary monomer with grafting to nano-silica demonstrated impressive performance at temperatures up to 260 °C (Jia et al., 2022). On the other hand, polystyrene-methyl methacrylate-acrylic acid/clay has a low tolerance to temperature up to 121.12 °C. Thus, the type monomers and nanoparticles involved are important when producing desirable nanopolymer properties (Al-Shargabi et al., 2022a; Rajak et al., 2022).

3. Synthetic polymers: characterization, manufacturing, classification, and applications

SPs are materials consisting of long molecular chains (macromolecules) and organic compounds derived from the processing of naturally occurring materials. They can also be synthesized from petrochemicals (Balaji et al., 2017).

3.1. Characterization of SP

SPs tend to be based on low molecular weight organic compounds (monomers) which form long chains as a result of polymerization or polycondensation reactions. The arrangement and configuration of molecular chains and the type of their bonding largely determine the mechanical characteristics of polymers (Balaji et al., 2017).

SPs typically display high elasticity - the ability to resist deformations and restore the original shape (Ali Khan et al., 2018). SPs can be characterized by their chemical composition; molecular weight; thermal stability; water solution; degree of polymerization; degree of crosslinking; tolerance to salinity; and, tolerance to shear (Balaji et al., 2017). Depending on the chemical composition, carbochain and heterochain polymers can be distinguished. Carbochain SPs are polymers in which the main chain consists of C atoms. Heterochain SP are polymers, whose main chain, apart from C atoms, also includes atoms of O$_2$, S, P, N$_2$, Si and other elements (Balaji et al., 2017).

SPs may dispay a variety of molecular weights until they are purified. Various approaches used to determine SP molecular weight result in various averages. The number-average and weight-average molecular weights are the two most widely referred to. The molecular weight of the SP directly affects the magnitude of the intermolecular interaction forces. Therefore, the higher it is, the more difficult it is to dissolve the SP (Balaji et al., 2017; Ebnesajjad, 2015). The same pattern can be observed in the same SP-homology series. Fractions with higher molecular weight are less soluble in the same solvent than fractions with lower molecular weight; a characteristic that can used to separate the SP into fractions (Balaji et al., 2017). The capacity of a SP to withstand the effects of heat and to keep its qualities, such as strength, toughness, and elasticity at a
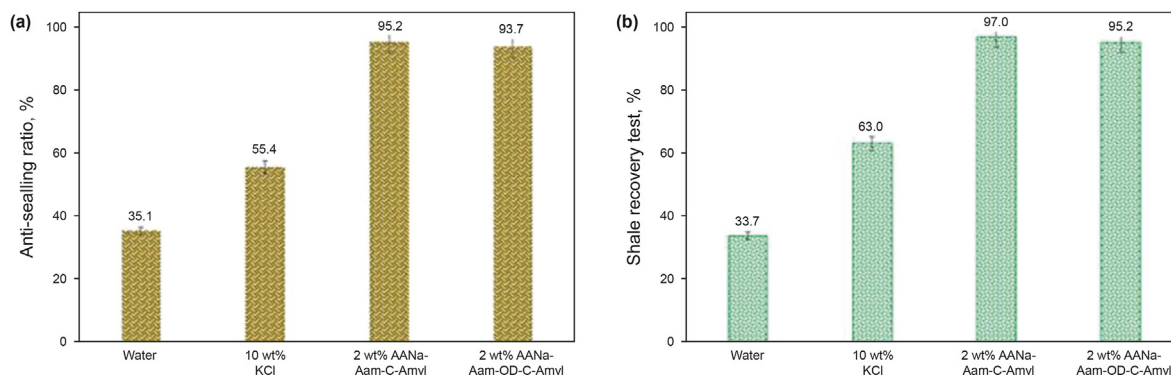
Fig. 4. Result of shale inhibition formation tests involving nanopolymers: (**a**) Anti-sealing ratio. (**b**) Shale recovery test. Reproduced from Elsevier (Saleh and Ibrahim, 2021).

specific temperature, is known as thermal stability. Ideally, the temperature affects the solubility of polymers in the usual way: as it increases, the solubility of polymers tends to improve, since the flexibility and mobility of macromolecules increases with temperature (Davoodi et al., 2022b). Thermogravimetric analysis is often used to assess the thermal stability of SP (Davoodi et al., 2019; Kariman Moghaddam et al., 2022). The SP water solution can be influenced by the polarity and flexibility of macromolecules (Zangari, 2017). The polarity of the polymer, depending on its chemical nature, significantly affects its solubility. The closer the polarity of the polymer and the liquid, the more likely the polymer is to be soluble. Polar polymers are most likely to be soluble in polar solvents, non-polar polymers in non-polar solvents. For example, non-polar polyvinyl alcohol is soluble in water, medium polar polystyrene is soluble in xylenes, non-polar polyethylene is soluble in higher-boiling-point aromatic hydrocarbons (McKeen, 2012).

The flexibility of macromolecules affects their solubility because the dissolution mechanism consists of the separation of macromolecule chains from each other and their diffusion into the solvent. Polymers with flexible macromolecules undergo this process more easily than polymers with rigid macromolecules (Zangari, 2017). Polymerization is another important characteristic of SP. SP can also be classified as polymers or copolymers according to the type of methods used in their synthesis (Balla et al., 2021).

Polymerization consists of combining homogeneous (or heterogeneous) monomers with the subsequent formation of a new high-molecular weight substance - polymer (without releasing any by-products). Polymerization is a continuous (chain) or step process. In copolymerization, two or more heterogeneous unsaturated monomers are polymerized (Balla et al., 2021). Polycondensation consists in the formation of a new high-molecular-weight substance - a polymer - and is accompanied by the release of many by-products (e.g., H_2O). Polycondensation is a stepwise process, where the intermediate products formed at each stage can be separated (Douka et al., 2018). The proportion of polymer chains that are linked in this network, that is the density of the gel component, controls the amount of crosslinking that takes place. More property changes arise from higher crosslink densities, which are caused by more links per length of polymer chain.

The degree of crosslinkage makes the different polymers more cohesive, increasing the viscosity of the SP. By joining numerous molecules together, a crosslinking agent substantially increases the molecular weight of the basic polymer, increasing the molecular weight of the linear gel (Balla et al., 2021). Water salinity and divalent ions like calcium and magnesium, which reduce the viscosity of the polymer solution, have an impact on polymer viscosity. The distance between the polymer chain and the molecules gets smaller as salinity rises. When salt is added to a polymer solution, a double layer of electrolytes forms to protect it against the repelling forces (Davoodi et al., 2022b). Hence, SPs have a wide range of characteristics, all of which depend on the structure and crystallinity of the polymer (Davoodi et al., 2022b).

3.2. SP manufacturing methods

The industrial synthesis of polymers can be carried out using different techniques, which are to a large extent responsible for the formation of a polymer's structure and properties (John et al., 2019). The molecular weight and molecular weight distribution of polymers, the ratio of differently structured units in the macromolecule and their mutual arrangement may change significantly, depending on the synthesis process adopted, while the reaction mechanism remains unchanged (Lin et al., 2021). This affects the viscosity of polymer solutions and melts, which determines processing conditions, which ultimately determines its operational properties: strength, density, hardness, flexibility, etc. The method of preparation determines the presence of impurities in the finished polymer (initiators, stabilisers, inhibitors, viscosifier, etc.), which, left in the polymer, significantly affect its properties, and the resistance of the polymer to oxidative, thermal and other influences to overcome in sub-surface environments (Balla et al., 2021; Fink, 2021). The technical methods of chain polymerization include gaseous polymerization and polymerization in mass of liquid and solid monomers, emulsions or suspensions (van Herk, 2013). Step polymerization is generally carried out in a monomer melt as well as in solution at the interface between two immiscible solvents and in the solid phase of the monomer or oligomer (Canfarotta et al., 2016).

The choice of polymerization method is determined by the specific requirements of the polymerization product as well as the nature of the monomer to be polymerized, the initiator used and the objectives of the polymerization process (John et al., 2019). The following manufacturing methods are commonly used:

1. **Addition Polymerization**: This method involves the addition of monomers to an initiator, which causes a chain reaction that leads to the formation of a polymer. Examples of addition polymerization include the polymerization of ethylene to form polyethylene and the polymerization of styrene to form polystyrene (Bergström, 2015). This method is applicable when working with monomers containing double or triple bonds, as it necessitates the use of heat or an initiator. In addition, the resulting polymers have the same repeating unit structure as the original monomers (Jain and Mahto, 2015).

2. **Condensation Polymerization**: In this method, two or more monomers react together with the elimination of a small

Table 1
Some applications of nanopolymers as additives in drilling fluids.

Type of nanopolymers	Fluid type	Work conditions/The properties of the nano-additive	Finding	Ref.
(Polystyrene-methyl methacrylate- acrylic acid)/clay	WBDF	2.1 MPa, 121.12 °C/Particle size: 1–2 nm, density: 300–370 kg/m^3, mineral type: montmorillonite, and specific surface area: 220–270 m^2/g	At 121.12 °C, the rheology of the composite nano clay/ NP wa stabilized. Compared to solid-based drilling fluid, composite NP decreased fluid losses in American petroleum institute (API) composite nano clay of NPs by 22%, and losses in polymer-based API decreased fluid losses by 65%. The introduction of terpolymer chains between clay nanolayers caused an increase in fluid-loss parameters. In an aqueous polar environment, clay NP interact with charged polymer chains, introducing clay NP into the structure of polymer. This acts to reduce the mobility of polymer chains, resulting in higher flow resistance.	Mohamadian et al. (2019)
Synthetic polymers plus ZnO NPs/carbon nanotubes	WBDF	3.5 MPa, 204.45 °C/N.G	At 204.45 °C, rheology stability and minimal filtering losses occurred. Fine filtration crusts with low permeability and minimum filtering losses were developed under low pressure/low temperature (LP/LT) conditions. Given NP are extremely small particles, they present a high surface area that acts to improve thermal stability, thermal conductivity and fluidity. This led to water permeability reducing by 25% and rheology being enhanced by 14%.	Ali Khan et al. (2018)
Polyanionic cellulose with acrylamide quaternary monomer and grafting to nano-silica (PAC-DDAS-SiO$_2$)	WBDF	690 KPa, 200–260 °C/Particle size: 200 nm, the nanopolymer morphology: micro-spherical.	Adding PAC-DDAS-SiO$_2$ to the base fluid increased PV from 4 to 30 MPa·s at 2% copolymer, raising the dynamic shear to 14.308 Pa. This is explained by the molecules of PAC-DDAS-SiO$_2$ being created at high temperatures. It occurs when the dissociative adsorption of water molecules by amide and sulfonic acid groups present on the graft copolymer's side chains increase, and the overall macromolecular side chains of the copolymer are broken. This leads to a reduction in the adsorption degree of on clay particles. Introduction of PAC-DDAS-SiO$_2$ (2 wt%) into fluid system decreased the volume of fluid loss from 20 to 5.4 mL before aging. After aging at 260 °C, the volume of fluid loss reduced from 38 to 7.2 mL, demonstrating that PAC-DDAS-SiO$_2$ can effectively control fluid loss at high temperature.	Jia et al. (2022)
Hydrophobic polymer-modified nanosilica	WBDF	3.44738 MPa, 100 °C/Particle size: 200 nm, the nanopolymer morphology: spherical and more dispersed.	PAM-SiO$_2$NPs-WBDF block the nanopores in the shale, preventing water penetration into the clay. As a result, the surface of the shale becomes hydrophobic, protecting it from water damage. PAM-SiO$_2$NPs- WBDF has demonstrated improved shale-inhibition performance compared to conventional drilling fluids and commercial shale inhibitor-based fluids. PAM-SiO$_2$NPs-WBDF extracted 86.6% of shale dispersion compared to 27.1%, 49.2%, 73.5% and 74.7% for water, aqueous Potassium chloride (KCl) solution, standard WBDF and commercial WBDF shale inhibitor, respectively. Compared with swelling in water, PAMSiO$_2$NPs-WBDF reduced the linear swelling of bentonite by 55%. Rheological analysis of PAM-SiO$_2$NPs-WBDF revealed reductions in PV, AV, YP, Gel$_{10\ sec}$ and Gel$_{10\ min}$ of 30.7%, 38.5%, 32.1%, 31.9% and 44.3%.	Saleh et al. (2022)
Nanopolymer based 2-acrylamide-2-methylpropane sulfonic acid, acrylamide, dimethyl diallyl ammonium chloride and nano-laponite	WBDF	3.4 MPa, 150, 160, 170, 180,190, and 200 °C/ Average diameter: 20 nm, average height: 1 nm.	This novel nanopolymer provides a high performance in terms of salt resistance and high thermal stability. This nanopolymer during thermal aging at 150 °C, saturated brine achieved 6.4 mL of fluid loss, whereas bentonite-based WBDF resulted in 10.4 mL of fluid loss after thermal aging at 200 °C. The mechanisms involve colloidal protection of nanopolymers and the colloidal structure of drilling fluid, which jointly enhance the aggregation stability of clay particles. This is advantageous for maintaining the content of fine particles in the drilling fluid and for forming a dense filter cake, thereby reducing filtration.	Dong et al. (2022)
Nano-sized poly(styrene-lauryl acrylate)	OBDF	690 KPa, 180 °C/Average particle size: 300 nm, morphology: spherical, the median particle size (D$_{50}$): 541 nm.	Utilizing styrene and lauryl acrylate through free emulsion polymerization, the nanopolymer poly(styrene-lauryl acrylate) rubber nanogels were obtained as a plugging agent to improve wellbore stability. the results demonstrated that at 3% the FLAPI was decreased from 3.6 to 2.8 mL while the FLHTHP was decreased from 10.2 to 7.8 mL As a result, it is reasonable to assume that the nanopolymer had	Du et al. (2022)

Table 1 (*continued*)

Type of nanopolymers	Fluid type	Work conditions/The properties of the nano-additive	Finding	Ref.
			improved its ability to manage filtration and rheological properties. The nanospheres have significant promise for OBDF because they can be used without negatively affecting the drilling fluid's qualities and can even enhance its rheological and filtration characteristics, especially after thermal aging.	
Nanopolymer based styrene, methyl methacrylate, butyl acrylate as raw materials.	OBDF	3.44738 MPa, 364 °C/Average size 108.70 nm, the particle size distribution:43.98—248.80, morphology: hexagonal prism.	This nanopolymer was obtained as a plugging agent for high temperature deployment up to 364 °C. The results demonstrated that the nanopolymer at concentration 0.5% was able to reduce filter cake permeability to 6.3×10^{-5} mD (72.12% of reduction) and the artificial core permeability was 4.1×10^{-4} mD (88.41% of reduction). The nanopolymer was able to fill the filter cake pores under the influence of formation pressure.	Yang et al. (2022)
Polymeric nanocomposites based multiwalled-carbon nanotubes and graphene-poly(lactic acid)	OBDF	3.44738 MPa, 148 °C for filtration test and 15.56—82.3 °C/N.G	These two polymeric composites demonstrated improved filtration characteristics which were 7 mL for graphene-poly(lactic acid) and 8 mL for multiwalled-carbon nanotubes. Moreover, these polymeric nanocomposites showed improved thermal stability, rheology, and mechanical performance.	Madkour et al. (2016)

molecule such as water. Examples of condensation polymerization include the polymerization of adipic acid and hexamethylenediamine to form nylon-6,6 and the polymerization of terephthalic acid and ethylene glycol to form polyethylene terephthalate (Hernandez and Reyes-Romero, 2019). The method is especially applicable when using monomers that contain functional groups capable of reacting to form dimers and losing small molecules. Heat is typically required to facilitate these reactions. The resulting polymers have a different repeating unit structure than that of the original monomers (Zhong et al., 2020a).

3. **Ring-Opening Polymerization**: This method involves the opening of cyclic monomers to form linear polymers. Examples of ring-opening polymerization include the polymerization of lactide to form polylactic acid and the polymerization of ε-caprolactone to form polycaprolactone (Nuyken and Pask, 2013). The method is applicable for producing linear polymers from cyclic monomers and requires the involvement of an initiator or catalyst to achieve the polymerization reaction. The reaction can be performed in the presence or absence of a solvent, depending on the specific monomer and initiator chosen at moderate temperatures and pressures (Utracki and Wilkie, 2014).

4. **Emulsion Polymerization**: This method involves the dispersion of monomers in an aqueous solution containing an emulsifying agent. The monomers are then polymerized to form a latex. Examples of emulsion polymerization include the polymerization of butadiene to form synthetic rubber and the polymerization of styrene to form latex (Zhong and Pan, 2022). This method is effective for producing polymers using immiscible monomers dissolved in water with the aid of a surfactant. An initiator is required to achieve the polymerization reaction, and agitation is needed for proper mixing of the monomers and reactants (Yamak, 2013).

5. **Suspension Polymerization**: This method involves the dispersion of monomers in a non-aqueous medium in the presence of a suspending agent. The monomers are then polymerized to form particles that are suspended in the medium. Examples of suspension polymerization include the polymerization of vinyl chloride to form polyvinyl chloride and the polymerization of methyl methacrylate to form polymethyl methacrylate (Jayaweera and Narayana, 2021). This method is particularly

effective for producing polymer particles with a narrow size distribution. It is performed by suspending monomer droplets in a liquid medium, typically water, using a stabilizer to prevent the droplets from coalescing and forming a single phase (Liu and Chen, 2014).

6. **Radical polymerization** is a method of synthesizing polymers through the initiation of a radical reaction. This method is particularly used for producing a wide variety of polymers with different properties using monomers that are able to form free radicals through the initiation process (Zhong and Pan, 2022). This method can be carried out in different phases, such as in the gas phase and in mass (bulk):

   a. In **gas-phase radical polymerization**, the monomer and initiator are vaporized and introduced into a reactor vessel. The vapor mixture is then heated to initiate the polymerization reaction (De Vos et al., 2021). The resulting polymer forms as a solid powder, which is collected and purified after the reaction. Gas-phase radical polymerization is often used to produce polymers with high molecular weight and narrow polydispersity (Cancelas et al., 2016).

   b. **Mass radical polymerization**, also known as bulk polymerization, is a method of synthesizing polymers in the absence of a solvent. The monomer and initiator are mixed together and heated to initiate the polymerization reaction. The resulting polymer forms as a solid, which can be collected and purified after the reaction. Mass radical polymerization is often used to produce thermoset polymers, which are cross-linked networks that are not soluble in any solvents (Fulcrand et al., 1996).

Subsections 3.2.1—3.2.4 explain in details the most applicable manufacturing methods for synthesizing the SPs suitable for drilling fluids. These are suspension polymerization (Chaudhary and Sharma, 2019), emulsion polymerization (Cummings et al., 2019; Yamak, 2013), solution free radial polymerization (Edeleva et al., 2021), and ring opening polymerization (Zhang et al., 2020).

3.2.1. Suspension polymerization

Suspension polymerization is a process in which polymer particles are formed in a liquid medium, suspended in the form of droplets, and then polymerized. The process involves the dispersion of monomers in a liquid medium containing a stabilizer and an

initiator, which are agitated to form droplets of monomer. The initiator then initiates polymerization within the droplets, resulting in the formation of polymer particles. The polymer particles remain suspended in the liquid medium and can be collected and used for a range of applications (Chaudhary and Sharma, 2019).

The main applications of suspension polymerization include: paints and coatings, plastics, adhesives, biomedical applications, and SP for drilling fluids (Utracki and Wilkie, 2014). The typical monomers used in suspension polymerization include styrene, vinyl chloride, and acrylonitrile, among others. The choice of monomer depends on the desired properties of the polymer and the intended application. The initiators used in suspension polymerization are typically water-soluble, such as potassium persulfate or ammonium persulfate, and are activated by a reducing agent, such as sodium sulfite or sodium metabisulfite. The stabilizers used in suspension polymerization are usually surfactants or other surface-active agents, such as polyvinyl alcohol or sodium lauryl sulfate.

The key mechanism of suspension polymerization involves the formation of small, uniform droplets of monomer in a liquid medium, which are stabilized by surfactants or other stabilizing agents (Liu and Chen, 2014). The initiators are added to the reaction mixture and triggers the polymerization of the monomer droplets, resulting in the formation of small polymer particles. As the reaction proceeds, the particles grow in size and eventually become too large to be stabilized by the surfactants, leading to agglomeration and the formation of larger particles. The reaction is typically terminated by cooling or by the addition of a terminating agent. The resulting polymer particles are then washed and dried to remove any residual solvent or other impurities (Liu and Chen, 2014).

Some of the common technical difficulties of suspension polymerization include: particle size control, agglomeration and coalescence which can occur if the reaction conditions are not properly controlled, heat transfer which can cause localized overheating and affect the particle size and distribution, environment contamination from impurities or microorganisms, and reactor design (Jayaweera and Narayana, 2021; Liu and Chen, 2014). The factors that can influence the performance and properties of the polymer particles produced by suspension polymerization include:

- **monomer concentration** can affect the rate of polymerization and the size and distribution of the resulting polymer particles;
- **stabilizer concentration** can affect the size and distribution of the polymer particles, as well as their stability and ability to resist agglomeration and coalescence;
- **agitation rate** can affect the size and distribution of the polymer particles by influencing the mixing of the reactants and the efficiency of heat transfer;
- **temperature** can affect the rate of polymerization, the size and distribution of the polymer particles, and the stability of the reaction mixture; and,
- **design of the reactor**, including its size, shape, and configuration of mixing and cooling systems, can affect the efficiency and quality of the suspension polymerization process (Utracki and Wilkie, 2014).

As an example of suspension polymerization, an oil-absorbent polymer (OAP) to be used in drilling fluids to mitigate lost circulation was manufactured containing monomers of methylmethacrylate (MMA) (6 g), BA and hexadecyl methacrylate (18 g), cross-linking reagent N,N'-Methylenebis (acrylamide) (0.3 g), porogen ethyl acetate (5 g), and initiator benzoyl peroxide (0.4 g), which can easily decompose into benzoyl and oxygen radicals, which can then initiate the polymerization of monomers (Zhong et al., 2018). Suspension polymerization was utilized in this case because it is highly economical and more environmentally friendly

than other forms of polymerization. It can also be used to make high-molecular-weight polymers in a short time period which is required to mitigate lost circulation (Zhong et al., 2018). The reaction was carried out in 0.5 L four-necked round-bottom flasks. These were equipped with and heating devices and mechanical stirrers. The polymerization process was carried out for 6 h at 80 °C at a 600-rpm stirring rate. Following the completion of the reaction, the products were washed multiple times with 100% ethanol, followed by numerous washes with hot deionized water (60—70 °C). The particle size may be adjusted by varying the monomer ratio and the rate of stirring in the process (Zhong et al., 2018). Fig. 5 displays the possible oil-absorbent polymer chemical reaction mechanism (OAP), and the (FT-IR) spectrum of suspension polymerization.

Suspension polymerization was also used to create a novel type of polymeric rheology modifier (PRM) due its ability to produce high-quality, uniform polymer particles with a high solids content, versatility, scalability, low cost, and allowing for precise control over particle size. These characteristics are important for producing polymeric rheology modifiers with consistent and predictable properties (Ma et al., 2018). To do so, methyl styrene, dimethyl azobis isobutyrate, methyl methacrylate, octadecyl acrylate, and 300 mL tetrahydrofuran were added to a 500 mL four-necked flask equipped with magnetic stirrers and nitrogen inlets. The mixture was swirled in nitrogen for 16 h at 80 °C. Following the removal of the solvent at low pressure, the product was washed several times with distilled water to remove residual tetrahydrofuran, dried for 24 h in a vacuum oven at 100 °C, pulverized through an 80100 grit sieve, and the PRM is recovered as a white-colored powder (Ma et al., 2018).

Suspension polymerization is the preferred technique for producing polymeric rheology modifiers for drilling fluids because it allows for precise control over particle size and yields high quantities of the product. It is also a relatively low-cost and solvent-free process, making it suitable for industrial-scale production (Chaudhary and Sharma, 2019).

3.2.2. Emulsion polymerization

Emulsion polymerization is a type of free radical polymerization that takes place in an aqueous medium. In this process, monomers are dispersed in water, along with a surfactant and a water-soluble initiator. The surfactant helps to stabilize the monomer droplets in water and prevent them from coalescing, while the initiator generates free radicals that initiate polymerization (Zhong and Pan, 2022). Emulsion polymerization is a radical process, involving the generation of free radicals, which are highly reactive species with an unpaired electron. These free radicals are generated through the use of initiators, which are typically water-soluble peroxides, such as potassium persulfate or ammonium persulfate, so it requires the use of real initiators, which are sources of radicals. The essential components required for emulsion polymerization include:

1. **Monomer**: The monomer is the starting material for the polymerization reaction. It should be water-insoluble, or only slightly soluble, to form an emulsion with the aqueous medium. Common monomers used in emulsion polymerization include styrene, butadiene, and methyl methacrylate.
2. **Emulsifier**: The emulsifier is a surfactant that is used to stabilize the emulsion and prevent the coalescence of the monomer droplets. It adsorbs onto the surface of the monomer droplets, creating a protective layer that prevents them from coming into contact with each other. Common emulsifiers used in emulsion polymerization include sodium lauryl sulfate and polyvinyl alcohol.
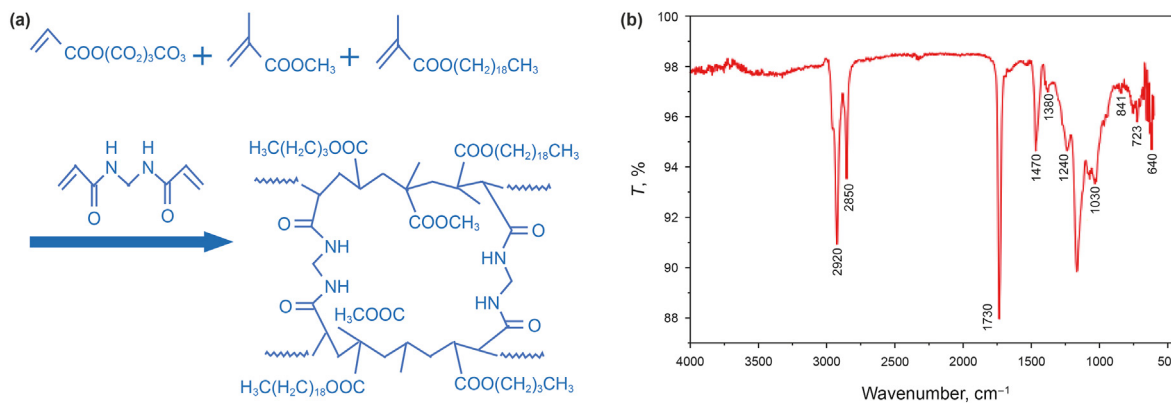
Fig. 5. (**a**) An oil-absorbent polymer (OAP) chemical reaction mechanism. (**b**) (FT-IR) spectrum of suspension polymerization. Modified after (Zhong et al., 2018).

3. **Initiator**: The initiator is a molecule that initiates the polymerization reaction by forming free radicals. It should be water-soluble, or only slightly soluble, to be able to initiate polymerization in the aqueous medium. Common initiators used in emulsion polymerization include ammonium persulfate and potassium persulfate.
4. **Water**: Water is the solvent and the dispersion medium for emulsion polymerization. It is used to dissolve the initiator and emulsifier and to maintain the emulsion stability.

In addition to these components, other additives such as co-monomers, cross-linkers, and chain transfer agents may be added to control certain polymer properties such as molecular weight, degree of branching, and morphology (Cummings et al., 2019; Yamak, 2013).

The mechanism of emulsion polymerization involves three distinct steps. 1) the monomer is dispersed in the aqueous medium, forming droplets that are stabilized by the surfactant or emulsifying agent. The surfactant molecules form a layer around the droplets, which prevents them from coalescing. 2) The initiator is added to the system. The initiator may be water-soluble or oil-soluble, depending on the type of monomer and surfactant used. When the initiator is activated, it generates free radicals or other reactive species that initiate polymerization within the micelles. As polymerization proceeds, the monomer droplets are consumed and the polymer particles grow in size. The surfactant or emulsifying agent continues to stabilize the particles, preventing them from coalescing or aggregating. 3) Once the polymerization process is complete, the resulting polymer particles can be isolated and used for a range of applications.

The mechanism of emulsion polymerization can vary depending on the specific type of monomer and surfactant used, as well as the conditions of the reaction. However, the basic principle of forming micelles around monomer droplets to stabilize them and initiate polymerization is common to all emulsion polymerization processes (Cummings et al., 2019; Yamak, 2013).

As an example of the emulsion polymerization, Davoodi et al. (2019) synthesized a synthetic copolymer based on acrylamide styrene monomers using inverse emulsion polymerization due to its water-based system, ability to produce polymer particles with a narrow size distribution, provide control over polymer morphology, versatility, and low energy consumption. Firstly, the hydrophobic monomer, styrene, was dissolved in an organic solvent to control the polymerization reaction by regulating the solubility of the monomers and the growing polymer chains, whereas acrylamide, the hydrophilic monomer, was dissolved in distilled water. Next, the polymer reaction was carried out in a three-necked

flask that was equipped with a mechanical stirrer, thermometer, a nitrogen inlet (Davoodi et al., 2019). One advantage of using aqueous emulsion polymerization for hydrophilic monomers is that no organic solvents are needed, which can reduce costs and minimize environmental concerns. However, the use of an organic solvent may still be necessary in certain cases to improve the solubility of the monomer or to provide additional control over the reaction (Zhong and Pan, 2022).

As a filtrate-loss-control agent, β-cyclodextrin polymer (β-CDP) microspheres were synthesized by mixing 12 g-CD in 20 mL solution sodium hydroxide aqueous through inverse emulsion polymerization (Zhong et al., 2020b). The use of sodium hydroxide in inverse emulsion polymerization can provide several benefits, including improved initiator activation, pH control, and monomer solubility. These factors can help to ensure the formation of high-quality polymer particles with desirable properties for various applications. After 20 min, 14.8 g of EPI was gently introduced into the solution and stirred for 1.5 h at a 60-rpm stirring rate at 30 °C. The dispersing phase was then produced. The continuous phase was made by magnetically swirling 0.5 g of Tween and 1.5 g of Span 80 into 80 g of kerosene. Vigorously agitating at 1000 rpm for 20 min, the dispersing phase was then mixed with the continuous phase solution to generate an inverse emulsion. The resulting mixture of the dispersing and continuous phase solution was then placed in a four-necked round flask (250 mL) fitted with a mechanical stirrer and a water bath. The temperature was raised to 70 °C and held there for 6 h. The speed of stirring was increased further to a stirring speed of 2000 rpm to improve the mixing and dispersion of the β-CDP in the water and facilitate the formation of smaller and more uniform microspheres. Following the reaction, the mixture was centrifuged and washed with diluted hydrochloric acid solution (10 wt%), absolute ethanol, deionized water, and acetone in that order. The subsequent washing steps were performed to remove any residual impurities and solvents that could affect the final properties of the microspheres. Finally, the β-CDP microspheres were produced after 24 h of drying in a vacuum oven at 60 °C to allow for the complete removal of any remaining moisture and solvents, resulting in the production of dry β-CDP microspheres (Fig. 6) (Zhong et al., 2020b).

3.2.3. Solution free radial polymerization

Radical polymerization is a process of polymer formation applying the free-radical mechanism with sequential attachment of monomer molecules to the growing macroradical. Radical polymerization is possible for most vinyl, vinylidene, diene monomers, as well as for some dense cyclic compounds. Some unsaturated monomers are unable to polymerize by the radical mechanism due
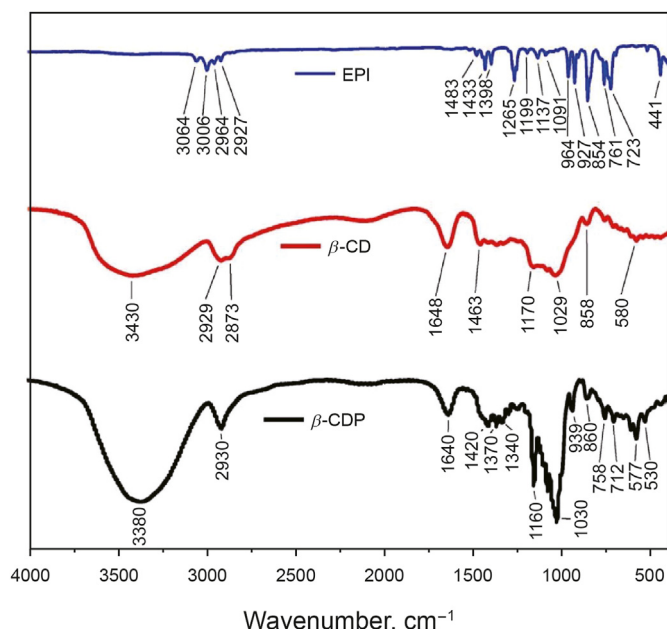
Fig. 6. FT-IR spectrum of epichlorohydrin (EPI), β-CD (β-cyclodextrin) and β-CDP (β-cyclodextrin polymer) microsphere. Reproduced from (Zhong et al., 2020b).

to steric difficulties (e.g., 1,2-disubstituted vinyl monomers) or because of degenerate chain transfer, for example propylene, allyl monomers (Edeleva et al., 2021). The mechanism of free radical polymerization involves several steps:

1. **Initiation**: This step involves the formation of free radicals that will initiate the polymerization process. This can be achieved by various methods such as thermal decomposition, photochemical or redox reactions. For example, a common initiator for free radical polymerization is benzoyl peroxide, which is thermally decomposed to form benzoyl radicals.
2. **Propagation**: This step involves the addition of monomers to the active center of the free radical, resulting in the growth of the polymer chain. The addition of monomers leads to the formation of a new radical at the end of the growing polymer chain.
3. **Termination:** This step halts the polymerization process, where the free radicals are either consumed by chain termination reactions or by combining with another free radical. This results in the formation of a polymer with a defined molecular weight and distribution (Krzysztof and Thomas, 2002).

Several factors can affect free radical polymerization including:

- **Temperature.** The rate of polymerization increases with an increase in temperature, but high temperatures can also lead to side reactions such as chain transfer and chain termination.
- **Monomer concentration.** Higher monomer concentrations can lead to faster polymerization rates, but can also result in a higher degree of branching and crosslinking.
- **Initiator concentration.** The rate of polymerization is proportional to the concentration of initiator used. Fourthly, the
- **Presence of impurities**. Certain impurities in the reaction mixture can inhibit or interfere with the polymerization process.
- **Solvent effects.** The choice of solvent can affect the rate of polymerization, as well as the molecular weight and distribution of the resulting polymer.

Overall, free radical polymerization is a versatile and popular method for synthesizing polymers with a wide range of properties (Edeleva et al., 2021; Krzysztof and Thomas, 2002). Many SP for use in drilling fluids have been created by solution free radial polymerization such as the novel graft copolymer (Lei et al., 2021b), viscosifier (SDKP) (Xie et al., 2018), and PAAN-G (A polymer/graphene oxide (GO) composite) (Ma et al., 2021a). Solution free radical polymerization is extensively used for synthesizing SPs used in drilling fluids. This technique involves polymerizing monomers in the absence of solvents or dispersants, and using thermal or chemical initiators to generate free radicals that initiate polymerization. This method can be used to synthesize a wide range of polymers, including copolymers, copolymers, and graft copolymers, which can be tailored to provide specific properties such as rheology control, thermal stability, and fluid loss control in drilling fluids. Overall, solution free radical polymerization is a versatile and widely used method for synthesizing SPs for use in drilling fluids (Edeleva et al., 2021; Lei et al., 2021b).

For instance, a low-molecular-weight quadripolymer to act as a viscosifier additive was synthesized by solution free radial polymerization. AA plus 2-acryl-amido-2-methyl-1-propane sulfonic acid (AMPS) plus methyl acrylate plus dimethyl diallyl ammonium chloride were used to produce the quadripolymer in a 500 mL glass reactor equipped with a teflon stirrer, thermometer, condenser, and nitrogen inlet (Huang et al., 2015). The four monomers used in the synthesis of low-molecular-weight quadripolymers can be chosen based on their desired properties, such as their reactivity, solubility, and compatibility with the other monomers. During the polymerization reaction, the monomers react with each other to form a copolymer with a specific molecular weight and composition. The properties of the resulting quadripolymer can be tuned by adjusting the reaction conditions, such as the temperature, initiator concentration, and monomer feed ratios (Huang et al., 2015).

3.2.4. Ring opening (RO) polymerization

RO is a type of polymerization reaction that involves the opening of cyclic monomers through the use of an initiator or catalyst. RO can be divided into two types: cationic RO and anionic RO.

- **Catonic RO.** In cationic RO, a Lewis acid catalyst is used to initiate the opening of the cyclic monomer. The monomer is typically an epoxide, such as ethylene oxide or propylene oxide. The cationic RO reaction proceeds by the coordination of the catalyst with the epoxide, which results in the activation of the epoxide ring. The activated epoxide then reacts with a nucleophile, such as a water molecule or an alcohol, leading to the formation of a polymer chain.
- **Anionic RO**, in anionic RO, a nucleophilic initiator, such as an organolithium compound or an alkoxide, is used to initiate the opening of the cyclic monomer. The monomer is typically a lactone, such as ε-caprolactone or lactide. The anionic RO reaction proceeds by the coordination of the initiator with the lactone, which results in the activation of the lactone ring. The activated lactone then reacts with a nucleophile, such as the initiator or a chain-terminating agent, leading to the formation of a polymer chain (Takasu and Hayashi, 2015; Zhang et al., 2020).

The essential components required for RO include:

1. **Monomer.** The cyclic monomer is the starting material for the polymerization reaction. Examples of cyclic monomers used in RO include lactones, lactams, and cyclic carbonates.
2. **Initiator/Catalyst**, The initiator or catalyst is used to initiate the RO reaction. Initiators such as alcohols or amines can be used in

the absence of a catalyst for certain RO reactions. Catalysts can be divided into two categories: metal-based catalysts and organic-based catalysts. Examples of metal-based catalysts include titanium and zinc compounds, while examples of organic-based catalysts include organocatalysts and enzymes.

3. **Solvent**: The solvent is used to dissolve the monomer and the initiator/catalyst, and to control the reaction rate. Common solvents used in RO include toluene, tetrahydrofuran, and dimethylformamide.

In the RO mechanism, the cyclic monomer is opened by the initiator or catalyst, leading to the formation of an activated monomer. The activated monomer then reacts with additional monomer molecules, leading to chain growth and the formation of a polymer. Factors affecting RO include the rate and selectivity of RO can be influenced by several factors, including the type of monomer, the initiator or catalyst, the solvent, temperature, and pressure (Nuyken and Pask, 2013; Takasu and Hayashi, 2015). Some technical difficulties are associated with the RO process:

1. **Control of molecular weight and polydispersity**/Controlling the molecular weight and polydispersity of the polymer can be challenging due to the complex nature of the RO reaction.
2. **Catalyst poisoning.** Catalyst poisoning can occur due to the presence of impurities in the monomer or solvent, which can result in the deactivation of the catalyst.
3. **Side reactions.** Side reactions such as chain transfer, termination, and backbiting can occur during RO, leading to undesired polymer properties.
4. **Stereoselectivity.** Some RO reactions can exhibit stereoselectivity, leading to the formation of specific isomers or enantiomers. However, achieving high stereoselectivity can be challenging due to the complex nature of the reaction (He et al., 2021).

For drilling fluid applications, RO polymerization is used to synthesize polymers for filtration control, viscosification, and/or as inhibition additives; for example, polyethyleneimine (PEI) (Guancheng et al., 2016). Two SP, branched Polyethyleneimine (BPEI) and hexamethylenediamine, were synthesized by RO polymerization for use as an inhibition additive. They achieved inhibition efficiency of 65% due to the substantial number of primary amine groups. This leads to a reduction in amine group adsorption on bentonite, enabling it to adsorb more water (Xie et al., 2017). Additionally, the amine groups present in BPEI and hexamethylenediamine are highly reactive and can form strong bonds with clay particles, further enhancing the inhibition efficiency of these polymers. The use of these polymers as inhibition additives can also help to reduce the adsorption of other additives onto clay particles, improving the overall performance of the drilling fluid. Inhibition additives synthesized through RO can be effective in reducing water adsorption and improving the performance of drilling fluids by forming a protective layer around clay particles and reducing their interaction with water. The high molecular weight of the polymers synthesized through RO allows them to effectively adsorb onto clay particles, forming a stable and protective layer that inhibits clay swelling and improves the stability of the drilling fluid (Xie et al., 2017).

For instance, the SP called SNF-FLOERGER has been used to synthesize three polymers (copolymers P1, P2 and P3) using the RO method (Ahmad et al., 2018). P1 is a copolymer of AMPS and acrylamide containing 10% degree of hydrolysis (DOH). P2 is a 25% DOH copolymer of 2-acrylamido-2-methylpropane sulfonic acid and acrylamide. P3 is a copolymer of acrylamide and AA containing 15% DOH (degree of hydrolysis) (Ahmad et al., 2018). The first phase of the experimental procedure involves the preparation of polymer

solutions using a magnetic stirrer. The stirring helps to dissolve the polymer into the water, creating a homogeneous solution. The concentration of the polymer in the solution is 0.25 wt%, which means that there are 0.25 g of polymer for every 100 g of solution. After stirring for 3 h, the solution is left undisturbed for the next 3 h to allow for complete hydration of the polymers for surrounding and interacting with the polymer chains, resulting in the formation of a gel-like structure. The time given for hydration is important as it allows the polymer chains to fully absorb water and swell, which is necessary for the polymer to perform its intended function in the bentonite (BT)/polymer dispersions. In the second phase, bentonite/polymer dispersions are prepared by dispersing 5 wt% bentonite in deionized water using a mechanical stirrer. The stirring helps to disperse the bentonite particles throughout the water, creating a homogeneous suspension. The concentration of bentonite in the dispersion is 5 wt%, which means that there are 5 g of bentonite for every 100 g of water. The 0.25 wt% polymer solutions prepared in the first phase are then mixed with the bentonite dispersions to prepare three bentonite/polymer dispersions: BT/P1, BT/P2, and BT/P3. The stirring is applied for 30 min to ensure complete homogenization of the bentonite with the polymer for creating a uniform mixture of the bentonite and polymer. This is important for obtaining consistent and reproducible results in the rheological experiments. Finally, after homogenization, the dispersions are left undisturbed for 24 h before starting rheological experiments. This time is given to allow the bentonite/polymer dispersions to stabilize and reach equilibrium (Ahmad et al., 2018). Incorporating high molecular weight polymer into the drilling fluid under investigation, improved thermal stability, enhanced rheology, and superior filtration properties were observed. However, the study also highlighted a significant concern regarding the presence of a high proportion of electrolyte, as this has an adverse effect on both the rheology and filtration characteristics (Ahmad et al., 2018).

Graft copolymerization is often used to create SPs suitable for drilling fluids (Abdollahi et al., 2018). Graft copolymerization is a process in which one or more monomers are polymerized onto an existing polymer backbone, resulting in a hybrid copolymer. This technique is commonly used to modify the properties of the original polymer by introducing new functional groups or enhancing its molecular weight. The mechanism of graft copolymerization typically involves the following steps:

1. **Initiation.** The reaction is initiated by a suitable initiator, which generates free radicals that can react with the monomer.
2. **Adsorption.** The monomer is adsorbed onto the surface of the polymer backbone, usually through physical adsorption or chemical bonding.
3. **Polymerization.** The monomer is polymerized onto the polymer backbone, forming a graft copolymer.

Factors that can affect the success of graft copolymerization include the type and concentration of the initiator, the nature of the monomer and polymer backbone, reaction temperature and time, and the presence of any additives or impurities (Thakur, 2018). In the context of drilling fluids, graft copolymerization can be used to improve the properties of the fluid, such as its rheological properties and stability. However, there are several technical difficulties associated with this technique. For example, it can be challenging to achieve a high degree of grafting without compromising the stability or performance of the drilling fluid. Additionally, the presence of impurities or contaminants in the drilling fluid can interfere with the grafting process, leading to lower yields and reduced performance (Abdollahi et al., 2018; Jain et al., 2017).

As an example, graft copolymerization was used to synthesize

lignosulfonate plus acrylamide graft copolymers (LS-g-PAAm) (Abdollahi et al., 2018). They selected acrylamide concentration and initiator type as variables for their experiment. They prepared a solution of lignosulfonate, $CaCl_2$, and distilled water, then added a specific amount of acrylamide dissolved in water to the reaction mixture. Nitrogen gas was bubbled into the solution for 30 min while stirring, followed by the addition of a specific amount of H_2O_2, which was purged with nitrogen gas for an additional 10 min. The reaction mixture was sealed in a flask, immersed in a water bath at 30 °C, and left to react for 48 h. To stop the reaction, a hydroquinone aqueous solution (1 wt%) was added as an inhibitor. The mixture was diluted with water and slowly added to acetone with an excess amount (about five times relative to the aqueous solution) under stirring to precipitate the graft polymer, as well as any potential free homopolymers. The precipitate was separated from the solution, dissolved in water, and precipitated again in excess acetone. The purified solid product was then dried under vacuum at 60 °C for 24 h (Abdollahi et al., 2018).

Semi-continuous polymerization is another method that can be used to synthesize SP for drilling fluids (Lei et al., 2021a). Semi-continuous polymerization is a process that involves the continuous addition of monomers and initiators into a reaction vessel. The mechanism of semi-continuous polymerization involves the initiation, propagation, and termination steps. In the initiation step, a free radical initiator is added to the reaction vessel to start the reaction. Then, monomers are added continuously to the reaction vessel to undergo polymerization through the propagation step. The reaction is terminated by adding a termination agent, which stops the polymerization process. Several factors can influence the semi-continuous polymerization process, including the concentration of monomers, initiators, and termination agents, the temperature, and the stirring rate. The monomer concentration can affect the molecular weight and the properties of the resulting polymer. The initiator concentration can impact the rate of polymerization and the size of the polymer particles. The temperature can affect the reaction rate and the molecular weight of the polymer, while the stirring rate can influence the size and distribution of the polymer particles (Jönsson et al., 2007; Xu et al., 2013a, b). Some technical difficulties that can arise during semi-continuous polymerization for drilling fluids include controlling the reaction conditions, achieving a uniform distribution of the polymer particles, and minimizing the formation of by-products. These challenges can affect the quality and performance of the resulting polymer, which is crucial for the effectiveness of the drilling fluid (Jönsson et al., 2007; Xu et al., 2013a, b).

As an example, the semi-continuous polymerization was used to synthesize self-crosslinking soap-free latexes (PMS) (Lei et al., 2021a). The process involved adding MMA and styrene monomers into a water solution containing $NaHCO_3$ and 3-aminopropiltrimetoksisilan (APMS) under intensive stirring. The resulting mixture was then transferred into a 250 mL four-necked round-bottomed flask and stirred under N_2 atmosphere at 340 rpm for 20 min. The temperature was then raised to 75 °C, and a quarter of ammonium persulfate (APS) solution was added to initiate the polymerization. After 30 min, a hydrophobic monomer mixture consisting of MMA and styrene and a water solution containing the remaining APS, AMPS, and variable amounts of N-(hydroxymethyl)acrylamide were added simultaneously at constant rates over a period of 3–3.5 h. The reaction was allowed to proceed for an additional 2 h at 85 °C to consume the residual monomers. The resulting latexes were cooled, filtered, and purified to obtain self-crosslinking soap-free PMS latexes with different N-(hydroxymethyl)acrylamide contents (1, 3, 5, and 7 wt%). The PMS latexes were designated as PMS-N1, PMS-N3, PMS-N5, and PMS-N7, respectively. Technical difficulties in this process may include

controlling the addition rate of monomers and maintaining a consistent temperature and N_2 flow rate throughout the reaction (Lei et al., 2021a). The use of self-crosslinking latexes had a positive impact on the rheological and microporous filtration properties of the drilling fluid that was based on bentonite. These latexes had stronger interparticle interactions, which resulted in better viscosity-increasing effects after thermal treatment and stronger ability to reduce fluid loss at high temperatures. The microporous plugging mechanism was found to involve both heat deformation and self-crosslinking film formation, in addition to physical bridging and filling (Lei et al., 2021a).

Table 2 describes the main manufacturing methods used to synthesize polymers and their advantages and disadvantages. Table 2 describes each method together with its advantages and disadvantages, and the choice of method depends on the specific properties desired for the polymer and the intended application. The most preferable manufacturing method for SPs in drilling fluids depends on the specific type of polymer and the desired properties of the drilling fluid. The most common manufacturing methods include solution polymerization, emulsion polymerization, suspension polymerization, and inverse emulsion polymerization. The solution method is often used for producing high molecular weight polymers. Emulsion polymerization method is commonly used for producing latexes and other types of polymers that have low molecular weight and are water-soluble. Suspension polymerization method is used for producing polymers that are insoluble in water. Inverse emulsion method is used for producing polymers that are soluble in organic solvents but insoluble in water (Bergström, 2015; John et al., 2019). Graft copolymerization is sometimes preferred to produce SP suitable for drilling-fluid applications because it allows for the creation of a polymer that has both a backbone and pendant chains. This unique structure provides the polymer with enhanced performance characteristics, such as improved rheological properties, filtration control, and stability at high temperatures and pressures (Thakur, 2018).

The choice of polymerization method for drilling fluids also depends on factors such as the desired molecular weight, polydispersity, and particle size distribution of the polymer, as well as the cost and availability of raw materials. Other factors that may influence the choice of polymerization method include the stability of the polymer in harsh drilling conditions, its resistance to degradation by high temperature and pressure, high salinity and its compatibility with other drilling fluid components (Balla et al., 2021; Fink, 2021).

4. Synthetic polymer contributions to drilling fluids

4.1. Types of SP used in drilling fluids

4.1.1. SP in water-based fluid

SPs are widely used in the drilling industry, and they make significant contributions to different types of drilling fluids (Balaga and Kulkarni, 2022). Ideally, A WBDF that uses SPs typically includes several components: (i) either a single SP or multiple SPs, (ii) API-grade bentonite, (iii) weighting agents like barite, calcium carbonate, ilmenite, or hematite, (iv) loss circulation agents such as micronized cellulose, bagasse, or mica flakes, (v) lubricants such as PHPA, beads, graphite, poly-α-olefin, or crude tall oil, (vi) hole stabilizers like PHPA, sodium silicate, or polyalkylene-glycols, (vii) corrosion inhibitors like amides, imidazolines, polyoxylated amines, zinc carbonate, or ammonium bisulfite, (viii) salts including sodium chloride or potassium chloride, (ix) deflocculants such as lignosulfonate, sodium acid pyrophosphate, or quebracho, (x) pH control agents like magnesium oxide, caustic soda, caustic potash, soda ash, or sodium bicarbonate, and (xi) surfactants such

Table 2
Main manufacturing methods for synthesizing polymers and their advantages and disadvantages.

Method	Chemical definition	Advantages	Disadvantages	Ref.
Suspension polymerization	The monomer is dispersed in water in the form of fine droplets. The monomer must be water-soluble.	Efficient heat dissipation from the reaction system. Control of kinetic chain length (limiting the molecular weight distribution). Ease of separation from water. Easy processing of the finished product.	The main problem is the need to keep the system in a dispersed state. The need for slurry stabilizers. The need for solvent regeneration and wastewater treatment. The need to remove stabilizer residues from the polymer.	Jayaweera and Narayana (2021)
Emulsion polymerization	The monomer is dispersed in the aqueous phase as a homogeneous emulsion.	High polymerization rate. Low viscosity variation. Easy control of heat transfer. Use of water as solvent. Possibility to produce high molecular weight compounds displaying a narrow molecular-weight distribution. Possibility to adjust the molecular weight by the ratio monomer/surfactant/water. Possibility to use obtained emulsions of polymers for production of components applying a wetting method.	The need to use additional substances (surfactants, emulsifiers). Treatment of large quantities of wastewater. A coagulant is needed to separate the polymer from the emulsion.	Zhong and Pan (2022)
Solution free radial polymerization	The monomer, initiator and chain transfer agent are dissolved in an inert solvent.	Process takes place with simultaneous heat dissipation. Possibility to vary the monomer concentration in the solution. Possibility to vary the temperature across a wide range. Possibility to produce highly viscous polymers. Ability to produce oligomers with reactive end groups. Possibility to produce varnishes and concentrated polymer solutions.	The need for solvent separation and drying of the polymer. The need for solvent regeneration. Significant energy costs. There is a finite probability of chain transfer to the solvent, making it difficult to obtain very high molecular weight products.	De Vos et al. (2021)
Radical polymerization in the gas phase	Used if the monomer is characterized by a low critical boiling point.	No need to use solvents. Photo and radio initiation can be effectively applied.	The need for high pressure; Very poor heat dissipation; Change of polymerization kinetics when a solid phase appears.	Cancelas et al. (2016)
Radical polymerization in mass	The monomer is a liquid. The initiator and chain transfer agent are dissolved in the monomer.	Minimum number of components. No polymer extraction step from the reaction medium. Allows polymers to be obtained with a high degree of purity. The only way to produce optical organic glass. Minimal environmental contamination.	Difficulty in dissipating heat when the degree of conversion is deep. Thermal fluctuations result in a wide molecular weight distribution. Local temperature fluctuations can lead to degradation. Local evaporation of monomers and formation of defects (shells).	Fulcrand et al. (1996)
Ring opening (RO) polymerization	It is a chain process consisting of the initiation, growth, and chain limitation stages. In most cases, it is characterized by signs of "live" ionic processes leading to linear molecular-weight growth of polymers with increasing monomer conversion to form blocks of copolymer when an "alien" monomer is added to the reaction mixture at limiting conversions.	Because of the low melt viscosity of the cyclic oligomers, reactive injection molding is preferred over prefabricated high-molecular-weight polymers (cyclomers).	The process is determined by monomer concentration and conversion, and initiator concentration (as in "live" ionic polymerization).	Nuyken and Pask (2013)
Addition Polymerization	It is a type of polymerization reaction where monomers are added together to form a polymer. In this process, the double bonds in the monomers are broken and replaced with single bonds, forming a long chain polymer. Addition polymerization can be initiated by heat, light, or a chemical initiator.	High yield simple reaction conditions. Can produce polymers with high molecular weight and narrow polydispersity. Allows for the incorporation of functional groups in the polymer chain	Limited to certain monomers. Can produce low-quality polymers with impurities. Can require the use of toxic initiators.	Bergström (2015)
Condensation Polymerization	It is a type of polymerization reaction where monomers join together by forming covalent bonds and releasing small molecules. In this process, two or more different monomers react with each other to form a polymer with a repeating unit that contains atoms from both monomers.	Versatile method that can be used to produce a wide range of polymers. Can produce high-quality polymers with a narrow molecular weight distribution. Can produce polymers with desirable properties such as thermal stability and biocompatibility.	Can be a complex and lengthy process. Requires the removal of the small molecule by-product, which can be challenging.	Hernandez and Reyes-Romero (2019)
Semi-continuous polymerization	This process is often used for the synthesis of polymer particles or latexes with specific size, shape, and composition, and is commonly employed in the production of polymer dispersions for various applications such as coatings, adhesives, and paints.	Better control over particle size and morphology. Improved product quality. Increased production efficiency.	Complexity of the process. Limited scope of applications. Risk of contamination.	(Jönsson et al., 2007; Xu et al., 2013a, b)
Graft copolymerization	It is a type of polymerization reaction where one or more monomers are polymerized in the presence of an already formed polymer backbone. The result is a copolymer with branches of one or more monomers attached to the main polymer chain. This type of copolymerization can be achieved through a variety of methods, including radiation-induced grafting, chemical grafting, and surface-initiated polymerization.	The main advantage of this method of making grafted copolymers is that the side chains can be made from off-the-shelf polymers with the desired properties.	The disadvantages are low condensation rate and small yields of graft copolymers due to difficulties in performing the reaction until the complete transformation of the reagents	(Abdollahi et al., 2018; Jain et al., 2017)

as fatty alcohol ether sulfate or alkyl ether sulfate (Fink, 2021).

SPs in WBDF are mainly used as viscosifiers to increase the viscosity and carrying capacity of the fluid (Huang et al., 2015). In addition to viscosity, SP can also provide filtration control, which is essential for preventing the loss of drilling fluids into the formation (Davoodi et al., 2022b; Dias et al., 2015). This is achieved by forming a thin, impermeable filter cake on the walls of the borehole and can also be formulated to provide shale inhibition, which is important in formations that are prone to swelling or disintegration (Imohiosen and Akintola, 2021). The SPs can coat the shale particles and prevent them from absorbing water, which can cause the formation to swell or break apart (Jain and Mahto, 2015). For instance, a zwitterionic copolymer through free-radical polymerization using acrylamide (AM), AMPS, diallyl dimethyl ammonium chloride (DMDAAC), and the betaine-type monomer vinyl-phenyl sulfonate (VPS), which they synthesized by mixing 1,3 propane sultone and 1-vinyl imidazole (MW$_\text{W}$: $5.8 \cdot 10^6$ Da, MW$_\text{N}$: $2.56 \cdot 10^6$ Da, and PDI: 2.27). The composition of the fluid consists of 4.0 wt% of bentonite for controlling rheology, 0.24 wt% of sodium carbonate as a calcium ion inhibitor, and 1.5 wt% of a mixture containing the novel copolymer for controlling fluid loss.

VPS, the primary constituent of the copolymer, contains an aromatic heterocyclic imidazole ring linked with propyl-sulfonic acid and hydrophobic vinyl end groups. The sulfonic acid group provides hydrolytic stability in high salt contamination, while the cationic quaternary ammonium group improves the stability of bentonite-based fluid by being absorbed on negatively charged bentonite surfaces at high temperature, thus preventing coalescence and enhancing hydration dispersion of clay particles. The copolymer also has multiple adsorptions points that aid in forming a networked structure and controlling filtration loss and salt tolerance. The copolymer's effectiveness in controlling rheology and filtration loss was evaluated under high-temperature and high-salinity conditions using freshwater, saturated brine, and composite brine-based fluid. The copolymer was observed to maintain stable rheology up to 200 °C and control filtration loss more effectively than other common commercial filtration control additives (Ma et al., 2017).

SPs for WBDF are expected to have specific traits such as solubility in water, the ability to withstand high pressure and high-temperature conditions without degrading, ease of thickening, rheology modification, controlling fluid loss, and resistance to salt, and reactive shale. These traits can be found in a single copolymer or a blend of several polymers/copolymers (Davoodi et al., 2022b).

A new WBDF system called high-performance water-based fluid (HPWBF) that aims to improve drilling performance compared to conventional WBDF and emulsion-based fluid systems. The HPWBF has been field tested on difficult onshore, deepwater, and continental shelf wells that would typically require the use of OBDF or SBDFs (Dye et al., 2006). The HPWBF utilizes an innovative technique that involves both mechanical and chemical methods to create a selective membrane. A micronized and flexible sealing polymer is used to mechanically connect shale pore throats and microfractures. This polymer maintains a stable size distribution even when exposed to high salt concentrations. Its flexible nature allows it to mold itself to the shape of fractures, improving its ability to plug gaps. Additionally, the use of SP PHPA polymer helps to prevent the disintegration of cuttings when they are circulated from the annulus. These anionic molecules attach to positive sites on the cuttings and form a protective layer around them, minimizing disintegration and making them easier to remove through the solids control equipment available at the drilling rig (Dye et al., 2006).

4.1.2. SP in oil-based fluid

In OBDF, SPs are used for a variety of functions, including viscosity control, filtration control, and shale inhibition (Apaleke et al., 2012; Li et al., 2016c). The formulation and composition of OBDF can vary depending on the specific drilling conditions and requirements, However some general characteristics are:

- **Base Oil** such as diesel oil, mineral oil, synthetic paraffin (mineral oil), and low aromatic mineral oil.
- **Weighting Agents** which include barite, calcium carbonate, and hematite.
- **Emulsifiers** including non-ionic surfactants and fatty acid.
- **Wetting agents** such as barite. Rheology modifiers like organophilic clays and polymers.
- **Stabilizers**, including biocides and pH control agents.

Other additives may be added to the fluid to improve its performance or address specific drilling challenges. Examples include lubricants, corrosion inhibitors, and shale inhibitors (Fink, 2021).

The selection and use of SPs in OBDF can be more complex than in WBDF for two main reasons. 1) the compatibility of the polymers with the non-aqueous base fluid is crucial in OBDFs. The polymer must be soluble in the base fluid and not adversely affect its performance. This can limit the choice of polymers available for use in OBDFs. 2) the temperature and pressure conditions encountered in OBDFs can affect the performance of SPs.

SPs that are soluble in water are hydrophilic, meaning they have an affinity for water molecules (Apaleke et al., 2012; Zhong et al., 2019). These polymers typically have polar functional groups, such as hydroxyl ($-OH$) or amine ($-NH_2$) groups, which can interact with water molecules through hydrogen bonding. On the other hand, OBDFs are non-aqueous fluids composed of hydrophobic liquids, such as mineral oil or synthetic hydrocarbons. SPs that are soluble in OBDF are typically hydrophobic, meaning they have an affinity for hydrophobic molecules, such as oil (Balaga and Kulkarni, 2022; Zhong et al., 2019).

As an example, the composition in OBDF was compared with that of WBDF in the presence of SP. For this purpose the composition of the drilling fluid consisted of 90% white oil as the continuous phase and 10% calcium chloride solution as the dispersed phase. To control the rheology, 3% organic clay and 1% of a product made from poly acid and polyethene polyamine were used. The primary emulsifier was composed of 3% amidoamine, while the secondary emulsifier consisted of 3% fatty acid. A wetting agent was included at 2% concentration, and an emulsifier activator at 2% calcium oxide was also used (Zhong et al., 2019). To this composition the swellable polymer mesosphere-based MMA, BA, and lauryl methacrylate was utilized as fluid loss controller agent (Zhong et al., 2019). The copolymer that was produced displayed the ability to swell and absorb base oil, resulting in deformation and compression under high pressure and shear stress. This led to the formation of a close-packed filter cake with other fine solids, which was effective in reducing filtration loss and minimizing solid invasion. When the concentration of the synthesized copolymer was less than 1.5 w/v%, it did not have any effect on the rheology, but it still managed to reduce HPHT filtration loss volume by 79% at 200 °C (Zhong et al., 2019).

In case of low toxic drilling fluids, a non-aqueous system-based paraffin was utilized with a modified starch (Dias et al., 2015). The study aimed to assess the feasibility of using modified starch derivatives with vinyl esters from fatty acids as additives for controlling filtrate in invert-emulsion (W/O) drilling fluids. The findings showed that none of the tested formulations exhibited flocculation or progressive gelification. The emulsions produced by the additives with molar ratios of 2:1 and 3:1 of vinyl ester/starch

were more stable and had lower filtrate volumes compared to the standard commercial fluid, even after aging. The incorporation of the modified starch resulted in a significant reduction in the filtrate volume, with reductions ranging from 40% to 75% and 61%–76% for non-aged and aged systems formulated with 8.5 kg/m³ of filtrate controller, and 43%–85% and 62%–83% for non-aged and aged systems formulated with 14.2 kg/m³ of filtrate controller (Dias et al., 2015).

4.1.3. SP in synthetic-based fluid

As advantages of using SBDF is that they are less damaging to the environment than OBDF, and they have better chemical stability than WBDFs. SBDFs can be used in high-temperature and high-pressure drilling environments where WBDF may not be suitable. SBDFs overcome the drawbacks of conventional WBDFs by impeding the clays from absorbing water when the formation is exposed to synthetic liquid. Unlike OBDFs, SBDFs solve the challenge of disposing of OBDF drill cuttings by allowing them to be discharged into the marine environment. Additionally, SBDFs exhibit lower gas solubility than OBDFs, which makes it easier to detect kicks (Zevallos et al., 1996).

There are four main classifications of SBDFs: synthetic hydrocarbons, ethers, esters, and acetals. Of these, ester-based drilling fluids are highly regarded for their superior environmental performance and complete biodegradability (Dardir et al., 2014). SPs are also used in SBDF for similar functions as in WBDF and OBDF, such as viscosity control, filtration control, and shale inhibition. SBDF are typically composed of a synthetic hydrocarbon liquid as the continuous phase and water as the dispersed phase. For instance, the associative polymer (AP) based dimer acid, triethylenetetramine and polyoxyethylene lauramine was developed and utilized in SBDF. The emulsions formulation of the fluid containing water and oil (C14 linear alpha olefin) in ratios of 70:30 and 80:20 were prepared. Auxiliary treatment agents, such as 2 wt% organic clay, 1.5 wt% wetting agent, and 1.5 wt% CaO, were added sequentially, followed by the addition of 35 wt% and 85 wt% barite to create SBDF with two different densities. To evaluate the impact of AP on the SBDF, 2.0 wt% polymers were added to the SBDFs (Han et al., 2014). Moreover, the addition of AP at a normal dosage of 2.0 wt% does not significantly alter the rheology of the emulsion, as the yield point (YP) and gel strength (Gel) values remain low (<2). However, when organic clay is added, the YP and Gel values increase significantly. Without the addition of APs, the YP and Gel values decreased by over 50% from 4 to 65 °C. In contrast, with the addition of 2.0 wt% APs, the YP and Gel values only decreased by less than 15%. The reason for changes in the rheology of drilling fluid is primarily due to the disordered state that is observed when the molecular chains of AP are distributed within clay layers. This distribution can lead to a disorganized state, which can affect the rheology of the drilling fluid (Han et al., 2014). These results demonstrated that AP can be affected by the others additives utilized in formulating the drilling fluids. Also, the interaction of the SPs with the base fluid is different from that in WBDF, as the SPs are required to be compatible with the base fluid and maintain their properties over a wide range of temperatures and pressures. Therefore, the mechanism involved may depend on the specific combinations of drilling fluid components and the type of drilling fluid and SP used (Dye et al., 2006). However, the SPs are not easy to classify but in general terms can be classified into three categories (Fig. 7), which are based on:

1. chemical ingredients (homopolymers such as cross-linked polystyrene microspheres (Wang et al., 2011), and copolymers (or terpolymer if containing three types of repeated units) such as carboxymethyl-graft-polyacrylamide copolymer (Jain et al., 2017));
2. type of reaction, such as addition polymerization used to generate polyacrylamide/clay composite (Jain and Mahto, 2015), and condensation polymerization used to generate β-cyclodextrin polymer microspheres (Zhong et al., 2020a); and,
3. reaction to heating, such as thermoplastics forming polypropylene composites (Luz et al., 2008), and thermosets forming shape memory polymers (blended smart polymer) used for lost circulation (Li et al., 2021)) (see Fig. 7).

To evaluate the SP performance in drilling fluids, rheological analysis helps to determine the fluid's behavior and its flow characteristics under different shear rates and temperatures. Filtration analysis determines the ability of the drilling fluid to maintain the desired properties of the drilled formation while removing the drill cuttings and to evaluate the fluid loss performance of SP. Additionally, chemical analysis is used to determine the chemical composition of the drilling fluid and to identify any potential incompatibility issues with SPs (Davoodi et al., 2022b; Fink, 2021; Li et al., 2015; Morariu et al., 2022; Yahya et al., 2022). These analyses demonstrate the fundamental features with which to establish whether an SP is applicable for use in drilling fluids (Zhong et al., 2019).

Incompatibility between SPs and other drilling fluid additives can lead to a loss of performance, such as reduced viscosity or increased fluid loss. To address this, the following solutions can be used:

(i) Compatibility testing can help to identify any incompatibility issues between different additives.
(ii) Adjusting the formulation of the drilling fluid can help to address incompatibility issues. For example, reducing the concentration of an incompatible additive or replacing it with a compatible one can help to improve performance.
(iii) A buffer system can be used to maintain a stable pH level in the drilling fluid, which can help to reduce incompatibility issues between different additives.
(iv) Diluting the drilling fluid with water or another compatible fluid can help to reduce the concentration of incompatible additives and improve performance (Abbas et al., 2021; Aboulrous et al., 2022; Davoodi et al., 2022b; Gautam et al., 2022; M-I SWACO, 2009).

One successful example of natural polymers in drilling fluids is the use of xanthan gum. Xanthan gum is a water-soluble polymer that has excellent stability and rheological properties, making it suitable for use in a wide range of drilling conditions (Akpan et al., 2020). Another successful example is the use of SP, such as sulfonated styrene maleic anhydride (SSMA) copolymer with a low molecular weight (MW: 1000–5000 Da), which has superior filtration control and compatibility with other drilling fluid additives even at high temperatures. The high charge density provided by the sulfonate functional groups in SSMA copolymer allows it to remain absorbed on the edges of clay platelets even at high temperatures, which helps to keep the fluid deflocculated. The thermal stability of the copolymer is enhanced by the presence of a five-member heterocyclic furan ring in maleic anhydride and a benzene ring in the sodium p-styrenesulfonate (SSS) monomer. A study using thermogravimetric analysis has revealed that the copolymer's thermal decomposition temperature is greater than 400 °C (Chesser and Enright, 1980).

Table 3 provides a summary of the most used SP, together with the functions they are deployed to achieve as additives to drilling fluids. It reveals that each SPs provides different functions. For

instance, PHPA is commonly used in drilling fluids as a viscosifier, fluid loss control agent, and shale inhibitor. It is highly effective in improving the rheological properties of drilling fluids, such as increasing their viscosity and improving their fluid loss characteristics (Wang J. et al., 2022). Overall, SPs play a vital role in improving the performance of drilling fluids and achieving various drilling objectives. Their effectiveness depends on their concentration, molecular weight, and the specific drilling conditions in which they are used.

Table 4 describes the properties of the most common applicable SPs used in drilling fluids based on acrylate derivatives (Davoodi et al., 2022b). Acrylic acid and its derivatives in WBDF, and in some cases OBDF, can be utilized in complex wells or high temperature deep wells (Ge et al., 2012). Anionic acrylate and nonionic acrylamide monomer, an SP also referred to as PHPA, has a very high adsorption capacity on clay surfaces. It is one of the most applicable SPs for drilling fluids applications (Davoodi et al., 2022b; Gautam et al., 2022; M-I SWACO, 2009) due to its high adsorption capacity on clay surfaces, combined with good lubrication and anti-flocculation characteristics. In addition, the dense filter cake formed on the borehole walls in the presence of the reagent contributes to the stability of the borehole, preventing caving and collapse (Davoodi et al., 2022b; Jiang et al., 2015). However, its higher molecular weight also provides it with an equilibrium thickness of its adsorption layers. These adsorption characteristics allow it to be used in drilling fluids as a highly effective colloidal phase flocculant (Davoodi et al., 2022b).

Subsections 4.2–4.6 describe the main types of SPs and their application in different types of drilling fluids.

4.2. SPs deployed to improve rheology

Key rheological characteristics of drilling fluids are viscosity and gel strength. These characteristics determine a drilling fluid's abilities in bottomhole cleaning, cooling the bottom-hole assembly, cuttings carrying capacity and hydraulic resistance throughout the wellbore fluid circulation system (Agwu et al., 2021a). The main rheological properties of the drilling fluid include plastic viscosity (PV) and apparent viscosity (AV), static and dynamic shear stress, YP, alkalinity of the filtrate, content of sand, mineral salts and hydrogen ions (Agwu et al., 2021a; Zhang et al., 2020). These rheological properties can be controlled by using modified natural polymers and SP to adjust fluidity at different levels of shear stress. Hence, they play a major role in optimizing drilling performance. Polymers are mainly required to control filtration and changes viscosity (Davoodi et al., 2019).

Controlling fluid loss is a critical requirement in drilling operations as it can help reduce the amount of drilling fluid lost to the formation, which in turn helps maintain wellbore stability and prevent formation damage. Polymers such as starch and poly-anionic cellulose work by forming a filter cake on the wellbore surface, which helps to reduce fluid loss (Konstantin et al., 2018). Additionally, polymers can enhance several rheological properties, particularly PV, AV, YP, and gel strength, of drilling fluids through their ability to interact with the fluid molecules and form a network structure. When a polymer is added to a drilling fluid, it can increase the concentration of long-chain molecules in the fluid, which leads to increased viscosity and other rheological properties. The specific mechanism by which polymers enhance rheological properties depends on the type of polymer and the drilling fluid composition (Davoodi et al., 2019; Kariman Moghaddam et al., 2022).

However, along with natural and modified polymers, SP are widely used in both water- and hydrocarbon-based drilling fluids. They are used as clay and shale inhibitors (by encapsulation),

drilling-fluid thickeners, flocculants, water reducing agents and lubricants (Fink, 2021). For instance, the addition of a novel graft copolymer (CSGO) to a Na-bentonite dispersion increased viscosity and decreased filtration volume by aggregating bentonite particles and producing a polymer film, as evidenced by SEM and particle size distributions measurements (Lei et al., 2021b). The effects of CSGO on filtration and rheological characteristics are concentration dependent. The greater the concentration, the greater the viscosity and the lower the filtration volume. Because of the enhanced inter-particle electrostatic repulsion, particle aggregations were shown to disassemble in the opposite direction at 3 wt% CSGO concentration (Lei et al., 2021b). Another SP, poly(SSS/AM/AMPS), has been synthesized through inverse emulsion polymerization. It was synthesized from sodium p-styrenesulfonate (SSS)/AM/AMPS. Poly(SSS/AM/AMPS) impacts rheology by improving a drilling fluid's AV, PV, and gel rate as SP concentrations increase up to 1.2 wt%. Furthermore, the values of YP and YP/PV ratio were shown to satisfy the API standard values. Abundant non-ionic amide and sulfonic acid molecular groups caused the adsorption action of poly(SSS/AM/AMPS) to be strong, and clay particles to be well dispersed in the drilling fluids tested. As a result, the rheological characteristics of the drilling fluid systems were enhanced by the addition of poly(SSS/AM/AMPS) (Fig. 8) (Huo et al., 2018).

This indicates that the colloidal stability of the fluid was excellent. The micro-structure analysis showed that the copolymer helped reduce filtration loss by physically plugging the pores. The copolymer contains the surface-active monomer SSS, which has a benzene sulfonate unit that makes it effective as a salt-resistant and high-temperature deflocculant. The thermal stability of SSS is attributed to the resonance stabilization of its benzene sulfonate unit (Huo et al., 2018). However, the performance of the copolymer-based drilling fluid was not significantly affected by exposure to high temperatures of 160 °C, as seen by the stable rheological and filtration parameters (Huo et al., 2018).

SPs influences on drilling fluid viscosity can be explained partly in terms of interactions between SP chain length and fluid properties: as the SP chain length increases so does the fluid viscosity. Also, water adsorption, effectively increases the size of the SP molecules thereby acting to increase viscosity. Moreover, interactions between SP molecules and other drilling-fluid solids tend to create an interconnected network acting to increase fluid viscosity (Davoodi et al., 2022b). For example, reactive clay drilling cuttings and high molecular weight polyacrylamides enter into crosslinking reactions with SP chains (Gautam et al., 2022).

Unsatisfactory rheological properties can lead to such serious complications as hole plugging, bottomhole zone plugging, reduced mechanical drilling speed, stuck drill string, wellbore wall and core column washout and shale hollowing (Davoodi et al., 2022b). Salt contamination plays a very important role in determining SP performance and can lead to a rapid degeneration of rheological properties and reduced tolerance to temperature of SP used in drilling fluids. Salt-contamination effects can vary depending on the specific polymer and the conditions under which it is used (Mao et al., 2021). Chlorides and other salts inhibit polymer unfolding that occurs when a soluble polymer is added to water. Instead of unfolding and expanding, the polymer takes on a compact spherical shape and the solubility of the polymer is reduced. This occurs as a result of the polymer molecules "fighting" for water. Salt limits the amount of free water in which the polymer can hydrate and expand. As salinity increases, the amount of water attached to the polymer decreases and the viscosity does not increase as dramatically. When salt is added to a freshwater drilling fluid with fully expanded polymers, a jump in viscosity is usually observed. As the salt dissolves, it takes up water from the polymers and inhibits fluid loses stability for a period of time; this is when the viscosity

increases. The polymers intertwine with drill cuttings and other polymers, at the same time they decrease in size and return to their original spherical shape. Once in the spherical shape, viscosity is greatly reduced (Davoodi et al., 2022b).

Normally the performance of polymers in a salty environment is not good, but this problem can be solved by the utilizing monomers in SP synthesis that are able to overcome the influence of salts (Sun et al., 2022). For instance, the monomers AM, SSS, maleic anhydride (MA), and lauryl methacrylate (LMA) were used to create a SP called hydrophobic ASML (Sun et al., 2022). ASML with 30% of NaCl showed a high performance of rheological properties because the hydrophobic association units in ASML solutions form various spatial bridge structures that display excellent viscosity-enhancing effects. These hydrophobic moieties are also responsible for the shear thinning behavior of ASML solutions (Sun et al., 2022).

AM, AMPS, DMDAAC, and SSS monomers were utilized to obtain the copolymer called AADS (Huang et al., 2019). At 240 °C and 30 wt % NaCl, AADS showed a high performance with respect to salt resistance and the rheological properties were stable due to the presence of carboxylic acid and sulfonic acid salts (Huang et al., 2019). The zwitterionic copolymer called DCS was synthesized through radical copolymerization by utilizing the N, N-dimethyl acrylamide, 1-(2-carboxyethyl)-3-vinyl imidazolium chloride, sulfobetaine vinyl imidazole monomers for use as a fluid-loss reducer (Li et al., 2023). In the presence of NaCl, the addition of 2% DCS to different concentrations of NaCl showed that the transmittance became gradually cleaner. This phenomenon can be attributed to the anionic groups which mainly are sulfonate and carboxylate and cationic groups which is imidazolium cation in the DCS chain, or between different DCS chains being electrostatically connected in fresh water. This causes the DCS chain to curl and entangle, which reduces the DCS copolymer's solubility (Fig. 9(a)). However, when NaCl electrolyte was added, the sodium ions and chloride ions disrupted the "internal salt link" established by the anionic and cationic groups, which in turn encouraged the expansion of the polymer chain and enhanced the solubility of DCS in saline water. Furthermore, when shear rate increased, the viscosity of the DCS solution was reduced (Fig. 9(b)), demonstrating superior shear-thinning behavior, which was advantageous for breaking rock at a high shear rate and conveying drill cuttings at a low shear rate (Li et al., 2023).

Lignosulfonate combined with acrylamide-graft copolymer was utilized in drill fluids for its strong resistance to salinity and high temperatures due to its chemical structure (Abdollahi et al., 2018). The results demonstrated that at concentrations of 2.45–3.50 g per 350 mL water, the grafted copolymer enhanced the rheological behavior of drilling fluid and reduced fluid losses. It also controlled pH values in the temperature range of 25.5–121.1 °C (Abdollahi et al., 2018).

Most SP can provide a high-performance rheological property in salt-contamination condition. However, it highly depends on the utilized monomers, for instance, the DCS zwitterionic copolymer (Li et al., 2023) and hydrophobic ASML (Sun et al., 2022) showed a high performance of viscosity in the presence of NaCl even at high concentrations (up to 30%) but in the presence of CaCl$_2$ showed poor calcium contamination tolerance. This may be due to the greater impact of Ca^{2+} on the extent of polymer molecular coiling. Ca^{2+} with a greater valence number than Na$^+$ is better able to balance the negative charge on the polymer surface than Na$^+$. however, further research is required to establish whether hydrophobic monomers can achieve high salt resistance (Davoodi et al., 2022b).

Table 5 describes recent research assessing the deployment of SPs to improve drilling fluid rheology. Amphoteric polymer (PEX) showed the highest tolerance to temperature (up to 220 °C) due to

the presence of inflexible monomers in PEX and their contribution to PEX's tangled molecular framework (Adnan Hamad et al., 2020).

4.3. SPs deployed to improve fluid filtration

Filtration in drilling fluids is the process of removing solids and other impurities from the fluids as they flow through the formation being drilled. The filtration mechanism in drilling fluids is primarily governed by the pore size and permeability of the formation, the particle size and distribution of the solids in the fluid, and other properties of the drilling fluid, such as its viscosity and filtration control agents. The filtration process in drilling fluids typically involves three stages (Ali et al., 2022; Osipov et al., 2022): (i) **Filter cake formation**: As the drilling fluid flows through the formation, the solids in the fluid begin to deposit on the surface of the formation, forming a thin layer of solids, called the filter cake. The filter cake acts as a physical barrier that prevents further solids from passing through it into the formation (Fig. 10). (ii) **Filter cake consolidation**: Over time, the filter cake becomes denser and more consolidated, reducing its permeability and further preventing solids from passing through it. (iii) **Fluid loss**: As the drilling fluid is filtered through the formation, some of the fluid is lost to the formation. This loss of fluid can lead to changes in the properties of the drilling fluid, such as an increase in viscosity and changes in its solids content (Ali et al., 2022; Balaga and Kulkarni, 2022; Osipov et al., 2022).

To control the filtration mechanism in drilling fluids, various additives are used, including filtration control agents, which help to reduce the permeability of the filter cake and improve the retention of solids in the fluid. These additives can be bentonite, polymers, starches, or thinners. Polymers were some of the earliest and most commonly used drilling fluid additives, and are still used today for a variety of purposes such as controlling fluid loss and viscosity, as well as functioning as flocculants and surfactants due to their reactive groups and structural properties (Ali et al., 2022). SPs are mainly used in drilling fluids to control filtration and viscosity. For filtration control purposes, SPs are usually added to bentonite (Davoodi et al., 2021). SPs used for this purpose are PHPA (Kuma et al., 2020), polyanionic cellulose (Li et al., 2016), and sodium 4-styrenesulfonate (Chu and Lin, 2019). The ASML based Acrylamide, sodium p-styrenesulfonate, maleic anhydride, maleic anhydride and lauryl methacrylate was synthesized applying the emulsion polymerization method. This combined SSS, AM, lauryl methacrylate and maleic anhydride monomers (Sun et al., 2022). Fig. 11 shows diagrammatically the role of ASML in improving the performances of drilling fluids under extreme salinity and temperature conditions.

Hydrophobic side chains and hydrophilic groups associated with the ASML copolymer allow it to bind to the surface of bentonite and forming hydrophobic structures in the aqueous solutions. The presence of such structures increase the hydrodynamic radii, causing fluid viscosity to increase. With introduction of salt and temperature aging treatments, NaCl increases water polarity and promotes the hydrophobic interaction of ASML, resulting in stable rheology. In addition, bentonite particles become dispersed in the WBDF. This reduces filtration and maintains borehole stability, thereby improving wellbore integrity. Moreover, at 200 °C and 30% NaCl, the fluid loss recorded for ASML fluids was only 5 mL, representing about 95% less than the fluid loss recorded for drilling fluid that contained carboxymethylcellulose (Sun et al., 2022).

Synthetic acrylamide-styrene copolymer (SBASC) has been used to improve fluid filtration of drilling fluid (Davoodi et al., 2019). It was developed through inverse-emulsion polymerization, with the hydrophobic monomer, styrene, and hydrophilic monomer, acrylamide, were dissolved in organic solvent and in water, respectively.
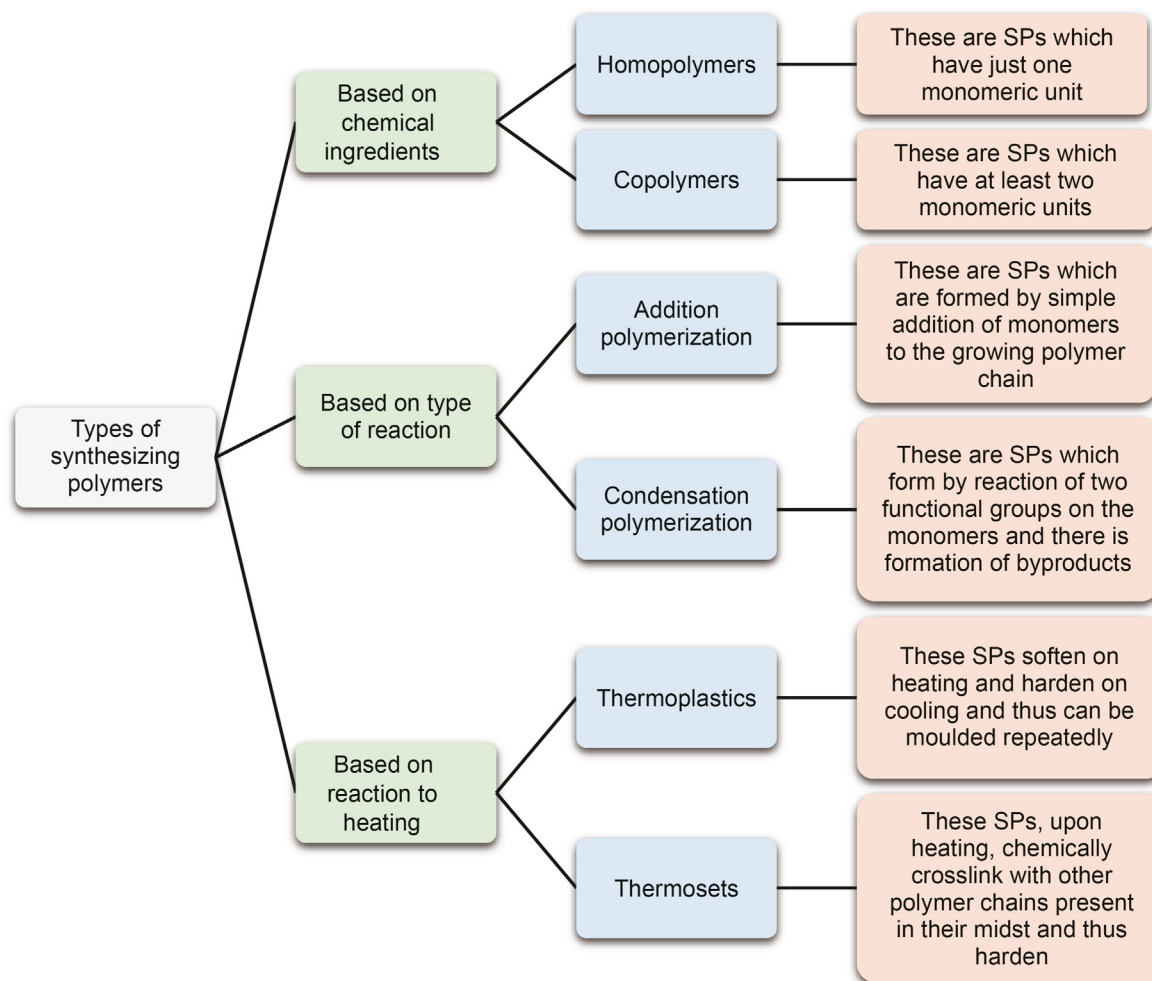
Fig. 7. Types of synthetic polymers.

The polymer reaction was carried out in a three-neck flask equipped with a mechanical stirrer, thermometer, and baffle to introduce nitrogen. 3 g of SBASC added to the fluid decreased the LP-LT fluid loss volume by 66%. The decrease in volume of fluid loss was attributed to the adsorption of polymer chains on the surface of the dispersed solids. The long polymer chains adsorbed and located between the solid particles tend to clog the pores of the filter cake, resulting in a significant reduction in the permeability of the filter cake, thereby reducing liquid loss from the drilling fluid (Fig. 12). The results indicate that synthetic acrylamido-styrene copolymers can be usefully deployed as an impervious additive for use in WBDF. Moreover, synthetic acrylamido-styrene copolymers are superior to starch in terms of leachate volume reduction (Davoodi et al., 2019).

In OBDF in HPHT conditions, SP additives can also be effective. Swelling polymer microspheres (SPM), can be synthesized by suspension polymerization, involving a mixture of BA, and lauryl methacrylate, MMA (Zhong et al., 2019). Oil adsorption capacity measurements were used to describe the SPM's swelling characteristics. Following hot rolling (200 °C), an OBDF sample with 1 wt% SPM showed an 85% reduction in LTLP fluid loss and a 79% reduction in HTHP filtration loss in comparison with the base fluid. When the base fluid contained 1 wt% asphalt-containing additive, modified lignite and SPM, the LP-LT fluid loss was reduced by 2%, 24% and 53% respectively, and HTHP filtration loss was reduced by 42%, 54% and 65% after hot rolling at 180 °C (Zhong et al., 2019). SPM can

absorb base oil and swell significantly to increase its volume. Moreover, SPM advantageously deforms and compresses under pressure or shear stress because of its elastic and swellable nature. This makes it more effective, when packed with other fine solids, in creating a filter cake, advantageously and efficiently filling void spaces and decreasing the permeability of the created filter cake. That mechanism is responsible for low filtration loss and solids migration in the drilling fluids tested with SPM additives (Fig. 13) (Zhong et al., 2019).
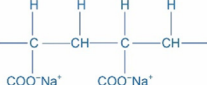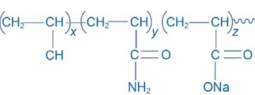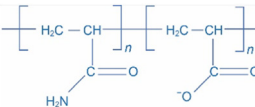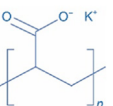
An oil-absorbent polymer (OAP) composed of MMA, BA, and hexadecyl methacrylate (HMA) was developed for use in OBDF (Zhong et al., 2018). The OAP particles formed had a spherical and porous structure, and were able to absorb white oil and diesel oil many times their own weight at temperatures between room temperature and 120 °C. Under downhole conditions, OAP particles were found to effectively reduce the FL_{HTHP} and improve the sealing ability of OBDFs (120 °C, 3.4 MPa). When used in isolation, OAP particles had limited capacity to seal fractures, but when used in combination with calcium carbonate particles, rubbers, and fibers, a synergistic effect was observed and fluid loss was effectively reduced. Over time, the volume of OAP in the OBDF increased, causing the viscosity of the fluid to increase and slowing down the rate of fluid loss. Swollen and deformable OAP particles were able to enter small openings of various shapes and conform to their size and shape (Zhong et al., 2018).

Table 3
Description of the most widely used SPs and their function in drilling fluids.

Name	Viscosity	Fluid Loss Control	Flocculation/Deflocculation (Thinning)	Shale Inhibition	Lubricity	Ref.
Polyacrylates	+	+	+	−	−	M-I SWACO (2009)
Sodium polyacrylate	+	+	+	−	−	M-I SWACO (2009)
Partially hydrolyzed polyacrylamide	+	+	+	+	+	Wang H. et al. (2022)
Styrene butadiene latexesin in oil based fluids	+	+	−	−	+	Li et al. (2020)
Sodium acrylate/acrylamide	−	+	−	+	−	Singh and Singhal (2013)

*+ = Polymer used (as one of its primary functions), *- = Polymer not used for that function.

Table 4
The properties of commonly used SPs in drilling fluids based on acrylate derivatives.

Type of synthetic polymer/Ref.	Type of chemical structure	Chemical formula/ Degradation temperature	Field of application	Advantages	Disadvantages
Sodium polyacrylate (M-I SWACO, 2009)		$(C_3H_3NaO_2)_n/$ >260 °C (M-I SWACO, 2009).	Low molecular weight sodium polyacrylate is designed to reduce water retention in fresh and saline WBDFs, to encapsulate drilled rock cuttings, and to strengthen wellbore walls.	Thermally stable, salt-resistant and not susceptible to bacterial decomposition, in contrast to natural polymers. It also displays rapid solubility. It is non-toxic with low environmental impacts.	Sodium polyacrylate can cause severe plugging and substantially increases the risk differentially stuck drill pipe.
Polyhydrolyzed (Na-HPAN) (Gu et al., 2019)		$(C_3H_3NaN)/90$ −150 °C (Li et al., 2019).	Mainly used for fluid-loss control.	Features: good thermal stability, controllable gel formation time, no cross-linking at room temperature, low surface viscosity, easy pumping, high gel strength, water scouring resistance and no special requirements for water-based preparations.	Mostly used for drilling coalbed methane reservoir. The polymer is temperature sensitive and intolerant of sub-surface contaminants.
Partially hydrolyzed polyacrylamide (PHPA) (M-I SWACO, 2009; Pinho De Aguiar et al., 2020)		$CONH_2[CH_2CH]_n/$ 149 °C (M-I SWACO, 2009; Pinho De Aguiar et al., 2020)	It is used as a shale inhibitor and solids encapsulant in fresh water, seawater, KCl, Sodium chloride (NaCl) based solutions. In addition to its shale inhibiting properties, it also provides encapsulation of drilled rock cuttings and viscosity control in fresh water-based systems.	It has a high molecular weight and a relatively long molecular structure, enabling it to bond to several sections along the wellbore. The result is a layer on the borehole walls that limits water penetration into the clay. It also acts as a selective flocculant, minimizing contents of the colloidal clay phase in solutions. PHPA improves lubricating properties of solutions, and is highly soluble in water.	It is not recommended to increase the pH of the solution more above 10.5 or the content of divalent cations (total hardness) above 500 mg/L. PHPA concentration must be increased to induce substantial changes in filtrate viscosity in saline environments.
Potassium polyacrylate (NPA or NH4-HPAN) Qi (2014)		$(C_3H_3KO_2)_n/$ 180 °C	The main applications of potassium polyacrylate are to inhibit lost circulation, and for fluid retention or pore blocking.	It has a low specific gravity. It is highly soluble in water, so it is used for preparing many types of drilling fluid solutions.	Potassium polyacrylate solution offers limited benefits for drilling fluids. Solution qualities need to be adjusted to suit specific applications. It can be used in solutions saturated with salts or with fresh water, and in solutions of different density and viscosity. In some circumstances it can cause formation damage.

*n - Degree of polymerization.

SP can also function effectively in SBDF. For instance, a polysaccharide was modified with hydrophobic properties by reacting carboxymethylcellulose with dodecylamine in water (Lima et al., 2022). This modified polysaccharide, known as CMC-DDA, was tested as an environmentally friendly additive in an olefin-based fluid. CMC-DDA had a larger hydrodynamic volume than CMC in water and became cloudy in water and saline solutions due to intermolecular interactions between hydrophobically modified polyelectrolytes. Despite being unstable in organic solvents, CMC-DDA was able to swell in pure olefin, indicating that the hydrophobic groups on the CMC backbone can interact with nonpolar solvents. The modified polymer was found to help stabilize emulsions in brine-in-oil drilling fluids, making it a useful additive. CMC-DDA also showed promising results as a rheological modifier for non-aqueous drilling fluids, reducing filtrate loss under high temperature and high pressure conditions (93 °C, 3.4 MPa). The CMC-DDA olefin-based fluid had the lowest filtrate value (2.6 mL) and no water was observed in any of the filtrates, indicating that the emulsions formed were stable (Lima et al., 2022).

Table 6 describes research studies testing SPs capable of positively adjusting drilling fluid filtration. Two SPs, β-CDPMs (β-cyclodextrin polymer microspheres) (Zhong et al., 2020a) and

copolymer AM/AMPS/DMDAAC/SSS (Huang et al., 2019) demonstrated their high performance in controlling filtration (Table 6). The creation of nano-carbon spheres and nanostructured composites in the β-CDPMs (β-cyclodextrin polymer microspheres) allows for the formation of a bridge that effectively reduces the volume of fluid loss (Zhong et al., 2020a). The copolymer AM/AMPS/DMDAAC/SSS molecules contain carboxyl groups, amide groups, sulfonic acid groups, and benzene rings, which impart strong polarity to the molecules. This results in the formation of a durable polarization layer that effectively blocks water molecules from filtering out of the drilling fluid (Huang et al., 2019).

4.4. SPs deployed to improve fluid lubricity

Lubricants play a critical role in drilling fluids by reducing friction and wear between the drill bit and the formation, protecting the drill bit from damage, and enhancing drilling efficiency (Kania et al., 2015). The main evaluation indicators for lubricants in drilling fluids are:

1. **Coefficient of friction (COF).** COF measures the friction between the drill bit and the formation. Lower COF indicates better lubricity;
2. **Wear scar diameter (WSD).** WSD measures the wear on the drill bit surface. Lower WSD indicates better wear protection;
3. **Hot rolling contact fatigue (HRCF).** HRCF measures the ability of the lubricant to prevent heat-induced wear on the drill bit. Higher HRCF indicates better heat resistance;
4. **Four-ball wear test (FBWT).** FBWT measures the wear protection of the lubricant. Lower wear scar diameter indicates better wear protection;
5. **Timken OK load test.** This test measures the load-carrying capacity of the lubricant. Higher OK load indicates better load-carrying capacity;
6. **Copper corrosion test.** This test measures the corrosiveness of the lubricant to copper. Lower copper corrosion rating indicates less corrosiveness;
7. **Emulsion stability test.** This test measures the ability of the lubricant to maintain stability in the presence of water. Higher emulsion stability indicates better water resistance;
8. **Thermal stability test:** This test measures the ability of the lubricant to maintain stability at high temperatures. Higher thermal stability indicates better heat resistance.

These evaluation indicators are important to ensure the lubricants in drilling fluids are effective in reducing friction and wear between the drill bit and the formation, protecting the drill bit from damage, and maintaining stability under different drilling conditions (Kania et al., 2015; Ma et al., 2021b; Zhao et al., 2022). Furthermore, good lubrication properties of drilling fluids increase bit life, reduce torque and possibly reduce the risk of drill-string differential sticking. Difficulties due to high torque forces are a particular problem in inclined and horizontal well sections with convoluted wellbore trajectories. In such conditions, the drill string tends to rest, due to gravity, on the bottom wall of the wellbore and has a large contact area with the formation and/or the casing. Under these conditions, the use of a lubricant additive can provide significant benefits, provided other drilling fluid properties are optimal and good drilling techniques are employed (Al-Shargabi et al., 2022a; Kania et al., 2015; Zheng et al., 2021).

On the other hand, the choice of lubricant additives may be limited by environmental and economic considerations, as well as additive compatibility with base drilling fluids. If experience in drilling similar wells does not allow a particular choice to be made, certain SP can be deployed to improve drilling efficiency and avoid

problems while drilling, such as inhibiting stuck pipe and improving hole cleaning. The SP provides similar functional benefits as lubricant additives (Al-Muhailan et al., 2014).

The mechanisms of SP lubricants in drilling fluids are mainly related to the formation of a protective layer between the drill bit and the formation. SPs are long-chain molecules with a high molecular weight, which makes them excellent lubricants due to their ability to reduce friction and wear. The mechanism of action of SP lubricants in drilling fluids involves adsorption onto the surface of the drill bit and the formation. This adsorption creates a lubricating film that reduces the frictional forces between the drill bit and the formation. As the drill bit rotates, the lubricant is sheared, forming a layer that continuously protects the drill bit from wear (Al-Shargabi et al., 2022a; Kania et al., 2015; Ma et al., 2021b; Zhao et al., 2022; Zheng et al., 2021).

In addition to reducing friction and wear, SP lubricants in drilling fluids can also enhance the stability of the drilling fluid by reducing the aggregation of particles in the fluid. SPs are also able to withstand high temperatures and pressures, making them suitable for use in HPHT drilling applications. Overall, the use of SP lubricants in drilling fluids improves drilling efficiency by reducing friction and wear, protecting the drill bit from damage, and enhancing the stability of the drilling fluid (Al-Shargabi et al., 2022a; Kania et al., 2015; Zheng et al., 2021).

Some SPs have been tested in HP conditions for mitigating differential-sticking-related problems by acting to minimize pore-pressure transfers (Mirabbasi et al., 2022). High differential pressures resulting in wellbore tightness, casing failure, induced losses and differential stuck pipe contribute to significant non-productive time in many drilling operations. In an example well, the presence of HP salt zone situated beneath a problematic interval, and the use of a casing configuration involving seven strings, eliminated the possibility of isolating zones with additional casing (Al-Muhailan et al., 2014). Traditionally, petroleum-based fluids containing various sizes of calcium carbonate have been used to reduce fluid intrusion, but without much success. The borehole formation was an extremely permeable sandstone/shale sequence formation (A1) that exists below approximately 2743.2 m in deep wells in Kuwait (Fig. 14), and is drilled in a 16-inch hole section in deep wells. The minimum pore pressure above this reservoir is 1042.49 kg/m³ of equivalent drilling-fluid weight, but the required drilling-fluid weight at the outlet of this section exceeds 2156.88 kg/m³.

The high pressure drop over the porous sandstone creates optimum conditions for differential pipe bridging. Frequent pipe sticking accidents in this formation resulted in significant rig downtime and sometimes the loss of the entire 16-inch section, leading to sidetracking. In the troubled shale-sand sequence in the 16-inch section of two deep Kuwait wells, a special SP (not specifically identified) combined with graphite and marble improved pore bridging and reduced pore pressure transfer, increasing wellbore stability. Concentrations of 10-μm and 50-μm marble at 7 and 8 pounds per barrel, respectively, together with 3 pounds per barrel of graphite and the specialized SP, were effective in overcoming the problems associated with drilling the A1 sand-shale sequence. Overpressure exceeding 24.13 MPa was effectively controlled without incidents of differential sticking (Al-Muhailan et al., 2014). However, using graphite/or nanographene with SPs such as PHPA can improve their lubricity (Aftab et al., 2017; Agwu et al., 2021b).

Applying potassium persulfate as an initiator, a novel polymer latex, called SDNL, was created via emulsion polymerizing (Xu et al., 2017a, b). Polymerization was conducted in a four-necked flask that was fitted with a mechanical stirrer, reflux condenser, thermometer, and feed inlet tube. By introducing 2.0 w/v % of SDNL to the drilling fluid at the ratio of lubrication reduced by 64.4%,
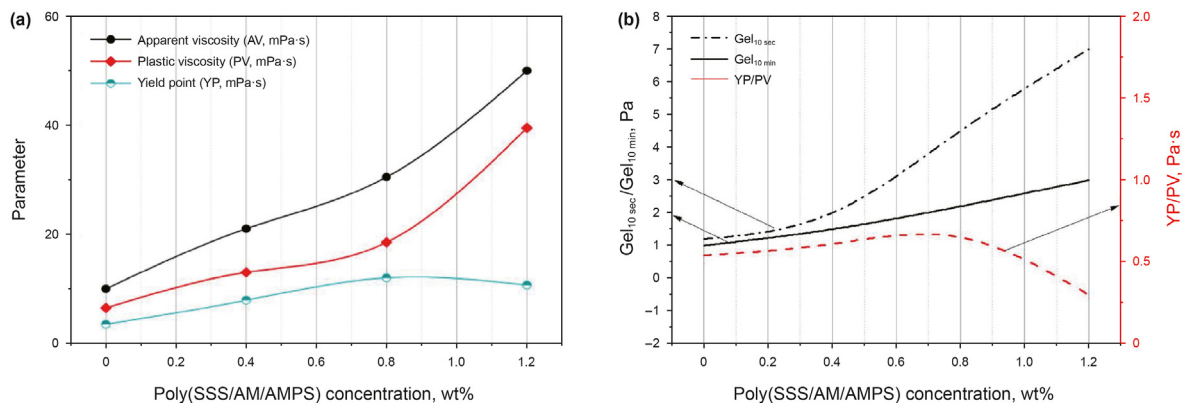
Fig. 8. Effects of synthetic poly(sodium p-styrenesulfonate (SSS)/acrylamide (AM)/2-acrylamido-2-methy-l-propanesulfonic acid (AMPS)) polymer on rheological parameters. ((**a**): AV, PV, YP, (**b**): $Gel_{10 \, min}$, $Gel_{10 \, sec}$ and YP/PV). Reproduced from Elsevier (Huo et al., 2018).

demonstrating that SDNL has strong lubricating properties. SDNL's lubrication mechanisms vary from that of conventional lubricants (Fig. 15), as SDNL relies on micro "rolling" and "film creation." The tiny NPs have a spherical form and may easily roll between the friction pairs. They function essentially as "roller bearings" converting sliding friction to rolling friction and therefore lowering torque. Furthermore, polymeric NP distributed throughout the drilling fluid may readily compress and deform during the friction process. This enables them to generate a dense and thin boundary lubricating layer on the friction surface, which aids in friction reduction and wear prevention. As a result, SDNL may effectively enhance the lubricating properties of drilling fluids in shale drilling, which can assist in minimizing torque and drag during drilling, and, consequently, minimizing tool wear (Xu et al., 2017a, b). The lubricating ability of the drilling fluids was evaluated by measuring their lubrication coefficients. In the pressure transmission test, when the drilling fluid containing 2.0 w/v% SDNL was exposed to the base fluid, the pore pressure remained stable at 1.8 MPa for 16,300 s, even when the temperature varied between room temperature and 150 °C. This suggests that a dense film was formed over the shale surface, indicating that SDNL is highly effective in plugging and delaying the transmission of pore pressure, which helps to maintain shale stability (Xu et al., 2017a, b).

Poly(vinyl alcohol) is another water-soluble SP which can be applied as an environmentally friendly lubricant additive in drilling fluids (Li et al., 2004; Zhang et al., 2021). It demonstrates good lubricating performance and shale inhibiting performance. This lubrication inhibitor can be used to prepare fresh water or brine or saturated brine drilling fluid, in which the lubrication inhibitor accounts for 1%−10% of the weight of the drilling fluid, preferably 1%−5% (Li et al., 2004).

SPs which contain AMPS can provide lubricity properties due to the hydrolytic stability in the monomer's structure (Gautam and Guria, 2020; Xian and Oren, 2012). For instance, A polyanionic cellulose was synthesized through radical polymerization utilizing AM, AMPS, and SSS monomers. Its lubrication characteristics were enhanced by the increased concentration of the AMPS monomer and acrylamide−AMPS, as well as by the AMPS−SSS interacting effect. The PAC graft also displays high filtration control performance and favorable rheological properties due to the presence of a hydrophobic polysaccharide backbone and hydrophilic carboxyl groups (Gautam and Guria, 2020). However, much more research and testing of the lubricity properties of other novel SPs is required. Available information suggests that itaconic acid, fatty acid esters, acrylamide, diallyl dimethyl ammonium chloride, and sulfonate also have beneficial properties with the potential to improve the lubricity properties of drilling fluids (Davoodi et al., 2022b; Gautam et al., 2022; Lin and Luo, 2015).

4.5. SPs deployed to improve hole cleaning capabilities

Ineffective wellbore cleaning especially for horizontal and
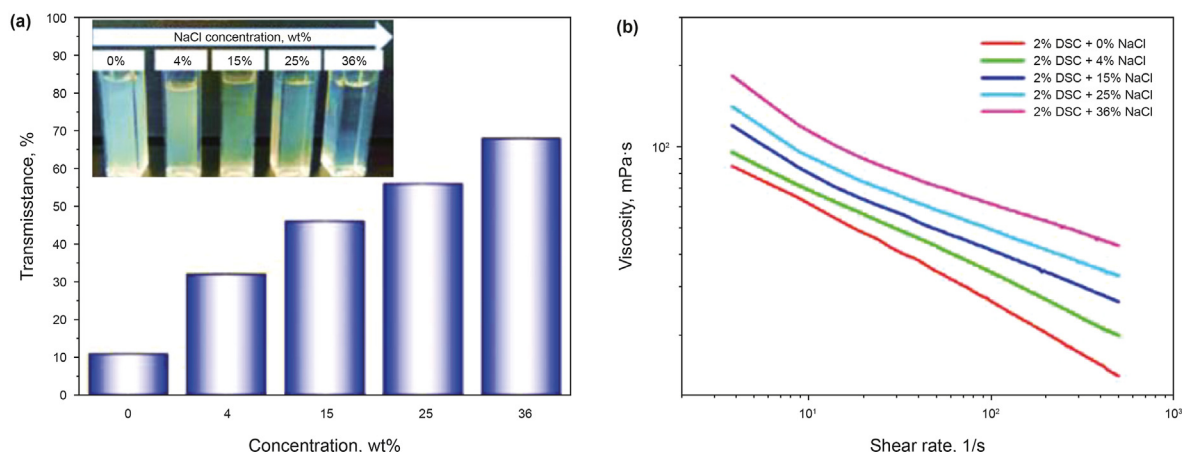
Fig. 9. DCS copolymer performance in different concentrations of NaCl solution: (**a**) The DCS copolymer transmittance, (**b**) The DCS copolymer viscosity curves in NaCl solutions. Reproduced from Elsevier (Li et al., 2023).

Table 5
Recent studies assessing deployments of SPs to improve drilling fluid rheology.
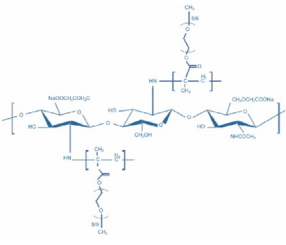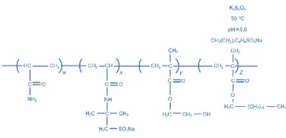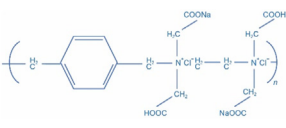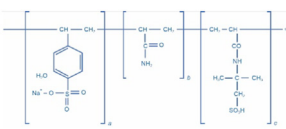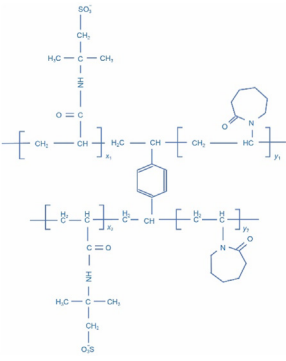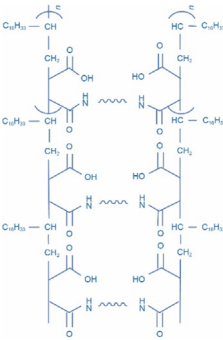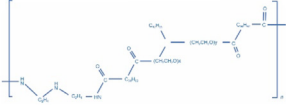
Type of SP	Chemical structure	Optimal concentration/The properties of the SP	Work condition	Finding	Ref.
Novel graft copolymer CSGO		1 wt% CSGO/N.G	Laboratory conditions (40—120 °C, 0.5—1.0 MPa)	Through free radical polymerization, a new graft copolymer (CSGO) was developed using carboxymethyl chitosan (CMCS). It contained a side chain of thermosensitive poly (oligo (ethylene glycol) methyl ether methacrylate) (POEGMA). The findings revealed that CSGO enhanced the filtration and rheological behaviors of Na-bentonite dispersion before and after hot rolling at a temperature of 120 °C. This was caused by the integrated impacts of aggregation and film-forming actions on the bentonite particles. More intriguingly, the thermally induced transition of hydrophilic-to-hydrophobic behavior resulted in the creation of partially desorbed polymer aggregates and association of Na-bentonite/CSGO flocculants. These contributed to lower filtration losses, a beneficial thermo-thickening rheology, and improved shale inhibition at high temperatures.	Lei et al. (2021b)
HAH-Polymer (The hydrophobically associating heteropolymer)		0.8 wt% HAH/N.G	Laboratory conditions (150 °C, 0.10 MPa)	In micellar media, free-radical polymerization was applied for creating HAH-Polymer, which contains sodium 2-acrylamido-2-methylpropanesulfonate, acrylamide, hydroxyethyl methacrylate, and lauryl methacrylate. The HAH-polymers can improve the rheological characteristics, thermal and salt stability of drilling fluid systems up to 150 °C (YP: 8.0 lb/100 ft^2, PV: 22.0 cP, and AV: 25.0 cP). This feature is ascribed to the presence of the large AMPS side chain's dimethyl and sulfomethyl groups, which offer steric hindrance to the amide functionality as well as hydrolytic, salt, and thermal stability in the HAH-Polymer−drilling fluid.	Nagre et al. (2021)
Amphoteric polymer (PEX)		1.2 wt% PEX/IDT: 245 °C, Type: amphoteric	Laboratory conditions (180—220 °C, 3.4 MPa)	The rheological properties increased significantly until they reached the optimum concentration (0.3 wt%). Above that concentration rheological properties decreased. This outcome was attributed to two substantial interactions related to PEX incorporation: the cationic and anionic groups provided excellent dispersion and increased particle friction, improving particle contact within the system. It appears that increased contact improves fluid rheology with increasing PEX content up to a concentration of 0.3 wt%).	Adnan Hamad et al. (2020)
Poly(sodium p-styrenesulfonate/acrylamide/2-acrylamido-2-methy-l-propanesulfonic acid) poly(SSS/AM/AMPS)		1.2 wt% Poly(SSS/AM/AMPS)/MW$_W$: 2.3 · 10^6 Da, MW$_N$: 1.4 · 10^6 Da, PDI: 1.653, IDT: >267.778 °C	Laboratory conditions (160 °C for 16 h, 0.69 MPa)	Substantial quantities of non-ionic amide and sulfonic acid molecular groups increase the adsorption effect of poly(SSS/AM/AMPS). Also clay particles were well distributed in the drilling fluid system, improving its rheology. Poly(SSS/AM/AMPS) is thermally stable, with drilling-fluid FL$_{API}$ pre- and post-thermal aging tests being 9.2 and 9.4 mL, respectively, at 1.2 wt% concentration.	Huo et al. (2018)
Novel viscosifier (SDKP)		1.0 wt% SDKP/MW$_W$: 8.9 · 10^6 Da, MW$_N$: 6.2 · 10^6 Da, PDI: 1.458, IDT: >330 °C	Laboratory conditions (180—220 °C, 3.4 MPa)	The copolymer viscosifier (SDKP) was synthesized by micellar radical polymerization from N-vinylcaprolactam (98%), (AMPS, 99%), sodium dodecyl sulfate, sodium hydroxide (NaOH), divinyl benzene (DVB) and acetone for bentonite-free water-based drilling. SDKP improved the rheological characteristics of bentonite-free fluids. Furthermore, the strong tolerance to salt and temperature in enhancing fluid rheological behaviors made SDKP more appealing at high temperatures ranging from 80 to 140 °C, even in systems with high salinity. The AV, PV, and YP of bentonite-free base fluids (BFBF) with SDKP rose dramatically with increasing concentrations, especially at higher copolymer concentrations. These findings demonstrated that SDKP aided the formation of	Xie et al. (2018)

Table 5 (*continued*)

Type of SP	Chemical structure	Optimal concentration/The properties of the SP	Work condition	Finding	Ref.
				fluid network structures, hence increasing rheological characteristics. SDKP was more successful in enhancing the rheological behavior of BFBF in general. This was considered unusual because the molecular weight of SDKP was lower than that of HE300 (rheology modifier).	
An amine cross-linked polymeric fluid-loss-control material (ACP)		3 g of ACP/MW_W: 1.56 · 10^6 Da, MW_N: 9.34 · 10^6 Da, PDI: 1.67.	Laboratory conditions (232 °C, 3.4 MPa)	The ACP was created by combining poly(maleic anhydride-alt-1-octadecene) with amine in a process called cross-linking for OBDFs. The hydrophilic amino molecules in the resulting crosslinked polymer ACP form a dense structure that prevents oil from passing through the polymer network, thus reducing filtration loss effectively. Before hot rolling, the drilling fluid's AV, PV, and YP values were relatively low. However, after hot rolling at 232 °C, the viscosity of OBDFs increased. This increase is because the ACP polymer does not fully swell at room temperature, but after hot rolling, the ACP fully absorbs oil, leading to an increase in the viscosity of the drilling fluid.	Chen et al. (2021)
A novel associative polymer (AP)		2~2.5 wt% of AP/N.G	Laboratory conditions (4 –65 °C)	The SP AP for use in SBDF was created using dimer acid, triethylenetetramine, and polyoxyethylene lauramine through chemical modification in an aqueous environment. The mud-making tests were conducted at two densities and oil/water ratios to assess the rheology performance of AP. This AP can greatly enhance the rheology of SBDF at low temperatures, particularly barite-weighted drilling fluid. By analyzing the mechanism above, the associative polymer is seen to effectively decrease the specific surface area of organic clay and minimize the force between the organic clay and dispersed water droplets due to its unique amphiphilic structure. This leads to reduced joint strength between clay particles and liquid droplets and less friction between barite particles and clay particles. As a result, the slipping and dispersion between the layers of particles and water droplets are increased.	(Han et al., 2014)

*n - Degree of polymerization; N.G- Not given.

directional well causes cuttings to accumulate downhole, thereby significantly reducing drilling efficiency and potentially causing costly problems. Well-designed drilling fluid additives can mitigate these problems at relatively low cost (Ahmed et al., 2020; Ji et al., 2021).

Drilling fluids with acceptable rheology (high yield strength, low plastic viscosity, adequate gel strength) facilitate efficient cuttings transport throughout the drilling process and this can be achieved in some cases by using SP (Ahmed et al., 2020; Ji et al., 2021; Osipov et al., 2022). For instance, solution-free radical polymerization was used to synthesizes a quadri-polymer from AMPS, DMDAAC, SSS, and AM (Osipov et al., 2022). At a polymer concentration of 0.9 wt%, the quadri-polymer system displayed YP/PV ratios up to 0.80, reflecting its excellent shear thinning properties. A drilling fluid's gel strength reflects its ability to suspend drilling cuttings once the fluid pumps are turned off. The interactions between polymer molecules are responsible for the increased gel strength. As a result, a quadri-polymer drilling fluid, without bentonite, demonstrates an outstanding cutting carrying capabilities (Osipov et al., 2022).

The SP amphoteric polymer (PEX) also increased a drilling fluid's efficiency at carrying drilling cuttings and hole cleaning (Adnan Hamad et al., 2020). Under controlled thermal conditions in DMF (N,N-dimethylformamide), amphoteric polymer (PEX) was produced by quaternizing Na_2EDTA with a DPF quaternizing agent. 0.3 wt% PEX displayed a 3D-network molecular structure capable of enhancing flow resistance and fluid viscosity. A drilling fluid with a suitable viscosity minimizes the settling of drilling cuttings, thereby reducing risks of drill pipe sticking. Furthermore, when compared to other drilling fluids, WBDF with PEX displayed higher 10 s/10 min gel strengths. With that gel profile, the drilling fluid could maintain its cuttings carrying during periods of non-circulation (Adnan Hamad et al., 2020). This enhancement in carrying drilling cuttings and hole cleaning is due to the complex web-like structure that causes increased resistance to flow and higher fluid viscosity.

The inclusion of functional groups with positively charged ions (sodium salt), no charge (amide), and negatively charged ions (carboxylic salt) leads to effective dispersion in the formulation of the drilling fluid (Adnan Hamad et al., 2020). The presence of both cationic, neutral, and anionic functional groups in the drilling fluid formulation is beneficial for several reasons. The different types of functional groups provide a balanced charge distribution that helps to disperse the drilling fluid evenly throughout the wellbore. This allows the fluid to effectively carry the cuttings to the surface and
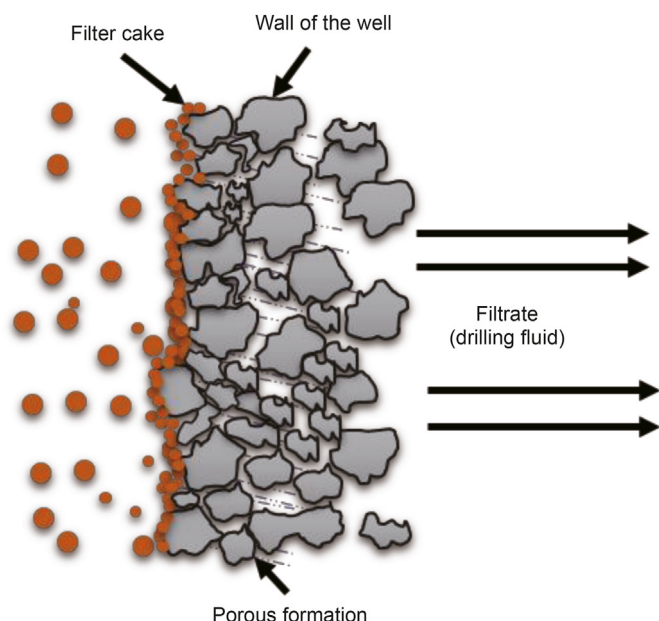
Fig. 10. The filtration mechanism from wellbore drilling fluids into a porous rock formation.

prevent them from settling, which enhances the hole cleaning process. Additionally, the neutral group (amide) can act as a surfactant and help to reduce interfacial tension between the drilling fluid and the rock surfaces, which further improves the fluid's ability to clean the wellbore. Also, the combination of these different functional groups can help to stabilize the fluid properties and prevent issues such as undesirable rheological properties, fluid loss or formation damage (Adnan Hamad et al., 2020; Davoodi et al., 2022b).

Another critical parameter in drilling fluid management is the equivalent cycling density (ECD), which refers to the pressure exerted on the formation by the drilling fluid. High ECD values can lead to lost circulation, formation damage, and other drilling problems. One of the main factors that contribute to high ECD is the viscosity of the drilling fluid, which can be increased by the addition of SP additives (Abdelgawad et al., 2019). SP additives can enhance the viscosity and yield strength of the drilling fluid, which can improve the suspension of cuttings and preventing them from settling in the wellbore. However, excessive amounts of SP additives can lead to high ECD and reduce the efficiency of the cuttings-carrying capability of the fluid. This can result in cuttings accumulation, reduced ROP, and other drilling problems.

The relationship between SP additives and ECD in drilling fluids is complex and depends on several factors, including the type and concentration of the SP, the drilling fluid properties, and the formation characteristics. In general, the addition of SPs to drilling fluids can increase the ECD due to the increase in fluid viscosity. The higher the concentration of SP in the drilling fluid, the higher the ECD will be. However, the increase in ECD due to the addition of SPs can be mitigated by optimizing the concentration of the polymer, the properties of the drilling fluid, and the drilling parameters. For example, reducing the concentration of SPs in the drilling fluid can reduce the ECD while still providing the desired rheological properties. Adjusting other drilling parameters such as the flow rate and drilling-fluid weight can also help to control the ECD. In general, the addition of SPs can increase the viscosity and yield strength of the drilling fluid, which can lead to higher ECD. More importantly, a balance must be struck between the desired rheological properties of the fluid and the potential impact on ECD and hole cleaning.

By selecting the appropriate SP additives and concentrations, drilling fluid engineers can improve the efficiency of the cuttings-carrying capability of the fluid while minimizing the risk of lost circulation and other drilling problems (Abdelgawad et al., 2019; Ezell et al., 2010; Gaurina-međimurec et al., 2021; Gautam and
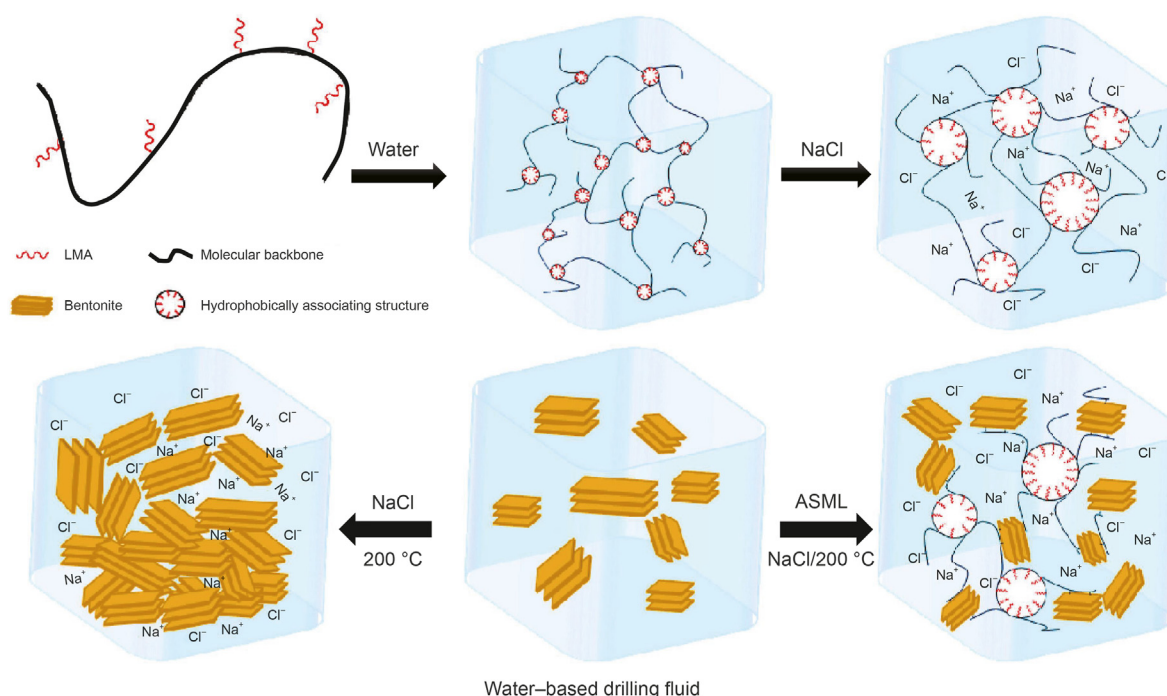
Fig. 11. The mechanism by which ASML improves the filtration behavior and rheology of drilling fluids under extreme saline and temperature conditions. Reproduced from Elsevier (Sun et al., 2022).
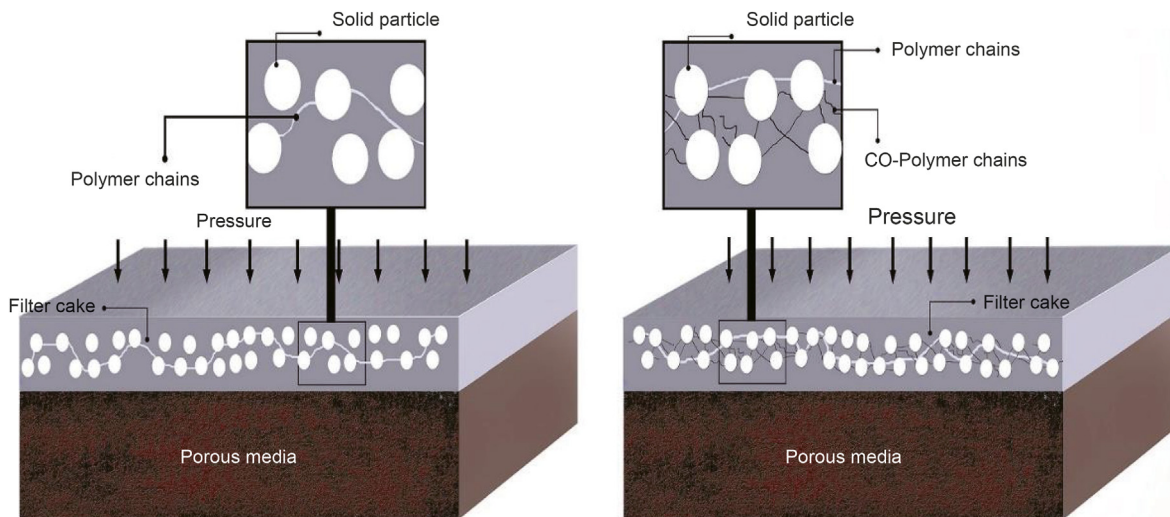
Fig. 12. Fluid loss reduction mechanism from drilling fluids involving long-chain SP additives. Reproduced from Elsevier (Davoodi et al., 2019).

Guria, 2020). Low molecular weight SPs, such as PHPA, can provide the desired rheological properties while having a lower impact on drilling-fluid ECD (M-I SWACO, 2009; Pinho De Aguiar et al., 2020). Copolymers made up of two or more different types of monomers, can be designed to provide the desired rheological properties while minimizing their impact on ECD. For example, a co-polymer of acrylamide and acrylic acid, created as inverse-emulsion polymers, can be designed to have a lower impact on ECD by forming smaller particles in the drilling fluid (Wan et al., 2011).

4.6. SPs deployed to stabilize clay formations

Shale formations can contain different types of clays with diverse mineral structures that can cause issues with wellbore instability and disintegration of cuttings due to their surface charge

and properties (Gholami et al., 2018). The commonly occurring clay minerals are usefully grouped as:

(i) **Smectites.** Montmorillonite is the main type of smectite encountered. It has a high cation exchange capacity that can influence the hydration of shales based on the type of cations present in the drilling fluid and its pH. Smectites consist of three repeating units: a silica tetrahedron, an alumina octa-hedron, and another silica tetrahedron. These clays tend to swell due to their weak bonding and the wide gaps between their layered units, but the swelling can be reduced by substituting counterions, such as Na^+ and Ca^{++} into the shales (Caenn et al., 2016).

(ii) **Illite.** This type of clay mineral has similar silica and alumina sheets to montmorillonite, but lacks an expanding lattice,
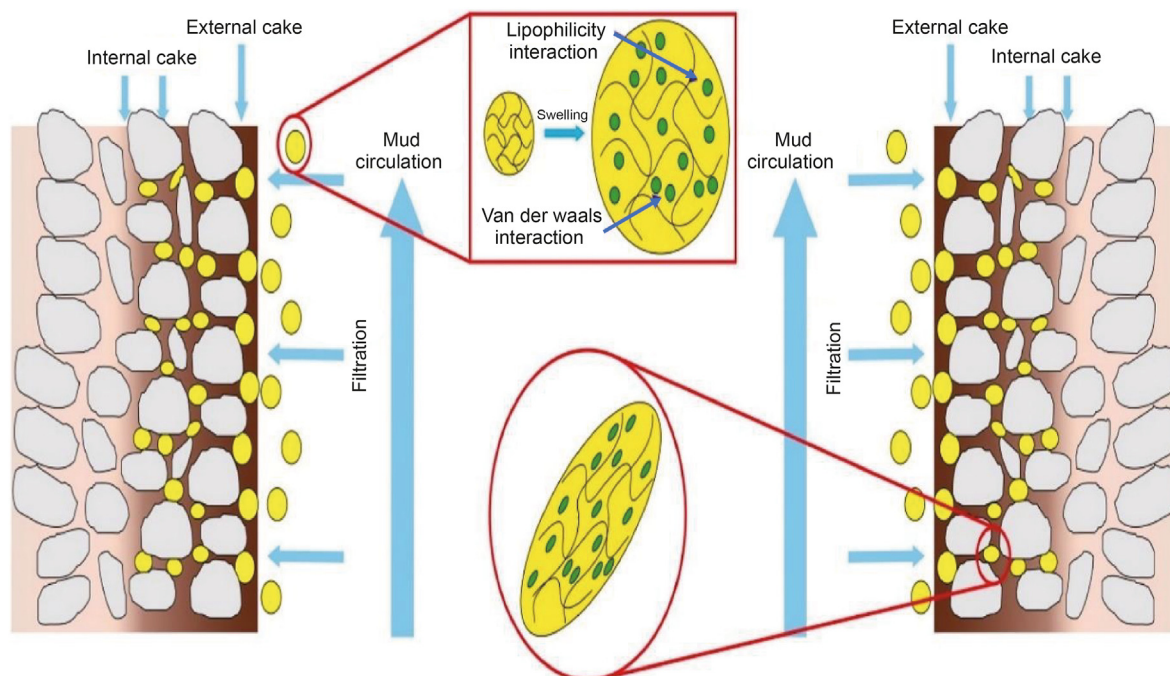
Fig. 13. The mechanism enabling SPM to beneficially influence drilling fluid filtration characteristics. Reproduced from Elsevier (Zhong et al., 2019).

preventing water from penetrating between its layers. While ion exchange can occur on the exterior surfaces of each layer, the increase in volume is less than that caused by hydration of montmorillonite. Illite forms from the degradation of muscovite and feldspar during weathering and in subsurface hydrothermal environments. Its lattice is occupied by poorly hydrated potassium cations, which act to prevent swelling (Patel et al., 2007).

(iii) *Chlorite and kaolinite.* This type of clay mineral is not able to hydrate or swell substantially, although kaolinite can disperse. Kaolinite has a low swelling tendency and poor cation exchange capacity and is produced by the chemical weathering of aluminum silicates such as feldspar. Shales with a considerable amount of kaolinite are brittle and can pose mechanical stability issues in wellbores (Anderson et al., 2010).

In order to maintain stability in the wellbore, it is necessary to prevent shale formations from hydrating and swelling. This can be achieved by neutralizing the reactive charges present on the surfaces and in the interlayers of clay minerals. Various inhibitors are added to WBDF fluids for this purpose, which act as physical, mechanical, or chemical inhibitors depending on their interaction with the shale formation. Inorganic salts, polymers, and ionic liquids are commonly used shale inhibitors, with polymers of different functional groups being the most effective. However, some of these polymers may not be efficient due to their high temperature degradation and less efficient functional group (Gholami et al., 2018). For example, polyethyleneimine can interact with clay through hydrogen bonding and electrostatic interaction, but it cannot withstand high temperatures above 120 °C, resulting in desorption from the shale surfaces, which subsequently swell (An and Yu, 2018).

Water is the most desirable dispersion phase for drilling and completion fluids, owing to its low cost and its beneficial environmental/safety attributes (Rana et al., 2019). In WBDF it is desirable to decrease the activity of the water in order to stabilize the clay in the borehole. The effect is achieved by chemically binding water molecules, preventing them from penetrating deep into clay formations. The rate of hydration and the response to different types of swelling inhibitors in plastic and non-plastic clays are not the same. Non-plastic clays bind a small amount of water and collapse immediately, making it imperative to reduce the rate of hydration, by reducing the activity of water molecules, to maintain formation stability in such clays (Rana et al., 2019).

Establishing an SP's ability to inhibit shale swelling is a prime concern. In this regard, SPs can be classified as follows:

1. *Water-soluble polymers* such as polyvinylpyrrolidone display an ability to adsorb onto the surface of the clay minerals in shale formations and reduce their swelling. Polyacrylamide can also interact with the clay minerals in shale formations and prevent water from penetrating into the interlayers.
2. *Cationic polymers* such as polyetheramine display an ability to neutralize the negative charges on the surface of the clay minerals in shale formations and reduce their swelling (Beg et al., 2019).
3. *Polymers that contain both positive and negative charges* such as polyampholytes also display an ability to interact with the clay minerals in shale formations and prevent water from penetrating into the interlayers (Ma et al., 2017).
4. *High molecular weight polymers* such as polyacrylamides display an ability to adsorb onto a shale formation's surface and form a protective layer, preventing water from penetrating into

the shale and its component clay minerals (Jain and Mahto, 2017).

An example field application involved an SP comprised of PHPA and KCL used to provide shale inhibition in high-density drilling fluid conditions (Gueciouer et al., 2017). It resulted in a reduced level of shale dispersion, which was attributed to the function of PHPA in encapsulating the shale, and the inhibition mechanism of K+ cation acting to prevent shale swelling (Gueciouer et al., 2017).

Fig. 16 provides a diagrammatic representation of the stabilization process of clay-rich formations in a borehole wall in the presence of SP-bearing WBDF. Initially, polar reagents, due to their low molecular weight, penetrate into the rock together with the aqueous phase of the solution. This contributes to neutralizing ions in the rock structure and stabilizing the pore pressure. Simultaneously, high-molecular-mass compounds (the SPs) are adsorbed onto the borehole walls, forming a protective layer inhibiting drilling-fluid penetration from its filtrate into the formation (Gholami et al., 2018; Rana et al., 2019).
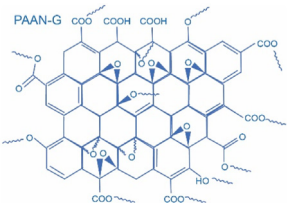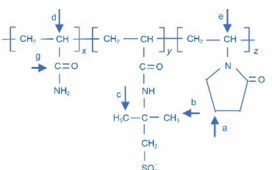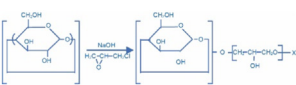
Wellbore stability is ensured through the use of sodium or potassium polyacrylates as part of the drilling fluid when combined with glycerine and with sodium formate (Chudinova et al., 2019). Polyvinylpyrrolidone tends to bind complex and low molecular weight compounds. Therefore, the introduction of polyvinylpyrrolidone into WBDF contributes to reduction of the dispersion medium's activity of the fluid. This acts to suppress pore pressure growth in the formations present in the borehole walls, thereby increasing borehole stability when drilling in clay-rich formations (Ma et al., 2022).

Acrylic-acid-grafted-activated carbon (C-g-AA-NH$_2$) was synthesized by free-radical polymerization (Ibrahim and Saleh, 2020). 16 g of AA and 1.5 g of C-A were added to 100 mL of deionized water and mixed in a three-neck flask equipped with a condenser, magnetic stirrer, and nitrogen gas. To remove dissolved oxygen, a nitrogen-gas purge (10 min) was necessary before reducing and maintaining the flow rate throughout the reaction. A solution made of 0.5 g of potassium persulfate dissolved in 10 mL deionized water was added gradually as an initiator to promote polymerization. After 3 h at 60 °C, 6.7 g ethylenediamine in 200 mL ethanol was introduced. The resulting solution was vigorously stirred for 24 h at room temperature. Fig. 17 illustrates that this caused the formation of hydrogen bonds and electrostatic interactions existing between the surface of clay and the grafted polymer part of −OH and −NH$_2$. A 2 wt% aqueous solution of C-g-AA-NH$_2$ develops a thin layer on the Na-Bt surface. Meanwhile, carbon NPs centered on the core help to prevent water penetration by sealing the nanopores. The ether group on the surface of the core-centered carbon NP further prevents the penetration of water into the clay, due to its hydrophobic nature (Ibrahim and Saleh, 2020).

The SP amidocyanogenesilanols (HAS) were introduced as a promising shale inhibitor after conversion of methacryloxypropyltrimethoxysilane with polyethylene polyamine (Chu et al., 2020). This created high-temperature stable shale inhibitors suitable for WBDF. HAS permeating into a clay interlayer tends to be adsorbed into more sites, reducing the affinity between water molecules and clay, and the degree of hydration degree at the clay surface (Fig. 18). HAS-bound neighboring clay plates also tend to eject some of adsorbed water molecules from the interlayers, thereby decreasing the osmotic hydration of the clay-rich formation (Chu et al., 2020).
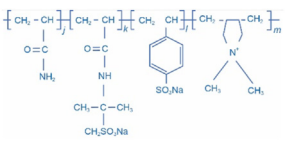
Table 7 describes selected research focused on improving the clay stabilization capabilities of drilling fluids. The polyampholyte (DAM) can tolerate heat up to 288 °C, but only provides 47% inhibition of shale. This low efficiency is due to its inability to diffuse charged clay minerals, which is attributed to its poor hydrogen-

Table 6
Selected studies of SP to enhance the filtration behavior of drilling fluids.

Type of SP/SP properties	Chemical structure	Optimal concentration	Work condition	Finding	Ref.
PAAN-G (A polymer/GO composite)/MW: 3500 Da		2.0 wt%PAAN-G	Laboratory conditions (25, 150, 180, and 240 °C, 3.5 MPa)	(PAAN-G) was generated by aqueous free radical polymerization to copolymerize 3 monomers: N-vinylpyrrolidone; AMPS; AM, in the presence of and GO. The volume of LTLP fluid loss of the base fluid with 2.0 wt% PAAN-0.5G or 2.0 wt% PAAN-0.2G was recorded ove the interval 180–240 °C. At 240 °C, the API filtration volume was only 12.5 and 12.3 mL, respectively. At 180 °C and at 1.0 wt %, the rate of change of AV, PV, and YP were 26.6%, 27.2%, 25.0%, respectively. In the presence of salt, 25% of NaCl at 150 °C and concentration 2.0 wt%, the AV, PV, and YP were 25, 17, 8 mPa·S, respectively. The results indicate that PAAN-0.5G and PAAN-0.2G can perform in ultra-high-temperatures. When the LTLP fluid loss volumes were compared the two forms of PAAN-G additive behaved in a similar manner. This indicated that increasing the GO concentration does not considerably improve the capacity of PAAN-G in filtration reduction. This may be a consequence of the GO's grafting rate on PAAN not increasing remarkably as GO concentration increased. After aging, PAAN-G adsorption enhanced the particle size distribution range of bentonite. Furthermore, because of the GO flake structure, the free PAAN-G was able to enter into the microscopic holes of filter cakes. This contributed to the filter cakes' compactness.	Ma et al. (2021a)
P (ANAN)(acrylamide, N-vinyl-2-pyrrolidone and 2-acrylamide-2-methylpropanesulfonic acid)/MW: $5.332 \cdot 10^6$ Da		0.8 wt%P (ANAN) fluid loss control: 1.5 wt% P(ANAN)	Laboratory conditions (180 °C, 4.1 MPa)	P (ANAN) was produced by free-radical polymerization triggered by 2,2′-Azobis (2-methylpropionamide) dihydrochloride. It can be deployed into WBDF, at high temperature conditions, for controlling magnesium and calcium contamination and reducing fluid loss. The performance deliverability after aging at 180 °C was YP: 4.0 N/m^2, PV: 19.0 mPa·S, and AV: 23.0 mPa·S, FL$_{API}$:2.4 mL, FL$_{HTHP}$: 28 mL). The results of fluid loss control mechanisms revealed that P (ANAN) had a greater contact with the bentonite particles at elevated temperatures. It could clearly enhance the colloidal dispersion capability of WBDF that has been polluted by salts leading to magnesium and calcium contamination, and invasion of acid gas under bottom-hole conditions. Because of the excellent quality of the filter cake, the filtration volume was lowered, and a high filtrate viscosity of the WBDF could be maintained at high-temperature conditions. As a result, P (ANAN) has the potential to be a viable additive in WBDFs for controlling fluid loss. It is suitable for deep and ultra-deep drilling operations.	Mao et al. (2021)
β-CDPMs (β-cyclodextrin polymer microspheres)/DT: 366.667 °C, Particle size(D_{50}): 74.49 μm		1.0 w/v% β-CDPM	Laboratory conditions (240 °C, 0.7 MPa)	β-CDPMs provided improved fluid loss control at temperatures of >160 °C. It could withstand temperatures up to 240 °C without significant rheological effect. When thermal ageing exceeded 160 °C, the hydrothermal process produces many nanocarbon spheres and nanostructured composites. These high-temperature resistant NP overlap the nanoscale gaps and promote the formation of a thick filter cake, resulting in good filtration control. The	Zhong et al. (2020a)

(*continued on next page*)

Table 6 (*continued*)

Type of SP/SP properties	Chemical structure	Optimal concentration	Work condition	Finding	Ref.
The synthetic copolymer AM/AMPS/DMDAAC/SSS is comprised of ADS, 2-acrylamide-2-methylpropanesulfonic acid, acrylamide, dimethyl diallylammonium chloride, and sodium styrene sulfonate,It is abbreviated here to AADS./MW_W: $1.161 \cdot 10^6$ Da, MW_N: $6.84 \cdot 10^6$ Da, PDI: 1.697, $MW\eta$: $1. \cdot 10^6$ Da		2 wt% AADS	Laboratory conditions (240 °C for 16 h, 3.5 MPa)	filtration control method used provides a new means of controlling HT filtration in WBDFs. The volume of filtrate was 17.2 mL, indicating 53.8% lower filtration. As the concentration of microspheres increased, the volume of filtration loss dropped somewhat. The performance deliverability results (AHR at 240 °C,16 h) at concentration 1.0 w/v% β-CDPM, were: YP: 13.5 Pa, PV: 39 mPa·S, and AV: 52.5 mPa·S. Two system of drilling fluids: (S1) 2 wt% of AADS+ 2 wt% NaCl; and (S2) 2 wt% of AADS+ 4 wt% NaCl) were prepared and tested. Their fluid losses at LTLP conditions reduced to 8.5 and 9.8 mL, respectively, in the presence of 2 wt% of AADS. Meanwhile, their fluid losses at HTHP conditions remained relatively low at 18.9 and 22.5 mL, respectively. The rheological properties results after adding the copolymer were YP: 10 Pa, PV: 19 mPa·S, and AV: 29.0 mPa·S. Moreover, the carboxyl groups, amide groups, sulfonic acid groups, and benzene ring, existing on copolymer molecules provides strong polarity that generates a robust polarization layer acting to prevent molecules of water from filtering out of the drilling fluid.	Huang et al. (2019)

*m and *n* are degrees of polymerization; for styrene copolymer $n \approx m$.
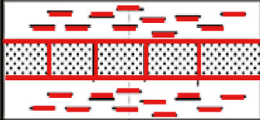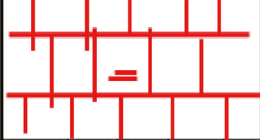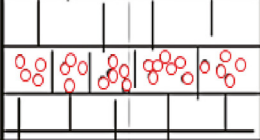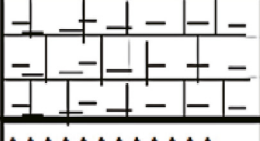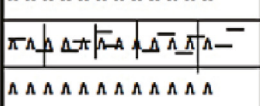
Stratigraphy	Lithology	PP	Formation description
Al		8.7–10.2	Soft clean fine grained sandstone interbedded with thin gray shale and some limestone
A2		10.2–13.2	Grayish green to dark gray shale with some layers of sandstone andlimestone
A3		13.2–13.8	Limestone with some shale
A4		13.8–14.7	Upper dense hard limestone middle oolitic limestone upper dense hard limestone
A5		14.7–16	Hard fine grained poorly sorted lime mud stone, yellowish brown at top and dark gray at base with some shale
A6		16–18.8	Thick sequence of anhydrite interbeded with limestone and someshale

Fig. 14. Sandstone/shale sequence in 16-inch-hole section of a problematic well (A1) drilled in Kuwait with drilling fluid lubricity improved by an SP additive. Modified after (Al-Muhailan et al., 2014).

bond-making ability. The polymer works better when combined with KCl, which helps neutralize clay charges through electrostatic interaction (Ma et al., 2017). Glycyrrhiza glabra root extract contains several functional groups like −OH, −COOH, and −CH$_3$, but requires higher concentrations to perform effectively as a shale inhibitor, which can negatively impact the rheological and filtration properties of drilling fluids (Moslemizadeh et al., 2017). Polymers containing amine, amide, imine, and hydroxyl groups are able to create electrostatic forces, helping them to achieve maximum shale inhibition up to 76%. Polymers based on ammonium, however, display lower inhibition, typically around 25% (Abbas et al., 2021; Gholami et al., 2018).

5. Environmental and economic aspects of SPs used in drilling fluids

5.1. Environmental considerations

Depending on the type of polymer or SP used and the specific environmental conditions of the drilling operation, some drilling fluid types can have greater environmental impacts than others. WBDFs are generally believed to be less harmful to the environment compared to OBDF or SBDF. OBDFs are typically more harmful to the environment than WBDFs because they are made with SPs that can be toxic to aquatic life and can lead to long-term damage to soil and water quality. SBDFs are designed to be more environmentally friendly than traditional OBDFs but they may still pose environmental risks if not managed appropriately and the additives they contained are not carefully selected (Bakke et al., 2013; Davoodi et al., 2022b; Fadairo et al., 2012). Using appropriately manufactured and handled polyacrylamide-based friction reducers in WBDF in preference to OBDF offers a more environmentally friendly alternative (Metwally et al., 2022). Environmental regulations now limit the use of OBDFs in many jurisdictions, placing more pressure on the industry to develop and use more environmentally-friendly WBDF and SBDF in place of OBDF (Metwally et al., 2022). Some of the SPs used in OBDF, such as polyalphaolefins, that are known to be toxic to aquatic life can also accumulate in the human food chain (Kania et al., 2015).

SPs used in various types of drilling fluids have environmental implications that need to be considered (Davoodi et al., 2022b). From an environmental perspective, it is preferable to preferentially apply polymerization processes in aqueous solutions when synthesizing polymers from acrylamide. That approach should lead to a reduction of energy costs for initial monomer separation, a decrease in environmental pollution, and the avoidance of a dissolution stage requiring some toxic polymer reagents (Rokhade et al., 2007). The drilling fluids with minimum solid phase content using biodegradable organic additives, including water-soluble polymers (natural or synthetic), such as CMC, starch and their derivatives and some acrylic polymers have substantially lower toxicity than traditional drilling fluid formulations (Daneshfar et al., 2018; Madani et al., 2022).

Furthermore, there are concerns that polyacrylamide (any polymer containing acrylamide monomers) used as a drilling-fluid can, if not handled appropriately, contaminate the environment (Dai and Zhao, 2018). Although polyacrylamide itself is non-toxic, because it is hydrophilic, its degradation products could potentially be widely transported to contaminate groundwater systems. SP, such as various modified cellulose, modified starch (and polyacrylamide) that are widely used in drilling fluids, display relatively low toxicity but further studies are required to determine the long-term biostability and impacts of such polymers in sub-surface environments (Dai and Zhao, 2018).

The creation and use of polymers can have direct and/or indirect impacts on the environment. If waste-materials containing certain polymers are buried in landfill waste sites there is a risk that they will contribute to soil and groundwater contamination as they decompose. Consequently, carefully designed treatments are required prior to disposal of drilling wastes to avoid such adverse outcomes (Lambert et al., 2014). More importantly, the manufacturing methods for SPs used in different types of drilling fluids can also have significant environmental impacts. The processes involved in producing these polymers can generate large amounts of waste, consume significant amounts of energy, and release harmful pollutants into the air, water, and soil. The manufacturing of SPs used in OBDF and SBDF can generate large amounts of waste and release harmful pollutants, which can have adverse effects on the environment. SBDF are designed to be more environmentally friendly, but their manufacturing still involves the use of various chemicals that need proper handling and disposal (Davoodi et al., 2022b; Gautam et al., 2022). When evaluating the toxicity, bioaccumulation, and biodegradation of SPs in drilling fluids before disposal, the following protocol is recommended:

1. **Toxicity testing.** Toxicity testing should be conducted to determine the potential adverse effects of the SP on aquatic organisms. This can include acute and chronic toxicity tests using different species of fish, invertebrates, and algae. The tests should follow standardized protocols, such as those recommended by the Organization for Economic Cooperation and Development (OECD), and measure parameters such as mortality, growth, and reproduction. Specifically, the applicable test protocols are: (i) ISO 10253 to examine the impact of drilling wastewater on the growth of single-celled marine algae Skeletonema and Phaeodactylum tricornutum in seawater, with a threshold of half maximal effective concentration (EC_{50}) (72 h) > 10,000 ppm deemed acceptable (ISO10253, 2006). (ii) ISO 14669 and ISO 16778 to assess the acute lethal toxicity of marine copepods Acertie tonsa, with an acceptable limit of
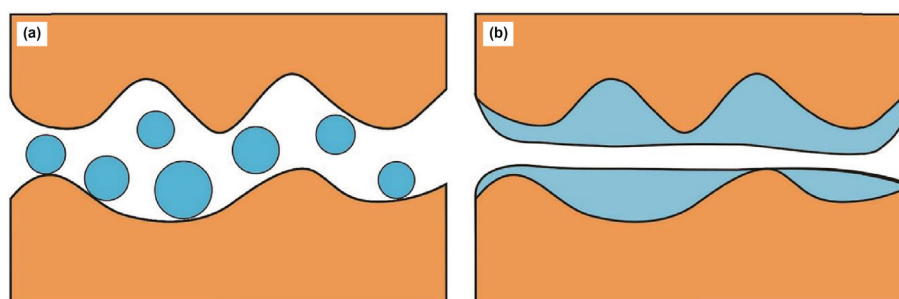
Fig. 15. Drilling fluid lubrication mechanisms: (**a**) "roller bearing" of polymer NP; and, (**b**) "lubrication film formation" of polymer NP. Reproduced from Elsevier (Xu et al., 2017a, b).

lethal concentration (LC$_{50}$) (48 h) > 10000 ppm (ISO14669, 1999; ISO16778, 2015). (iii) OSPAR utilizes an amphipod species Corophium sp. to investigate burrowing behavior and acute lethal toxicity, which determines the concentration of contaminants that kill 50% of the test organisms (OSPAR, 2006). (iv) EPA utilizes a test organism Mysidopsis bahia to define lethal contamination in suspended particulate phase of drilling fluid containing SP, which kills 50% of the test organisms within 96 h (EPA, 1993). (v) ASTM E1367 - 03 regulates the discharge of SBDF drill cuttings by utilizing a test organism L. plumulosus (ASTM E1367 - 03, 2014).

2. **Bioaccumulation testing.** Bioaccumulation testing is conducted to determine whether an SP is likely to accumulate in the tissues of aquatic organisms. This can include bioconcentration tests using fish or other aquatic organisms and measuring the concentration of the SP in the tissues over time. Specifically, the most applicable test protocols are: (i) OECD 117 evaluates the partition coefficient of a dissolved substance in a two-phase system (octanol and water) as a ratio of equilibrium concentrations. This ratio indicates the tendency of a chemical to partition into octane (fatty tissue of an organism) compared to water, and the acceptable limits are represented by a ratio value without a unit (log Kow) between 3.0 and 6.0 (OCED 117, 2004). (ii) OECD 305 evaluates the bioconcentration factor by exposing test organisms to a constant concentration of effluent in water until an equilibrium is reached between the concentration of effluent in water and the test organism. The acceptable limits for the bioconcentration factor are values < 3.0 (OCED305, 2012).

3. **Biodegradation testing**: Biodegradation testing is used to evaluate the potential of SPs to break down in the environment. Standardized tests, such as the OECD 301 Ready Biodegradability Test or the OECD 308 Aerobic and Anaerobic Transformation in Soil, can be used to determine the biodegradability of SPs. The tests involve exposing the SP to microorganisms under controlled conditions and measuring the rate of biodegradation (OCED 301, 1992).

Table 8 identifies certain polymers that have the potential to be hazardous to the environment and human/animal health. The hazard class of hazardous substances is a conventional value intended to provide a simplified classification of potentially hazardous substances in terms of their potential impact on the environment, human, and animal health (Davoodi et al., 2022b) and includes limiting value of harm (Byzov et al., 2019) and hazard value (ISO14971, 2015). For instance, the copolymer of methacrylate with butyl acrylate and methacrylic acid is categorized in the high hazard class (IV) with the potential for causing toxicological

environmental impacts. When polymerizing SPs, it is clearly beneficial to avoid or minimize the involvement/creation of these hazardous polymers and seek to identify non-hazardous and non-toxic alternatives (Lithner et al., 2011; Zhang and Dubé, 2018).

The technologies used to drill gas and oil wells results in substantial, difficult and costly to handle, waste materials, including: drilling cuttings, spent drilling fluids and produced formation water. The greatest difficulty is associated with handling spent drilling fluid and rock formation cuttings. Furthermore, the volumes of waste generated, particularly rock cuttings, is substantial. Up to 80% of the drill cuttings volume tends to be clay-rich/shale fine-grained rock material (Van Oort et al., 2015). Drilled rock particles tend to swell during hydro-transport from the bottomhole to the surface, and the volume of cuttings increases by about 20%–25% (Pereira et al., 2022). Treatments applied to drilling cuttings depend upon their physical and chemical properties, which will determine what can and cannot be readily reused (Boutammine et al., 2020; Pereira et al., 2022). The most commonly applied drilling fluids waste treatment are: physicochemical (Boutammine et al., 2020); bioremediation (Imam et al., 2019); thermal (Pham and Pakrasi, 2019); supercritical fluids (Manjare and Dhingra, 2019); electrokinetic (Adhami et al., 2021); and stabilization/solidification (Fig. 19) (Boutammine et al., 2020). The physicochemical properties of drilling wastes varies depending on the geological section drilled and with the various drilling fluid additives involved to deal with variable sub-surface environments. The drilling-fluid additives include various temperature stabilizers, surface-active substances, antifoam additives, specific gravity weighting agents, flowing agents, friction reducers, etc. Traditionally, some of these additives have not been environmentally friendly (e.g. diesel-based lubricants) or biodegradable. Inorganic contaminants are also present in drill cuttings, including various metals, in addition to complex materials such as sulfur-bearing compounds, asphaltenes, resins and heavy waxes deposited from some formation hydrocarbons (Manjare and Dhingra, 2019; Pereira et al., 2022).

In order to improve the environmental acceptability of SPs in drilling fluids, several strategies can be adopted. An obvious approach is to reduce the quantity of hazardous waste of SPs used in drilling fluids, and the many other chemicals involved in drilling activities, particularly those associated with uncertainties regarding their health and environmental impacts. To assess the hazardous potential of these chemicals, one can analyze the Fire and Explosion Damage Index, Toxicity Damage Index, Primary Dermal Irritation Index, and Eye Irritation Index (Draize Score) while developing drilling fluids. This information can assist in choosing the appropriate category of monomers, polymers, and additives for creating SPs that are effective drilling-fluid additives
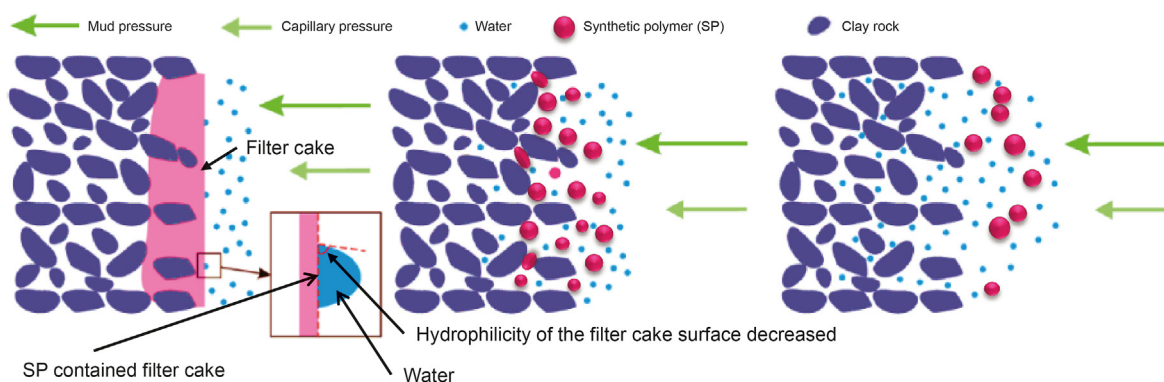
Fig. 16. Diagrammatic representation of the stabilization process of a clay-rich formation in the borehole walls in response to a WBDF containing SP.
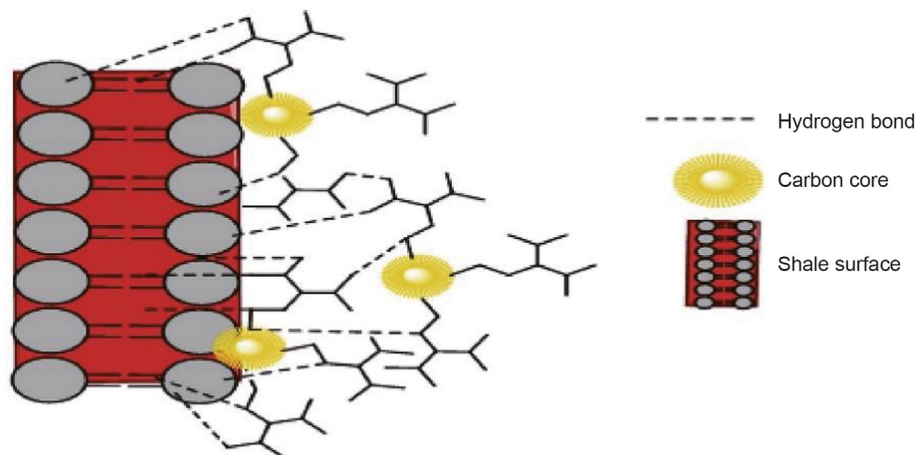
Fig. 17. The mechanism of inhibitor C-g-AA-NH$_2$. Reproduced from Elsevier (Ibrahim and Saleh, 2020).
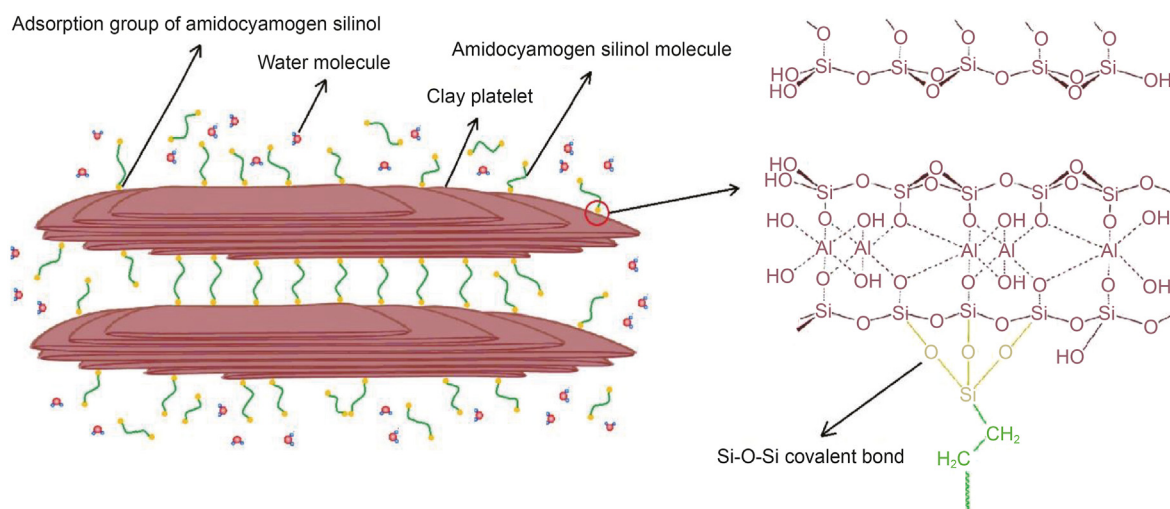
Fig. 18. The mechanism of interaction of amidocyanogenesilanol (HAS) with clay plates. Reproduced from Elsevier (Chu et al., 2020).

that can withstand high-pressure, high-temperature reservoir conditions (Tikadar et al., 2021a, b).

Preferentially using biodegradable polymers in drilling fluids can reduce their environmental impact. These polymers can be derived from natural sources such as starch, cellulose, and chitosan, or can be synthetic but designed to break down rapidly in the environment (Gautam and Guria, 2020). Also, by maintaining a low aromatic content (less than 1%) and n-paraffin content (less than 5%), it is possible to decrease the toxicity level of SBDF (Gautam et al., 2022). The implementation of appropriate disposal methods for SPs used in drilling fluids is essential to prevent contamination of the environment. This can be achieved by ensuring that the drilling fluids are properly contained and disposed of in designated locations, such as landfills or treatment facilities (Tikadar et al., 2021a, b) and that procedure is carefully monitored and regulated.

5.2. Economic considerations

Both natural and modified polymers are widely used as drilling fluid additives, particularly to improve rheology and filtration properties (Safi et al., 2016). These include xanthan gum, cellulose, guar gum, maleic anhydride and polyacrylate derivatives. However,

the benefits of the cheaper natural polymers are limited due to weak thermal stability, such as that of starch (Al-Hameedi et al., 2019) up to 120 °C, compared to that of SP Poly(SSS/AM/AMPS) 160 °C (Huo et al., 2018). Similarly natural polymers typically display low tolerance to salt, such as that of guar gum (Luqman Hasan et al., 2018), while the SP AADS displays high tolerance to NaCl (up to 100000 ppm) and CaCl$_2$ (up to 1000 ppm) (Huang et al., 2019). For instance (Konstantin et al., 2018), demonstrated that starch-based reagents are of limited use in reservoir drill-in fluid systems because starch-derived filter cakes become damaged by biodegradation and/or acid treatments, degrading the drilling fluids filtration properties.

When drilling the top-hole sections of oil/gas wells (surface/intermediate casing intervals), starch derivatives are rarely used as filtration reducers. If they are used, it tends to be in salt-water-based drilling fluids, or in saline conditions, reducing the rate of polymer biodegradation compared to freshwater systems. The synthetic introduction of a significant amount of carboxymethyl groups into the polymer structure can eliminate this drawback and increase thermal stability. Economic feasibility of this solution is provided by 30%−50% lower cost compared to low viscosity CMC. Most often CMC is produced from corn or potato starch (Konstantin et al., 2018). Consequently, such SP solutions offer significant

Table 7
Research involving drilling fluids with SP to improve the clay stabilization.
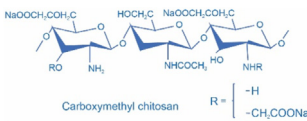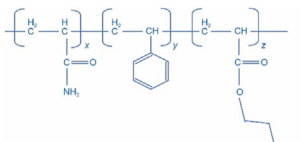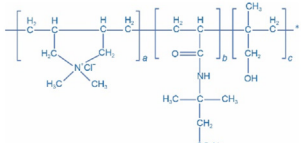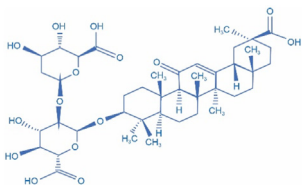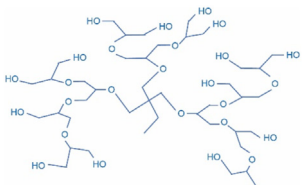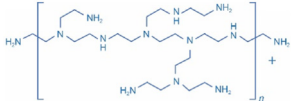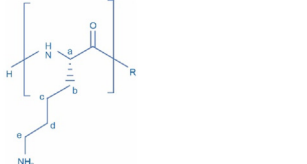
Type of SP	Chemical structure	Optimal concentration	Work condition	Finding	Ref.
Carboxymethyl chitosan (CMCS)		0.2 wt% CMCS	Laboratory conditions (150 °C)	They developed an environmentally friendly amphoteric inhibitor which was based on CMCS. The mechanism of inhibition of CMCS differs from that of conventional encapsulation and cationic inhibitors and inorganic salts. The greater CMCS's inhibition is attributed mostly to abundant NH_2 ($-NH_3^+$), $-OH$, and $-COO^-$, CMCS being easily adsorbed at many sites on Na-Bentonite particles. This occurs through hydrogen bonding and electrostatic interactions, partly neutralizing the clay surface with negative charges. Also, by firmly surrounding the clay particles, CMCS molecular chains form a continuous polymer film. This increases surface hydrophobicity and resists invasion by free water molecules.	Lei et al. (2020)
An amphoteric polymer (ASBA)		1.6 wt% ASBA	Laboratory conditions (150 °C)	Electrostatic interactions and hydrogen bonding with clay minerals are the most likely inhibition mechanisms involved. ASBA only inhibited shale swelling by 37.8%. It is not known what accounts for its relatively poor inhibition. It could be due to the inability of the active sites to neutralize reactive clay minerals. In addition, ASBA was incompatible with additives used in drilling fluids.	Zhang et al. (2018)
Polyampholyte (DAM)		2 wt% DAM, 3 wt% KCl	Laboratory conditions (288 °C)	The ability of this polymer to form hydrogen bonds is rather weak. Therefore, it could not completely suppress shale. It performed well in the presence of KCl, because the electrostatic contact neutralizes the clay charges.	Ma et al. (2017)
Glycyrrhiza glabra root extract (GGRE)		30 g/L GGRE	Laboratory conditions (82/105 °C)	Glycyrrhiza glabra is a tree with a highly effective saponin, a biosurfactant, that has been tested and proposed for enhanced oil recovery (EOR) purposes. Hydrophobic and hydrophilic groups provide Saponin with its surfactant properties. It is extracted from Glycyrrhiza glabra through a spray drying process. It contains many functional groups including $-COOH$, $-OH$, and $-CH_3$. A shale slurry inhibition test was used to determine the inhibition of shale slurry. The results showed that high concentrations of inhibitor are needed which is a disadvantage of its use. Moreover, at high concentrations, it impairs drilling fluids' rheology and filtration properties.	Moslemizadeh et al. (2017)
Partially Hydrophobized Hyperbranched Polyglycerols (HPG)		2 wt% HPG	Laboratory conditions (200 °C)	The inhibitor was created in a chemical reactor at 125 °C. The inhibitor's interaction mechanism involves electrostatic and hydrogen bonding. Abundant hydroxyl groups work as active sites to neutralize reactive clay particles and prevent water penetration. HPG achieved thermal stability up to 200 °C, although its effectiveness depends on its concentration. Significant interaction of the solution with the solvent above 2 wt% concentration caused agglomeration. This affected the fluid's rheology. In the absence of KCl, this polymer cannot inhibit effectively.	Ferreira et al. (2016)
Polyethyleneimine (PEI)		4 wt% PEI	Laboratory conditions (120 °C)	PEI was synthesized by ring polymerization of ethyleneimine. The ethylenimine group works as an active site to inhibit clay minerals. PEI was tested on montmorillonite clay (Mt-clay). It was found to inhibit Mt-clay through electrostatic interaction and hydrogen bonding. The swelling rate of the shale was estimated to be 76.2%. A possible explanation for the low efficiency is the dependence of inhibition on PEI's molecular weight. The higher its molecular weight, the higher the clay-mineral inhibition. However, high molecular weights resulted in lower water solubility.	Jiang et al. (2016)
Oligo (poly-L-lysine) (OPLL)		0.5 wt% OPLL	Laboratory conditions (180 °C, pH 7–10)	OPLL was synthesized by thermal co-polymerization. OPLL can be used as a high-performing, environmentally acceptable inhibitor for the hydration of shale. The remarkable efficiency of OPLL is related to the synergistic impacts of the inhibition of montmorillonite crystals and the decrease in the diffuse double-layer repulsion between the particles of clay. Linear swelling and shale dispersion experiments revealed that OPLL performs exceptionally well in montmorillonite- and illite-rich shales.	Xuan et al. (2015)
poly(oxypropylene)-amidoamine (POAA)		0.5 wt% POAA	Laboratory conditions (200 °C)	POAA was synthesized by condensing a low molar mass of polyoxypropylene diamine POP230 with diacids. The POAA compounds were then tested as possible shale inhibitors. POAA (POP230-ethane diacid) has the benefit of a simple	Zhong et al. (2012)

Table 7 (*continued*)

Type of SP	Chemical structure	Optimal concentration	Work condition	Finding	Ref.
				molecular structure and a low molecular weight. POAA acts to suppress shale swelling due to the monolayer polycation arrangement it forms in the interlayers of shales. POAA interacts with the surface of some clay minerals that convert it into a somewhat hydrophobic condition, giving it the ability to reduce hydration and swelling of shales. POAA was tested in various conditions, and observed to establish hydrogen-bond connections between amide and siloxane groups. Such bonds, together with van der Waals interactions and electrostatic forces, act as the primary variables responsible for reducing shale swelling and dispersion difficulties.	

*n Degrees of polymerization.

advantages in terms of resistance to biodegradation, stability, water solubility and cost of supply (Ma et al., 2017).

Nevertheless, many traditional SPs used in WBDF have many problems such as high operating costs, poor stability, high reactivity, and strong corrosion consequences. In addition, conventionally manufactured polymers readily degrade during high-temperature drilling, thus adversely impacting the rheological and filtration properties of the drilling fluid system. Many conventional SP provide good outcomes at temperatures below 150 °C. Therefore, in order to meet the requirements of drilling operations, it is necessary to develop more polymers with higher temperature resistance and that can be manufactured at lower costs of supply (Ghasemi et al., 2018; Khalil and Mohamed Jan, 2012).

Huo et al. (2018) synthesized the novel polymer poly(SSS/AM/AMPS). The monomers employed to produce that SP are quite inexpensive, such as AMPS, AM, and SSS, Some costly cationic monomers, such as DMDAAC, were not employed in synthesis. Thus, when compared to natural polymers such as xanthan gum (the cost of 1000 kg is approximately \$4300) and standard SPs ("Alibaba, 2023), the cost of 1000 kg of poly(SSS/AM/AMPS) is approximately \$4500 (Huo et al., 2018). However, when comparing poly(SSS/AM/AMPS) to xanthan gum, it should be taken into account that xanthan gum has weak thermal stability (120 °C), and low tolerance to salt (Agwu et al., 2021b). Another relatively low-cost SP application is WBDF with polyacrylamide-based friction reducer (AFR) additives, which has a lower cost of supply than OBDF. WBDF with AFR has outperformed the WBDF without AFR in terms of thermal stability and shear rate viscosity. Its beneficial properties improve hole cleaning, fluid rheology and stability, as wells limiting filtration losses to the formation, thereby reducing formation damage (Metwally et al., 2022).

Fig. 20 provides indicative costs (first quarter 2023) of selected SPs commonly used in drilling fluids. The SPs considered are PHPA, potassium polyacrylate (NPA Or NH$_4$-HPAN), sodium polyacrylate, polyhydrolyzed (Na-HPAN), and sodium acrylate/acrylamide (SAA). PHPA is the cheapest of the five considered, due to the low cost of the acrylamide monomer (approximately US\$1.5/g). SAA is the most expensive due to the high cost of sodium acrylate monomers (US\$21 to 27/g). In general, the cost of an SP depends largely on the cost of the monomer used in its production. The costs of common monomers are provided in Fig. 21. DMDAAC monomer is the most expensive (approximately US\$35\$/g). Thus, it can be inferred that any SPs developed containing high concentrations of DMDAAC will also be expensive. The costs reported in Figs. 20 and 21 are derived from the Alibaba website (Accessed in March 2023- https://www.alibaba.com) (Alibaba, 2023).

6. Recommendations for future research

The behavior of synthetic compounds in drilling fluids is influenced not only by the composition, structure and molecular weight of the particular polymer, but also by the composition and temperature of the system into which they are added. A particular polymer can work as a flocculant at low concentrations and as a filtration reducer at high concentrations. These variables make it necessary to conduct extensive testing programs before a new product can demonstrate its reliability and confidently enter the market.

Further research to develop novel and modified SPs is required for a number of reasons.

1. Modified-natural polymers in current usage have a number of disadvantages. These include sensitivity to formation lithology and fluid compositions, salinity, pH environment, water hardness and high temperature. In this regard, the search for inexpensive SPs with high encapsulating capacity, providing drilling fluids with a flat rheological profile and high viscosity at low shear rates remains a key ongoing research objective.

2. There are some disadvantages of the SPs in drilling fluids: (1) many geological factors can affect the performance of SP such as HPHT and salt contamination. Thus, to improve the SP performance it is beneficial to use suitable monomers. For example, in case of high temperature, monomers containing molecular groups such as sulfonate, methyl, phenyl, furan, lactam, and pyrrolidine can enhance SP thermal stability; for example, SP based sodium 4-styrene sulfonate in (Liu T. et al., 2020) which displays effective thermal stability up to 200 °C. On the other hand, monomers which contain carboxylic acid and sulfonic acid salts can highly enhance the salt tolerance of SP. such as the SP based AM, AMPS, DMDAAC, and SSS (Huang et al., 2019). (2) The monomers use to manufacture some SP are expensive. Therefore, part of SP synthesis planning should be to seek monomers that are inexpensive yet capable of providing the desired functionality. For example, poly(SSS/AM/AMPS) was developed by combining inexpensive monomers yet demonstrated its ability to enhance the filtration and rheological properties at high temperatures up to 160 °C (Huo et al., 2018). However, further research is required to develop additional low-cost SP which can be applicable in harsh condition. (3) The component monomers in some SPs are not environmentally friendly; for example, the copolymer based on methacrylate with butyl acrylate and methacrylic acid (Davoodi et al., 2022b). Therefore, it is necessary to conduct additional research to identify SPs composed of environmentally

Table 8
Limiting value and class of SP and natural polymers; the higher the hazard class the lower the toxicity (Buru Energy (Company), 2021; Lithner et al., 2011).

№	Name of Polymer	Limiting Value of Harm (LVH)	Hazard class
1	Copolymer of methacrylic acid and its ester	Toxicological/or	IV
		Sanitary and toxicological	II
2	Copolymer of methacrylate with butyl acrylate and methacrylic acid	Sanitary and toxicological	IV
3	Acrylamide copolymer and 75% sodium salt of acrylic acid	Toxicological	IV
4	Hydrolyzed polyacrylamide	Toxicological	IV
5	Cellulose derivative and synthetic polymeric polyalcohol	Toxicological	IV
6	Xanthan Gum	Non-toxicological	IV
7	N,N-dimethylacrylamide copolymer with calcium AMPS	Toxicological	II
8	Sulfonated organic polymer	Toxicological	II
9	Partially hydrolyzed polyacrylamide	Toxicological	IV

friendly monomers such as AMPS and AM that contain acrylamide and sulfonic acid groups (Davoodi et al., 2022b) for deployment in drilling fluids used in harsh conditions, e.g., high salt contamination, HPHT, and lost circulation.

3. There are two major disadvantages in using polymers based on polysaccharides as drilling fluid additives: (a) reaction with calcium and (b) insolubility. To overcome these issues, it is necessary to identify additional modifying additives that can withstand reactions with calcium and improve the solubility of polysaccharide-based polymers in drilling fluids. One approach is to modify the polysaccharides chemically to enhance their stability and solubility in the presence of divalent cations. Another approach is to combine polysaccharides with other materials, such as surfactants and/or nanoparticles, to improve their performance as drilling fluid additives.

4. In the process of developing a drilling fluid composition, it is necessary to consider the complex interactions between SPs and others chemical reagents present in the fluids, an SP's use should not adversely affect the other properties of the drilling fluid. Further research and testing is required to better delineate such interactions.

5. While using SP with WBDF and OBDF, the stability of the SP with bentonite and barite is limited. Moreover, some crosslinkers have unacceptable levels of toxicity, although polyethyleneimine is less toxic. Consequently, it is necessary to develop new environmentally-friendly crosslinkers.

6. Drilling fluid formulations with SP used to drill unstable clay-rich formations, have to provide sufficient inhibiting capacity combined with appropriate rheology and lubrication. In addition, a rock stability analysis must be performed in order to successfully drill wells in unstable clay-rich formations. New SPs are required that can deliver such properties under harsh sub-surface conditions which are mainly HPHT and salt contamination.

7. Many SPs, such as various modified cellulose, polyacrylamide, modified starch, used in drilling fluids display relatively low toxicity. However, more information is required regarding their biostability and long-term risks to the environment of their degradation products entering groundwater system.

8. Traditional SPs deployed in WBDF systems experience many problems such as high operating costs, poor stability, high reactivity, and strong corrosion. Therefore, in order to meet the requirements of drilling operations, it is necessary to develop new SPs with higher temperature resistance in WBDF that can be delivered at lower costs of supply.

9. The use of polymers as shale inhibitors is subject to certain limitations. High-temperature applications may cause polymer degradation, and the use of cationic polymers in WBDF can lead to the flocculation of bentonite clay, resulting in the segregation of drilling fluid components. There is, therefore, a need to develop biodegradable SPs that combine polymers and NPs, with low environmental impacts, that effectively control drilling fluid hydration by neutralizing reactive clay minerals and blocking pores.

10. Polymer-based materials, including SPs, polymer nanocomposites, and ionic liquids, which possess high thermal
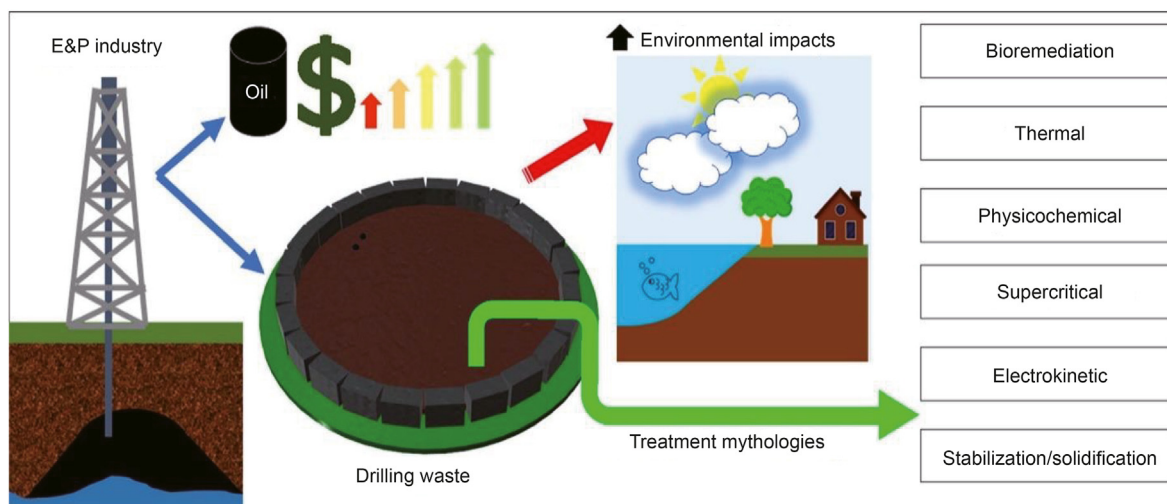
Fig. 19. Waste drilling fluid and rock cuttings treatment options. Reproduced from Elsevier (Pereira et al., 2022).

Type of SP
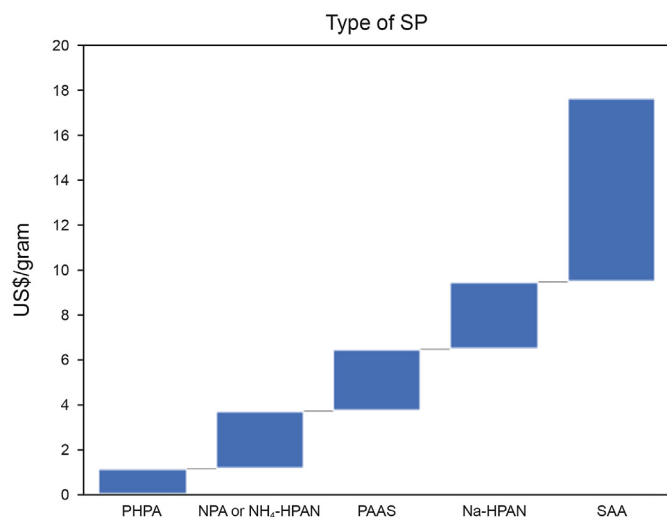
Fig. 20. Cost of commonly used SP in drilling fluids (Alibaba, 2023).

Name of monomers (purity>99%)
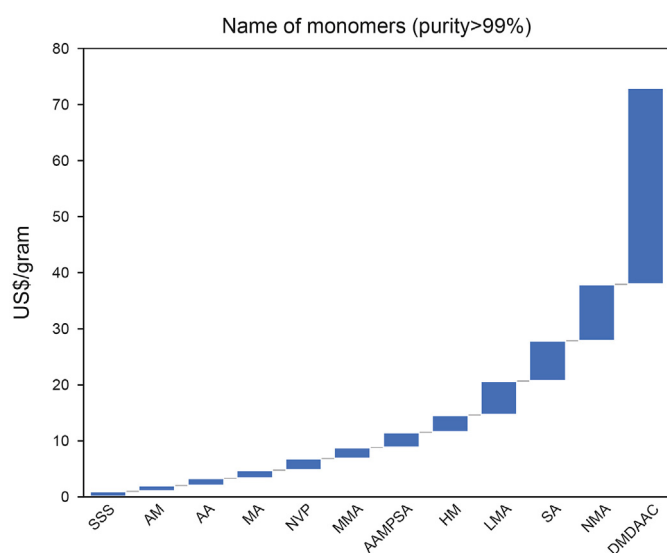
Fig. 21. Cost of common monomers used to synthesize SPs (the abbreviations can be found in the nomenclature) ("Alibaba Website," 2023).

stability, are regarded as potential shale inhibitors for use in the drilling of gas and oil reservoirs. However, the practicality of using these materials, specifically ionic liquids, co-polymers, and nanocomposites, as shale inhibitors in drilling fluid additives requires further evaluation. Factors such as the cost of synthesizing copolymers and polymer nano-composites, their toxicity, and hazard analysis for field applications should be taken into account. Although there is limited literature on the use of copolymers, polymer nano-composites, and ionic liquids as shale inhibitors, preliminary lab-scale studies have identified them as strong contenders for shale inhibition applications in WBDF.

11. Many monomers that are commonly used to synthesize polymers are extremely expensive, such as DMDAAC. Some monomers are inexpensive, such as AMPS, AM, and SSS. More effort is required to develop and utilize these lower-cost monomers in SP synthesis.
12. Current understanding of SP properties come from laboratory experiments. Many more field-scale tests are required

for the novel SPs identified in the laboratory in recent years. Moreover, many SPs designed for HPHT conditions are developed in laboratory conditions without due consideration of their cost of supply for commercial-scale deployments. Therefore, economic assessments should accompany laboratory tests associated with SPs, particularly those designed for HPHT conditions.

13. Operations associated with synthesizing polymers at commercial scales involve chemical hazards. The importance of avoiding environmental problems has led to stringent requirements for SP manufacturing technologies. It is necessary to further reinforce the requirements that production of SPs should be environmentally friendly, or at least have a minimal impact on the environment. Moreover, SPs considered for commercial-scale manufacture should be technologically recoverable and recyclable at the end of drilling operations, or rapidly biodegradable.
14. While polymerizing SPs for laboratory studies, inadequate attention is often paid to the type of monomer(s) involved, their unit costs and potential environmental/health impacts. It is essential that more attention be paid to such commercial, environmental and toxicological considerations when developing new SP for technically beneficial deployments in drilling fluids or for other industrial applications.

7. Summary and conclusions

This review presents a comprehensive assessment of SP applications as drilling fluid additives, the manufacturing methods used in SP synthesis, and their advantages and disadvantages. The main types of SPs tested in the field or in laboratory conditions are identified, with a focus on the novel SPs developed specifically to enhance drilling fluid performance. The applications of SPs in drilling fluids relating to fluid-loss reduction, viscosification, and clay/shale stabilization are addressed in detail. The environmental and economic consequences of SPs deployed in drilling fluids are also evaluated. The analysis leads to the following findings:

- The mechanisms of SPs in each type of drilling fluid are as follows: 1. WBDF: SPs provide a range of properties such as viscosity, fluid-loss control, and shale inhibition. The SPs interact with the water phase of the drilling fluid, providing a thickening effect that increases viscosity and reduces fluid loss. The SPs also adsorb onto the surface of the shale, preventing hydration and swelling, and reducing the risk of wellbore instability. 2. OBDF: SPs provide rheological properties such as viscosity, yield point, and gel strength. The SPs interact with the oil phase of the drilling fluid, improving the stability of the emulsion and preventing oil/water separation. The SPs also form a protective film on the borehole wall, reducing the risk of differential sticking and improving hole stability. 3. SBDF: SPs act as key components of the base fluid. SBDF typically contains synthetic hydrocarbon or ester-based fluids, which are less prone to contamination and provide improved environmental performance. The SPs provide a range of properties, including viscosity, fluid-loss control, and shale inhibition, similar to those involved in WBDF. However, the interaction of the SPs with the base fluid is different from that in WBDF, as the SPs are required to be compatible with the base fluid and maintain their properties over a wide range of temperatures and pressures. Overall, SPs play a critical role in improving the properties of drilling fluids and enhancing drilling efficiency in a range of drilling applications.
- The characteristics of SPs in drilling fluids are determined by the type of monomers used in their formation, as well as the

presence of cross-linking or branching groups within the polymer chain. These factors can impact the polymer's properties and its effectiveness in drilling fluids, such as its ability to inhibit shale hydration or control fluid loss. Additionally, the presence of cross-linking or branching groups can make SPs more or less susceptible to chemical alteration. The number of monomers employed in an SP's synthesis tend to determine its molecular weight.

- In terms of rheological properties, nano-polymer-based drilling fluids tend to outperform conventional drilling fluids under severe HPHT conditions. In addition, the enhanced sealing ability of nano-polymers preserves the formation by minimizing pressure transfer, increasing carrying capacity and reducing fluid contact between the wellbore wall and/or formation. By doing so it avoids formation damage and improves wellbore stability.

- SPs can be applied to improve drilling efficiency and avoid problems while drilling, such as stuck pipe or poor hole cleaning, thereby functioning as lubricant additives.

- Copolymers impart several desirable properties to low-solids solutions. As selective flocculants, these copolymers enhance the thickening properties of bentonite, thereby improving wellbore cleanup. Copolymers also improve cuttings separation from low-solids drilling fluids. In addition, they reduce friction losses in turbulent drilling-fluid-flow conditions.

- Based on worldwide experience, various chemical groups of monomers proved their high performance while synthesizing the SPs used in drilling fluids to improve their properties. For example, sulfonate, methyl, phenyl, furan, lactam, and pyrrolidine groups can enhance the thermal stability of SPs. Amide, hydroxyl, cellulose derivatives, quaternary ammonium, and acrylates can improve the rheological performance of SPs. Quaternary ammonium, pyridine, and cellulose derivatives help enhance the filtration control of SPs. Sulfonate, acrylamide, diallyl dimethyl ammonium chloride, itaconic acid, and fatty acid esters can improve the lubrication behavior of SPs. Carboxylate, sulfonate, quaternary ammonium, and polyoxyethylene chains help prevent flocculation of SPs at high temperatures. Also, carboxylic acid and sulfonic acid salts provide salt tolerance to SPs.

- In terms of environmental and cost aspects, SPs derived from acrylamide are best polymerized in aqueous solutions. This reduces energy costs involved in the separation of the initial monomers, reduces environmental pollution, and eliminates the dissolution of polymer reagents in aqueous solutions.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Nomenclature

Acronyms

AA	Acrylic acid
AA-AAm-C-Amyl	A grafted nanopolymer with Less Hydrophobic
AA-AAm-OD-C-Amyl	A grafted nanopolymer with More Hydrophobic
AADS	2-acrylamide-2-methylpropanesulfonic acid, acrylamide, dimethyl diallylammonium chloride, and sodium styrene sulfonate
AAMPSA	2-acryl-amido-2-methyl-1-propane sulfonic acid
AFR	Handled polyacrylamide-based friction reducers
AM	Acrylamide
AMPS	2-acrylamido-2-methy-l-propanesulfonic acid
AP	Associative Polymer Based Dimer Acid, Triethylenetetramine and Polyoxyethylene Lauramine
API	American petroleum institute
APS	Ammonium Persulfate
ASBA	Amphoteric polymer
ASML	Acrylamide, sodium p-styrenesulfonate, maleic anhydride, and lauryl methacrylate
BA	Butyl acrylate
BPEI	Polyethyleneimine
BPO	Initiator benzoyl peroxide
BT	Bentonite
$CaCl_2$	Calcium Chloride
CaO	Calcium Oxide
CD	Cyclodextrin
$C-g-AA-NH_2$	Acrylic acid grafted activated carbon
CMC	Carboxymethyl cellulose
CMC-DDA	Carboxymethylcellulose with Dodecylamine Polymer
CMCS	Carboxymethyl chitosan
CMS	Carboxy methyl starch
COF	Coefficient of Friction
CSGO	Novel graft copolymer
CuO	Copper oxide
DAM	Polyampholyte
DCS	Zwitterionic Copolymer
DMDAAC	Diallyl dimethyl ammonium chloride
DOH	Degree of hydrolysis
ECD	Equivalent Cycling Density
EOR	Enhanced oil recovery
EPI	Epichlorohydrin
FBWT	Four-Ball Wear Test
GGRE	Glycyrrhiza glabra root extract
GO	Graphene oxide
H_2O	Water
H_2O_2	Hydrogen Peroxide
HAH-Polymer	The hydrophobically associating heteropolymer
HAS	Amidocyanogenesilanols
HEC	Hydroxyethyl cellulose
HM	Hexadecyl methacrylate
HPG	Partially hydrophobized hyperbranched polyglycerols
HPWBDF	High-Performance water-based drilling fluid
HRCF	Hot Rolling Contact Fatigue
KCl	Potassium chloride
LHV	Limiting Value of Harm
LMA	Lauryl methacrylate
LS-g-PAAm	Lignosulfonate/acrylamide graft copolymers
MA	Methyl acrylate
MMA	Methyl methacrylate
Na-Bt	Sodium bentonite
NaCl	Sodium chloride
$NaHCO_3$	Bicarbonate of Soda
Na-HPAN	Polyhydrolyzed
$-NH_2$	Amino group
NMA	N'-methylenebis (acrylamide)
NP	Nanoparticle
NPA Or NH_4-HPAN	Potassium polyacrylate
NVCL	N-vinyl-ε-caprolactam
NVP	N-vinyl-2-pyrrolidone
OAP	Oil-absorbent polymer
OBDF	Oil-based drilling fluid
OECD	Economic Cooperation and Development
$-OH$	Hydroxyl group
OPLL	Oligo (poly-L-lysine)

P (ANAN)	Acrylamide, n-vinyl-2-pyrrolidone and 2-acrylamide-2-methylpropanesulfonic acid
PAAN-G	Polymer/graphene oxide composite
PAAS	Sodium polyacrylate
PAC	Polyanionic cellulose
PAC-DDAS-SiO$_2$	Polyanionic cellulose with acrylamide quaternary monomer and grafting to nano-silica
PAM-SiO$_2$NPs	Hydrophobic polymer-modified nanosilica
PEI	Polyethyleneimine
PEX	Amphoteric polymer
PHPA	Partially hydrolyzed poly-acrylamide
PMS	Self-Crosslinking Soap-Free Latexes
POAA	Poly(oxypropylene)-amidoamine
PRM	Polymeric rheology modifier
RO	Ring opening
ROP	Rate of penetration
SA	Sodium acrylate
SAA	Sodium acrylate/acrylamide
SBASC	Synthetic based acrylamide-styrene copolymer
SDKP	A copolymer viscosifier
SDNL	A novel polymer latex
SNF-FLOERGER	Copolymers with Different Degree of Hydrolysis
SiO$_2$	Silicon Dioxide
SNF-FLOERGER	SNF Holding Company Inc
SP	Synthetic polymers
SPM	Swelling polymer microspheres
SSMA	Sulfonated Styrene Maleic Anhydride Copolymer
SSS	Sodium p-styrenesulfonate
VPS	Vinyl-Phenyl Sulfonate
WBDF	Water-based drilling fluid
WSD	Wear Scar Diameter
ZnO	Zinc oxide
β-CD	β-Cyclodextrin
β-CDP	β-Cyclodextrin polymer
β-CDPMs	β-Cyclodextrin polymer microspheres

Parameters and variables

AV	Apparent viscosity
DT	Decomposition Temperature
Gel$_{10\ sec}$/Gel$_{10\ min}$	Gel strength per 10 sec/per 10 min
HPHT	High-pressure/high-temperature
LP-LT	Low pressure and low temperature
MW	Molecular weight
MW$_N$	Number Average Molecular Weight
MW$_W$	Weight Average Molecular Weight
MWη	Viscosity Average Molecular Weight
PDI	poly dispersity index
PV	Plastic viscosity
rpm	Revolutions per minute
YP	Yield points

References

Abbas, M.A., Zamir, A., Elraies, K.A., Mahmood, S.M., Rasool, M.H., 2021. A critical parametric review of polymers as shale inhibitors in water-based drilling fluids. J. Pet. Sci. Eng. 204, 108745. https://doi.org/10.1016/J.PETROL.2021.108745.

Abdelgawad, K.Z., Elzenary, M., Elkatatny, S., Mahmoud, M., Abdulraheem, A., Patil, S., 2019. New approach to evaluate the equivalent circulating density (ECD) using artificial intelligence techniques. J. Pet. Explor. Prod. Technol. 9, 1569–1578. https://doi.org/10.1007/S13202-018-0572-Y/FIGURES/11.

Abdollahi, M., Pourmahdi, M., Nasiri, A.R., 2018. Synthesis and characterization of lignosulfonate/acrylamide graft copolymers and their application in environmentally friendly water- based drilling fluid. J. Pet. Sci. Eng. 171, 484–494. https://doi.org/10.1016/J.PETROL.2018.07.065.

Aboulrous, A.A., Haddad, A.S., Rafati, R., Boyou, N.V., Alsabagh, A.M., 2022. Review of synthesis, characteristics and technical challenges of biodiesel based drilling fluids. J. Clean. Prod. 336, 130344. https://doi.org/10.1016/J.JCLEPRO.2021.130344.

Adhami, S., Jamshidi-Zanjani, A., Darban, A.K., 2021. Remediation of oil-based drilling waste using the electrokinetic-Fenton method. Process Saf. Environ. Protect. 149, 432–441. https://doi.org/10.1016/J.PSEP.2020.11.018.

Adnan Hamad, B., He, M., Xu, M., Liu, W., Mpelwa, M., Tang, S., Jin, L., Song, J., 2020. A novel amphoteric polymer as a rheology enhancer and fluid-loss control agent for water-based drilling muds at elevated temperatures. Cite This ACS Omega 5, 8495. https://doi.org/10.1021/acsomega.9b03774.

Aftab, A., Ismail, A.R., Ibupoto, Z.H., 2017. Enhancing the rheological properties and shale inhibition behavior of water-based mud using nanosilica, multi-walled carbon nanotube, and graphene nanoplatelet. Egypt. J. Petrol. 26, 291–299. https://doi.org/10.1016/J.EJPE.2016.05.004.

Agwu, O.E., Akpabio, J.U., Ekpenyong, M.E., Inyang, U.G., Asuquo, D.E., Eyoh, I.J., Adeoye, O.S., 2021a. A critical review of drilling mud rheological models. J. Pet. Sci. Eng. 203, 108659. https://doi.org/10.1016/J.PETROL.2021.108659.

Agwu, O.E., Akpabio, J.U., Ekpenyong, M.E., Inyang, U.G., Asuquo, D.E., Eyoh, I.J., Adeoye, O.S., 2021b. A comprehensive review of laboratory, field and modelling studies on drilling mud rheology in high temperature high pressure (HTHP) conditions. J. Nat. Gas Sci. Eng. 94, 104046. https://doi.org/10.1016/J.JNGSE.2021.104046.

Ahmad, H.M., Kamal, M.S., Al-Harthi, M.A., 2018. High molecular weight copolymers as rheology modifier and fluid loss additive for water-based drilling fluids. J. Mol. Liq. 252, 133–143. https://doi.org/10.1016/J.MOLLIQ.2017.12.135.

Ahmed, N., Alam, M.S., Salam, M.A., 2020. Experimental analysis of drilling fluid prepared by mixing iron (III) oxide nanoparticles with a KCl–Glycol–PHPA polymer-based mud used in drilling operation. J. Pet. Explor. Prod. Technol. 10, 3389–3397. https://doi.org/10.1007/s13202-020-00933-1.

Akpan, E.U., Enyi, G.C., Nasr, G.G., 2020. Enhancing the performance of xanthan gum in water-based mud systems using an environmentally friendly biopolymer. J. Pet. Explor. Prod. Technol. 10, 1933–1948. https://doi.org/10.1007/S13202-020-00837-0/FIGURES/14.

Al-Hameedi, A.T.T., Alkinani, H.H., Dunn-Norman, S., Al-Alwani, M.A., Alshammari, A.F., Albazzaz, H.W., Alkhamis, M.M., Mutar Rusul, A., Al-Bazzaz, W.H., 2019. Proposing a new eco-friendly drilling fluid additive to enhance the filtration properties of water-based drilling fluid systems. Soc. Pet. Eng.-SPE Gas Oil Technol. Showc. Conf. https://doi.org/10.2118/198651-MS, 2019, GOTS.

Al-Muhailan, M.S., Rajagopalan, A., Al-Shayji, A.K., Jadhav, P.B., Khatib, F.I., 2014. Successful application of customized fluid using specialized synthetic polymer in high pressured wells to mitigate differential stikcing problems by minimizing pore pressure transmission. Soc. Pet. Eng. - Int. Pet. Technol. Conf. 3, 1822–1834. https://doi.org/10.2523/IPTC-17913-MS.

Al-Shargabi, M., Davoodi, S., Wood, D.A., Al-Musai, A., Rukavishnikov, V.S., Minaev, K.M., 2022a. Nanoparticle applications as beneficial oil and gas drilling fluid additives: a review. J. Mol. Liq. 352, 118752. https://doi.org/10.1016/j.molliq.2022.118725.

Al-Shargabi, M., Davoodi, S., Wood, D.A., Rukavishnikov, V.S., Minaev, K.M., 2022b. Carbon Dioxide applications for enhanced oil recovery assisted by nano-particles: recent developments. ACS Omega 7 (12), 9984–9994. https://doi.org/10.1021/ACSOMEGA.1C07123.

Ali, I., Ahmad, M., Ganat, T., 2022. Biopolymeric formulations for filtrate control applications in water-based drilling muds: a review. J. Pet. Sci. Eng. 210, 110021. https://doi.org/10.1016/J.PETROL.2021.110021.

Ali Khan, M., Khan, M.A., Al-Salim, H.S., Arsanjani, L.N., Akademia Baru, P., 2018. Development of high temperature high pressure (HTHP) water based drilling mud using synthetic polymers, and nanoparticles. J. Adv. Res. Fluid Mech. Therm. Sci. 45, 99–108.

Alibaba, 2023. Website [WWW Document] URL. https://www.alibaba.com.

An, Y., Yu, P., 2018. A strong inhibition of polyethyleneimine as shale inhibitor in drilling fluid. J. Pet. Sci. Eng. 161, 1–8. https://doi.org/10.1016/J.PETROL.2017.11.029.

Anderson, R.L., Ratcliffe, I., Greenwell, H.C., Williams, P.A., Cliffe, S., Coveney, P.V., 2010. Clay swelling-A challenge in the oilfield. Earth Sci. Rev. 98, 201–216. https://doi.org/10.1016/J.EARSCIREV.2009.11.003.

Apaleke, A.S., Al-Majed, A., Hossain, M.E., 2012. Drilling fluid: state of the art and future. Trend. Soc. Pet. Eng. - North Africa Tech. Conf. Exhib. 2012, NATC 2012 Manag. Hydrocarb. Resour. a Chang. Environ. 1, 101–113. https://doi.org/10.2118/149555-MS.

ASTM E1367-03, 2014. Methods for Assessing the Toxicity of Sediment-Associated Contaminants with Estuarine and Marine Amphipods. ASTM Inter, West Conshohocken.

Austin, E.H., 1983. Drilling engineering handbook. Drill. Eng. Handb. https://doi.org/10.1007/978-94-009-7261-2.

Baba Hamed, S., Belhadri, M., 2009. Rheological properties of biopolymers drilling fluids. J. Pet. Sci. Eng. 67, 84–90. https://doi.org/10.1016/J.PETROL.2009.04.001.

Bakke, T., Klungsøyr, J., Sanni, S., 2013. Environmental impacts of produced water and drilling waste discharges from the Norwegian offshore petroleum industry. Mar. Environ. Res. 92, 154–169. https://doi.org/10.1016/J.MARENVRES.2013.09.012.

Balaga, D.K., Kulkarni, S.D., 2022. A review of synthetic polymers as filtration control additives for water-based drilling fluids for high-temperature applications. J. Pet. Sci. Eng. 215, 110712. https://doi.org/10.1016/J.PETROL.2022.110712.

Balaji, A.B., Pakalapati, H., Khalid, M., Walvekar, R., Siddiqui, H., 2017. Natural and synthetic biocompatible and biodegradable polymers. Biodegrad. Biocompatible Polym. Compos. Process. Prop. Appl. 3–32. https://doi.org/10.1016/B978-0-08-100970-3.00001-8.

Balla, E., Daniilidis, V., Karlioti, G., Kalamas, T., Stefanidou, M., Bikiaris, N.D., Vlachopoulos, A., Koumentakou, I., Bikiaris, D.N., 2021. Poly(lactic acid): a versatile biobased polymer for the future with multifunctional properties—from monomer synthesis, polymerization techniques and molecular weight increase to PLA applications. Polymers 13 (11), 1822. https://doi.org/10.3390/POLYM13111822.

Beg, M., Sharma, S., Ojha, U., 2018. Effect of cationic copolyelectrolyte additives on drilling fluids for shales. J. Pet. Sci. Eng. 161, 506–514. https://doi.org/10.1016/J.PETROL.2017.12.009.

Beg, M., Singh, P., Sharma, S., Ojha, U., 2019. Shale inhibition by low-molecular-weight cationic polymer in water-based mud. J. Pet. Explor. Prod. Technol. 9, 1995–2007. https://doi.org/10.1007/S13202-018-0592-7/TABLES/5.

Bergman, W.E., Fisher, H.B., 2002. Bentonite suspensions-Effect of sodium chloride, sodium hydroxide, quebracho, and sodium carboxymethylcellulose upon physical properties. Ind. Eng. Chem. 42, 1895–1900. https://doi.org/10.1021/IE50489A050.

Bergström, J., 2015. Mechanics of Solid Polymers, Mechanics of Solid Polymers. William Andrew Publishing, pp. 1–17. https://doi.org/10.1016/B978-0-323-31150-2.00001-7.

Bland, R., Mullen, G., Gonzalez, Y., Harvey, F., Pless, M., 2006. HP/HT Drilling Fluids Challenges. Proc. IADC/SPE Asia Pacific Drill. Technol. Conf. 2006 - Meet. Value Chall. Performance, Deliv. Cost, pp. 362–372. https://doi.org/10.2118/103731-MS.

Blkoor, S.O., Mohd Norddin, M.N.A., Ismail, I., Oseh, J.O., Agi, A., Gbadamosi, A.O., Okoli, N.O., Onyejekwe, I.M., Risal, A.R., 2022. Amphipathic anionic surfactant modified hydrophilic polyethylene glycol-nanosilica composite as effective viscosifier and filtration control agent for water-based drilling muds. Arab. J. Chem. 15, 103741. https://doi.org/10.1016/J.ARABJC.2022.103741.

Boutammine, H., Salem, Z., Khodja, M., 2020. Petroleum drill cuttings treatment using stabilization/solidification and biological process combination. Soil Sediment Contam.: Int. J. 29 (4), 369–383. https://doi.org/10.1080/15320383.2020.1722982.

Browning, W.C., 1955. Lignosulfonate stabilized emulsions in oil well drilling fluids. J. Petrol. Technol. 7, 9–15. https://doi.org/10.2118/393-G.

Buru Energy (Company), 2021. Well Drilling Environment Plan: Additional Chemical Disclosure Summary Document.

Byzov, A., Pak, A., Kuznetsova, D., Ostapenko, G., 2019. Analysis of the statistical correlation between the estimated value of individual risk and the hazard class of a hazardous production facility in the Russian Federation. E3S Web Conf 140. https://doi.org/10.1051/E3SCONF/201914008004.

Caenn, R., Darley, H.C.H., Gray, G.R., 2016. Composition and properties of drilling and completion fluids. In: Composition and Properties of Drilling and Completion Fluids, seventh ed. Gulf Professional Publishing. Seventh Edition.

Cancelas, A.J., Monteil, V., McKenna, T.F.L., 2016. Influence of activation conditions on the gas phase polymerisation of propylene. Macromol. Symp. 360, 133–141. https://doi.org/10.1002/MASY.201500099.

Canfarotta, F., Poma, A., Guerreiro, A., Piletsky, S., 2016. Solid-phase synthesis of molecularly imprinted nanoparticles. Nat. Protoc. 11, 443–455. https://doi.org/10.1038/nprot.2016.030.

Celino, K.N., Souza, E.A. de, Balaban, R. de C., 2022. Emulsions of glycerol in olefin: a critical evaluation for application in oil well drilling fluids. Fuel 308. https://doi.org/10.1016/j.fuel.2021.121959.

Chang, I., Lee, M., Tran, A.T.P., Lee, S., Kwon, Y.M., Im, J., Cho, G.C., 2020. Review on biopolymer-based soil treatment (BPST) technology in geotechnical engineering practices. Transp. Geotech. 24, 100385. https://doi.org/10.1016/J.TRGEO.2020.100385.

Chaudhary, V., Sharma, S., 2019. Suspension polymerization technique: parameters affecting polymer properties and application in oxidation reactions. J. Polym. Res. 26, 1–12. https://doi.org/10.1007/S10965-019-1767-8/TABLES/4.

Chen, Y., Wu, R., Zhou, J., Chen, H., Tan, Y., 2021. A novel hyper-cross-linked polymer for high-efficient fluid-loss control in oil-based drilling fluids. Colloids Surfaces A Physicochem. Eng. Asp. 626, 127004. https://doi.org/10.1016/J.COLSURFA.2021.127004.

Chesser, B.G., Enright, D.P., 1980. High-temperature stabilization of drilling fluids with a low-molecular-weight copolymer. J. Petrol. Technol. 32, 950–956. https://doi.org/10.2118/8224-PA.

Chu, Q., Lin, L., 2019. Effect of molecular flexibility on the rheological and filtration properties of synthetic polymers used as fluid loss additives in water-based drilling fluid. RSC Adv. 9, 8608–8619. https://doi.org/10.1039/C9RA00038K.

Chu, Q., Su, J., Lin, L., 2020. Inhibition performance of amidocyanogen silanol in water-based drilling fluid. Appl. Clay Sci. 185, 105315. https://doi.org/10.1016/J.CLAY.2019.105315.

Chudinova, I.V., Nikolaev, N.I., Petrov, A.A., 2019. Design of Domestic Compositions of Drilling Fluids for Drilling Wells in Shales.

Cummings, S., Zhang, Y., Smeets, N., Cunningham, M., Dubé, M.A., 2019. On the use of starch in emulsion polymerizations. Processes 7 (3), 140. https://doi.org/10.3390/PR7030140.

Dai, C., Zhao, F., 2018. Drilling fluid chemistry. Oilfield Chem. 21–84. https://doi.org/10.1007/978-981-13-2950-0_2.

Daneshfar, R., Moghadasi, J., Mojtaba Bassir, S., Kamranfar, P., Mohammadzadeh, H., 2018. Prediction of Petrophysical/Geophysical Parameters by Artificial Intelligence View Project Simulation of Low Salinity Water Injection Process in a Carbonate Reservoir in Southern Part of Iran: Case Study View Project Shale Hydration Inhibitive Materials a.

Dardir, M.M., Ibrahime, S., Soliman, M., Desouky, S.D., Hafiz, A.A., 2014. Preparation

and evaluation of some esteramides as synthetic based drilling fluids. Egypt. J. Petrol. 23, 35–43. https://doi.org/10.1016/J.EJPE.2014.02.006.

Davoodi, S., Ahmed Ramazani, S.A.A., Soleimanian, A., Fellah Jahromi, A., 2019. Application of a novel acrylamide copolymer containing highly hydrophobic comonomer as filtration control and rheology modifier additive in water-based drilling mud. J. Pet. Sci. Eng. 180, 747–755. https://doi.org/10.1016/J.PETROL.2019.04.069.

Davoodi, S., Ramazani, A., Rukavishnikov, V., Minaev, K., 2021. Insights into application of acorn shell powder in drilling fluid as environmentally friendly additive: filtration and rheology. Int. J. Environ. Sci. Technol. 18, 835–848. https://doi.org/10.1007/S13762-020-02880-0/FIGURES/8.

Davoodi, S., Al-Shargabi, M., Wood, D.A., Rukavishnikov, V.S., Minaev, K.M., 2022a. Experimental and field applications of nanotechnology for enhanced oil recovery purposes: a review. Fuel 324, 124669. https://doi.org/10.1016/J.FUEL.2022.124669.

Davoodi, S., Al-Shargabi, M., Woodc, D.A., Rukavishnikov, V.S., Minaev, K.M., 2022b. Thermally stable and salt-resistant synthetic polymers as drilling fluid additives for deployment in harsh sub-surface conditions: a review. J. Mol. Liq. 121117. https://doi.org/10.1016/J.MOLLIQ.2022.121117.

De Vos, L., Van de Voorde, B., Van Daele, L., Dubruel, P., Van Vlierberghe, S., 2021. Poly(alkylene terephthalate)s: from current developments in synthetic strategies towards applications. Eur. Polym. J. 161, 110840. https://doi.org/10.1016/J.EURPOLYMJ.2021.110840.

Deville, J.P., 2022. Drilling fluids. Fluid Chem. Drill. Complet. 115–185. https://doi.org/10.1016/B978-0-12-822721-3.00010-1.

Dias, F.T.G., Souza, R.R., Lucas, E.F., 2015. Influence of modified starches composition on their performance as fluid loss additives in invert-emulsion drilling fluids. Fuel 140, 711–716. https://doi.org/10.1016/j.fuel.2014.09.074.

Dong, X., Sun, J., Huang, X., Lv, K., Zhou, Z., Gao, C., 2022. Nano-laponite/polymer composite as filtration reducer on water-based drilling fluid and mechanism study. R. Soc. Open Sci. 9. https://doi.org/10.1098/RSOS.220385/.

Douka, A., Vouyiouka, S., Papaspyridi, L.M., Papaspyrides, C.D., 2018. A review on enzymatic polymerization to produce polycondensation polymers: the case of aliphatic polyesters, polyamides and polyesteramides. Prog. Polym. Sci. 79, 1–25. https://doi.org/10.1016/J.PROGPOLYMSCI.2017.10.001.

Du, H., Lv, K., Sun, J., Huang, X., Shen, H., 2022. Styrene-lauryl acrylate rubber nanogels as a plugging agent for oil-based drilling fluids with the function of improving emulsion stability. Gels 9, 23. https://doi.org/10.3390/GELS9010023/S1.

Dye, W., d'Augereau, K., Hansen, N., Otto, M., Shoults, L., Leaper, R., Clapper, D., Xiang, T., 2006. New water-based mud balances high-performance drilling and environmental compliance. SPE Drill. Complet. 21, 255–267. https://doi.org/10.2118/92367-PA.

Ebnesajjad, S., 2015. Polymerization and finishing of tetrafluoroethylene. In: Fluoroplastics. William Andrew Publishing, pp. 95–156. https://doi.org/10.1016/B978-1-4557-3199-2.00008-2.

Edeleva, M., Marien, Y.W., Van Steenberge, P.H.M., D'Hooge, D.R., 2021. Impact of side reactions on molar mass distribution, unsaturation level and branching density in solution free radical polymerization of n -butyl acrylate under well-defined lab-scale reactor conditions. Polym. Chem. 12, 2095–2114. https://doi.org/10.1039/D1PY00151E.

El-Hamshary, H., Fouda, M.M.G., Moydeen, M., Al-Deyab, S.S., 2014. Removal of heavy metal using poly (N-vinylimidazole)-grafted-carboxymethylated starch. Int. J. Biol. Macromol. 66, 289–294. https://doi.org/10.1016/J.IJBIOMAC.2014.02.047.

El-hoshoudy, A.N., Desouky, S.E.M., Al-Sabagh, A.M., Betiha, M.A., kady, M.Y.E., Mahmoud, S., 2017. Evaluation of solution and rheological properties for hydrophobically associated polyacrylamide copolymer as a promised enhanced oil recovery candidate. Egypt. J. Petrol. 26, 779–785. https://doi.org/10.1016/J.EJPE.2016.10.012.

EPA, 1993. Oil and Gas Extraction Point Source Category, Offshore Subcategory; Effluent Limitations Guidelines and New Source Performance Standards.

Ezell, R.G., Ezzat, A.M., Turner, J.K., Wu, J.J., 2010. New filtration-control polymer for improved brine-based reservoir drilling-fluids performance at temperatures in excess of 400°F and high pressure. Proc.-SPE Annu. Tech. Conf. Exhib. 1, 25–32. https://doi.org/10.2118/128119-MS.

Fadairo, A., Falode, O., Ako, C., Adeyemi, A., Ameloko, A., Fadairo, A., Falode, O., Ako, C., Adeyemi, A., Ameloko, A., 2012. Novel formulation of environmentally friendly oil based drilling mud. New Technol. Oil Gas Ind. https://doi.org/10.5772/51236.

Fagundes, K.R.S., Da Souza Luz, R.C., Fagundes, F.P., De Carvalho Balaban, R., 2018. Effect of carboxymethylcellulose on colloidal properties of calcite suspensions in drilling fluids. Polímeros 28, 373–379. https://doi.org/10.1590/0104-1428.11817.

Ferreira, C.C., Teixeira, G.T., Lachter, E.R., Nascimento, R.S.V., 2016. Partially hydrophobized hyperbranched polyglycerols as non-ionic reactive shale inhibitors for water-based drilling fluids. Appl. Clay Sci. 132–133, 122–132. https://doi.org/10.1016/J.CLAY.2016.05.025.

Fink, J.K., 2021. Petroleum Engineer's Guide to Oil Field Chemicals and Fluids. https://doi.org/10.1016/C2009-0-61871-7.

Friedheim, J., 1997. Second-generation synthetic drilling fluids. J. Petrol. Technol. 49, 724–728. https://doi.org/10.2118/38251-JPT.

Fulcrand, H., Doco, T., Es-Safi, N.E., Cheynier, V., Moutounet, M., 1996. Study of the acetaldehyde induced polymerisation of flavan-3-ols by liquid chromatography-ion spray mass spectrometry. J. Chromatogr. A 752, 85–91.

https://doi.org/10.1016/S0021-9673(96)00485-2.

Gaillard, N., Thomas, A., Bataille, S., Dupuis, G., Daguerre, F., Favéro, C., 2017. Advanced selection of polymers for EOR considering shear and hardness tolerance properties. In: IOR Norw. 2017-19th Eur. Symp. Improv. Oil Recover. Sustain. IOR a Low Oil Price World 2017, 1–18. https://doi.org/10.3997/2214-4609.201700333/CITE/REFWORKS.

Gaurina-medimurec, N., Pašić, B., Mijić, P., Medved, I., 2021. Drilling fluid and cement slurry design for naturally fractured reservoirs. Appl. Sci. 11 (2), 767. https://doi.org/10.3390/APP11020767.

Gautam, S., Guria, C., 2020. Optimal synthesis, characterization, and performance evaluation of high-pressure high-temperature polymer-based drilling fluid: the effect of viscoelasticity on cutting transport, filtration loss, and lubricity. SPE J. 25, 1333–1350. https://doi.org/10.2118/200487-PA.

Gautam, S., Guria, C., Rajak, V.K., 2022. A state of the art review on the performance of high-pressure and high-temperature drilling fluids: towards understanding the structure-property relationship of drilling fluid additives. J. Pet. Sci. Eng. 213, 110318. https://doi.org/10.1016/J.PETROL.2022.110318.

Ge, W.F., Chen, M., Jin, Y., Xie, S.X., Jiang, G.C., 2012. A "dual protection" drilling fluid system and its application. Petrol. Sci. Technol. 30, 1274–1284. https://doi.org/10.1080/10916466.2010.504934.

Geng, Y., Sun, J., Wang, J., Wang, R., Yang, J., Wang, Q., Ni, X., 2021. Modified nanopolystyrene as a plugging agent for oil-based drilling fluids applied in shale formation. Energy Fuel. 35, 16543–16552. https://doi.org/10.1021/ACS.E-NERGYFUELS.1C02546/ASSET/IMAGES/MEDIUM/EF1C02546_0017 (GIF).

Gerali, Francesco, 2018. Drilling Fluids, Residence at the. IEEE History Center.

Ghasemi, N., Mirzaee, M., Aghayari, R., Maddah, H., 2018. Investigating created properties of nanoparticles based drilling mud. Heat Mass Transf. und Stof-fuebertragung 54, 1381–1393. https://doi.org/10.1007/s00231-017-2229-7.

Ghazali, N.A., Naganawa, S., Masuda, Y., Ibrahim, W.A., Abu Bakar, N.F., 2018. Eco-friendly drilling fluid deflocculant for drilling high temperature well: a review. Proc. Int. Conf. Offshore Mech. Arct. Eng.-OMAE 8. https://doi.org/10.1115/OMAE2018-78149.

Gholami, R., Elochukwu, H., Fakhari, N., Sarmadivaleh, M., 2018. A review on borehole instability in active shale formations: interactions, mechanisms and inhibitors. Earth Sci. Rev. 177, 2–13. https://doi.org/10.1016/J.EARSCIREV.2017.11.002.

Grattan-Guinness, I., 2014. From anomaly to fundament: louis Poinsot's theories of the couple in mechanics. Hist. Math. 41, 82–102. https://doi.org/10.1016/J.HM.2013.08.002.

Gu, J., Gan, P., Dong, L., Wang, S., Tang, N., 2019. Prediction of water channeling along cement-aquifuge interface in CBM well: model development and experimental verification. J. Pet. Sci. Eng. 173, 536–546. https://doi.org/10.1016/J.PETROL.2018.10.040.

Gueciouer, A., Benmounah, A., Sekkiou, H., Kheribet, R., Safi, B., 2017. Valorization of KCl/PHPA system of water-based drilling fluid in presence of reactive clay: application on Algerian field. Appl. Clay Sci. 146, 291–296. https://doi.org/10.1016/J.CLAY.2017.06.007.

Hall, L.J., Deville, J.P., Santos, C.M., Rojas, O.J., Araujo, C.S., 2018. Nanocellulose and biopolymer blends for high-performance water-based drilling fluids. Soc. Pet. Eng.-IADC/SPE Drill. Conf. Exhib. DC. https://doi.org/10.2118/189577-MS.

Han, Z., Jiang, G., Li, Q., 2014. Application of a novel associative polymer on synthetic-based drilling muds for deepwater drilling. SOCAR Proc 2. https://doi.org/10.5510/OGP20140200193.

Hay, W.W., 2021. The earth is a sphere and rotates. Exp. a Small Planet 543–574. https://doi.org/10.1007/978-3-030-76339-8_24.

He, X., 2010. The Past, Present and future of aphron based drilling fluids. Proc. - SPE Annu. Tech. Conf. Exhib. 7, 5992–6005. https://doi.org/10.2118/141136-STU.

He, Y., Wu, Y., Zhang, M., Zhang, Y., Ding, H., Zhang, K., 2021. Controlled ring-opening polymerization of macrocyclic monomers based on the quinone methide elimination cascade reaction. Macromolecules 54, 5797–5805. https://doi.org/10.1021/ACS.MACROMOL.1C00872/SUPPL_FILE/MA1C00872_SI_001.PDF.

Hernandez, E.D.D., Reyes-Romero, J.R., 2019. Materials for Biomedical Engineering: Thermoset and Thermoplastic Polymers, Materials for Biomedical Engineering: Thermoset and Thermoplastic Polymers. Elsevier. https://doi.org/10.1016/B978-0-12-816874-5.00014-1.

Huang, W., Zhao, C., Qiu, Z., Leong, Y.K., Zhong, H., Cao, J., 2015. Synthesis, characterization and evaluation of a quadripolymer with low molecular weight as a water based drilling fluid viscosity reducer at high temperature (245 °C). Polym. Int. 64, 1352–1360. https://doi.org/10.1002/PI.4923.

Huang, Y., Zhang, D., Zheng, W., 2019. Synthetic copolymer (AM/AMPS/DMDAAC/SSS) as rheology modifier and fluid loss additive at HTHP for water-based drilling fluids. J. Appl. Polym. Sci. 136. https://doi.org/10.1002/APP.47813.

Huo, J.H., Peng, Z.G., Ye, Z.B., Feng, Q., Zheng, Y., Zhang, J., Liu, X., 2018. Investigation of synthesized polymer on the rheological and filtration performance of water-based drilling fluid system. J. Pet. Sci. Eng. 165, 655–663. https://doi.org/10.1016/J.PETROL.2018.03.003.

Ibrahim, M.A., Saleh, T.A., 2020. Partially aminated acrylic acid grafted activated carbon as inexpensive shale hydration inhibitor. Carbohydr. Res. 491, 107960. https://doi.org/10.1016/J.CARRES.2020.107960.

Ibrahim, D.S., Sami, N.A., Balasubramanian, N., 2017. Effect of barite and gas oil drilling fluid additives on the reservoir rock characteristics. J. Pet. Explor. Prod. Technol. 7, 281–292. https://doi.org/10.1007/S13202-016-0258-2/TABLES/12.

Ibrahim, A.O., Momoh, O.R., Isa, M.T., 2019. Improving rheological properties of Gambe clay for drilling fluid application using fermentable polymers. Niger. J. Technol. Dev. 15, 113–120. https://doi.org/10.4314/njtd.v15i4.2.

Imam, A., Suman, S.K., Ghosh, D., Kanaujia, P.K., 2019. Analytical approaches used in monitoring the bioremediation of hydrocarbons in petroleum-contaminated soil and sludge. TrAC, Trends Anal. Chem. 118, 50–64. https://doi.org/10.1016/J.TRAC.2019.05.023.

Imohiosen, O.U.O., Akintola, S.A., 2021. Effect of sodium carboxymethyl cellulose from delonix regia sawdust on rheological and filtration properties of water based drilling fluid. Soc. Pet. Eng. - SPE Niger. Annu. Int. Conf. Exhib. 2021. https://doi.org/10.2118/207200-MS.

ISO10253, 2006. Water Quality—Marine Algal Growth Inhibition Test with Skeletonema Costatum and Phaeodactylum Tricornutum (Geneva, Switzerland).

ISO14669, 1999. Water Quality — Determination of Acute Lethal Toxicity to Marine Copepods (Copepoda, Crustacea) (Geneva, Switzerland).

ISO14971, 2015. Hazard and Hazardous Situation [WWW Document]. Johner-Institute. URL. https://www.johner-institute.com/articles/risk-management-iso-14971/hazard-and-hazardous-situation/.

ISO16778, 2015. Water Quality — Calanoid Copepod Early-Life Stage Test with Acartia Tonsa (Geneva, Switzerland).

Jain, R., Mahto, V., 2015. Evaluation of polyacrylamide/clay composite as a potential drilling fluid additive in inhibitive water based drilling fluid system. J. Pet. Sci. Eng. 133, 612–621. https://doi.org/10.1016/J.PETROL.2015.07.009.

Jain, R., Mahto, V., 2017. Formulation of a water based drilling fluid system with synthesized graft copolymer for troublesome shale formations. J. Nat. Gas Sci. Eng. 38, 171–181. https://doi.org/10.1016/J.jngse.2016.12.018.

Jain, R., Paswan, B.K., Mahto, T.K., Mahto, V., 2017. Study the effect of synthesized graft copolymer on the inhibitive water based drilling fluid system. Egypt. J. Pet. 26, 875–883. https://doi.org/10.1016/J.EJPE.2015.03.016.

Jayaweera, C.D., Narayana, M., 2021. Multi-objective dynamic optimization of seeded suspension polymerization process. Chem. Eng. J. 426, 130797. https://doi.org/10.1016/J.CEJ.2021.130797.

Ji, G., Wang, H., Huang, H., Cui, M., Yulong, F., Ma, Y., Sun, X., 2021. Achieving Improved Drilling Performance with Hole Cleaning Technology in Horizontal Shale Gas Wells in Sichuan Basin of China. International Petroleum Technology Conference. https://doi.org/10.2523/IPTC-21214-MS.

Jia, X., Zhao, X., Chen, B., Egwu, S.B., Huang, Z., 2022. Polyanionic cellulose/hydrophilic monomer copolymer grafted silica nanocomposites as HTHP drilling fluid-loss control agent for water-based drilling fluids. Appl. Surf. Sci. 578, 152089. https://doi.org/10.1016/J.APSUSC.2021.152089.

Jiang, G., Li, Y., Kong, Y., Ling, L., Feng, C., Zeng, C., 2015. Application of acrylate copolymers in the drilling-in completion fluid for low and extra low permeability reservoirs. Energy Sources, Part A Recover. Util. Environ. Eff. 37, 633–641. https://doi.org/10.1080/15567036.2011.592905.

Jiang, G.C., Qi, Y.R., An, Y.X., Huang, X.B., Ren, Y.J., 2016. Polyethyleneimine as shale inhibitor in drilling fluid. Appl. Clay Sci. 127–128, 70–77. https://doi.org/10.1016/J.CLAY.2016.04.013.

Jiao, G., Zhu, S., Ye, Z., Shu, Z., Wang, X., Wang, D., 2023. The effect of shear on the properties of an associated polymer solution for oil displacement. Polymers 15 (3), 616. https://doi.org/10.3390/POLYM15030616.

John, G., Nagarajan, S., Vemula, P.K., Silverman, J.R., Pillai, C.K.S., 2019. Natural monomers: a mine for functional and sustainable materials – occurrence, chemical modification and polymerization. Prog. Polym. Sci. 92, 158–209. https://doi.org/10.1016/J.PROGPOLYMSCI.2019.02.008.

Jönsson, J.E., Karlsson, O.J., Hassander, H., Törnell, B., 2007. Semi-continuous emulsion polymerization of styrene in the presence of poly(methyl methacrylate) seed particles. Polymerization conditions giving core–shell particles. Eur. Polym. J. 43, 1322–1332. https://doi.org/10.1016/J.EURPOLYMJ.2007.01.027.

Kania, D., Yunus, R., Omar, R., Abdul Rashid, S., Mohamad Jan, B., 2015. A review of biolubricants in drilling fluids: recent research, performance, and applications. J. Pet. Sci. Eng. 135, 177–184. https://doi.org/10.1016/J.PETROL.2015.09.021.

Kariman Moghaddam, A., Davoodi, S., Ramazani, S.A.A., Minaev, K.M., 2022. Mesoscopic theoretical modeling and experimental study of rheological behavior of water-based drilling fluid containing associative synthetic polymer, bentonite, and limestone. J. Mol. Liq. 347, 117950. https://doi.org/10.1016/J.MOLLIQ.2021.117950.

Khalil, M., Mohamed Jan, B., 2012. Viscoplastic modeling of a novel lightweight biopolymer drilling fluid for underbalanced drilling. Ind. Eng. Chem. Res. 51, 4056–4068. https://doi.org/10.1021/IE200811Z.

Koh, J.K., Lai, C.W., Johan, M.R., Gan, S.S., Chua, W.W., 2022. Recent advances of modified polyacrylamide in drilling technology. J. Pet. Sci. Eng. 215, 110566. https://doi.org/10.1016/J.PETROL.2022.110566.

Konstantin, M.M., Vyacheslav, A.Y., Daria, O.M., Aleksey, S.Z., Rashid, R.S., Mikhail, O.A., Sushil, K.P., 2018. Comparative research of filtration reducers based on carboximethyl esters of starch and cellulose in modern drilling mud systems. Bull. Tomsk Polytech. Univ. Geo Assets Eng. 57–66.

Krzysztof, M., Thomas, P.D., 2002. Handbook of Radical Polymerization. John Wiley & Sons, Inc. John Wiley & Sons, Inc. https://doi.org/10.1002/0471220450.

Kuma, M., Das, B.M., Talukdar, P., 2020. The effect of salts and haematite on carboxymethyl cellulose–bentonite and partially hydrolyzed polyacrylamide–bentonite muds for an effective drilling in shale formations. J. Pet. Explor. Prod. Technol. 10, 395–405. https://doi.org/10.1007/S13202-019-0722-X/FIGURES/33.

Lambert, S., Sinclair, C., Boxall, A., 2014. Occurrence, degradation, and effect of polymer-based materials in the environment. Rev. Environ. Contam. Toxicol. 227, 1–53. https://doi.org/10.1007/978-3-319-01327-5_1/TABLES/7.

Lei, M., Huang, W., Sun, J., Shao, Z., Wu, T., Liu, J., Fan, Y., 2020. Synthesis of

carboxymethyl chitosan as an eco-friendly amphoteric shale inhibitor in water-based drilling fluid and an assessment of its inhibition mechanism. Appl. Clay Sci. 193, 105637. https://doi.org/10.1016/J.CLAY.2020.105637.

Lei, M., Huang, W., Sun, J., Shao, Z., Chen, Z., Chen, W., 2021a. Synthesis and characterization of high-temperature self-crosslinking polymer latexes and their application in water-based drilling fluid. Powder Technol. 389, 392–405. https://doi.org/10.1016/J.POWTEC.2021.05.045.

Lei, M., Huang, W., Sun, J., Shao, Z., Zhao, L., Zheng, K., Fang, Y., 2021b. Synthesis and characterization of thermo-responsive polymer based on carboxymethyl chitosan and its potential application in water-based drilling fluid. Colloids Surfaces A Physicochem. Eng. Asp. 629, 127478. https://doi.org/10.1016/J.COLSURFA.2021.127478.

Li, H., Xiao, H.Z., Zhang, R.D., He, G., Zhao, B., Zhu, J.Z., Yin, D., He, T., Song, L.H., 2004. A Kind of Polyalcohol Lubricating Inhibitor for Drilling Fluid.

Li, J., Sun, J., Lv, K., Ji, Y., Ji, J., Bai, Y., Wang, J., Jin, J., Shi, S., Huang, X., Liu, J., 2023. A zwitterionic copolymer as fluid loss reducer for water-based drilling fluids in high temperature and high salinity conditions. Geoenergy Sci. Eng. 222, 111200. https://doi.org/10.1016/J.PETROL.2022.111200.

Li, M.C., Wu, Q., Song, K., De Hoop, C.F., Lee, S., Qing, Y., Wu, Y., 2016. Cellulose nanocrystals and polyanionic cellulose as additives in bentonite water-based drilling fluids: rheological modeling and filtration mechanisms. Ind. Eng. Chem. Res. 55, 133–143. https://doi.org/10.1021/ACS.IECR.5B03510/SUPPL_FILE/IE5B03510_SI_001.PDF.

Li, P., Xu, Y., Liu, Y., Feng, J., Hui, B., Feng, Y., Hu, M., Guo, J., 2021. Terpolymer with rigid side chain as filtrate reducer for water-based drilling fluids. J. Appl. Polym. Sci. 138, 50237. https://doi.org/10.1002/APP.50237.

Li, W., Jiang, G., Ni, X., Li, Y., Wang, X., Luo, X., 2020. Styrene butadiene resin/nano-SiO2 composite as a water-and-oil-dispersible plugging agent for oil-based drilling fluid. Colloids Surfaces A Physicochem. Eng. Asp. 606, 125245. https://doi.org/10.1016/J.COLSURFA.2020.125245.

Li, W., Zhao, X., Li, Y., Ji, Y., Peng, H., Liu, L., Yang, Q., 2015. Laboratory investigations on the effects of surfactants on rate of penetration in rotary diamond drilling. J. Pet. Sci. Eng. 134, 114–122. https://doi.org/10.1016/J.PETROL.2015.07.027.

Li, W., Zhao, X., Ji, Y., Peng, H., Chen, B., Liu, L., Han, X., 2016a. Investigation of biodiesel-based drilling fluid, Part 2: formulation design, rheological study, and laboratory evaluation. SPE J. 21, 1767–1781. https://doi.org/10.2118/180926-PA.

Li, W., Zhao, X., Ji, Y., Peng, H., Chen, B., Liu, L., Han, X., 2016b. Investigation of biodiesel-based drilling fluid, Part 1: biodiesel evaluation, invert-emulsion properties, and development of a novel emulsifier package. SPE J. 21, 1755–1766. https://doi.org/10.2118/180918-PA.

Li, W., Zhao, X., Ji, Y., Peng, H., Li, Y., Liu, L., Han, X., 2016c. An investigation on environmentally friendly biodiesel-based invert emulsion drilling fluid. J. Pet. Explor. Prod. Technol. 6, 505–517. https://doi.org/10.1007/S13202-015-0205-7/FIGURES/10.

Li, X., Jiang, G., He, Y., Chen, G., 2021. Novel starch composite fluid loss additives and their applications in environmentally friendly water-based drilling fluids. Energy Fuel. 35, 2506–2513. https://doi.org/10.1021/ACS.ENERGYFUELS.0C03258/ASSET/IMAGES/ACS.ENERGYFUELS.0C03258.SOCIAL.

Li, X., Liu, Z., Zhu, L.Y., Miao, S.S., Fang, Z., Zhao, L.H., Guo, K., 2020. Carboxylic modification of welan gum. J. Appl. Polym. Sci. 137, 48301. https://doi.org/10.1002/APP.48301.

Li, Y.X., Li, Y.K., Peng, Y., Yu, Y., 2019. Water shutoff and profile control in China over 60 years. Oil Drill. Prod. Technol. 41, 773–787. https://doi.org/10.13639/J.ODPT.2019.06.016.

Lima, B.L.B., Marques, N.N., Souza, E.A., Balaban, R.C., 2022. Polysaccharide derivative as an additive in Olefin-Based drilling fluid. J. Mol. Liq. 364, 120023. https://doi.org/10.1016/J.MOLLIQ.2022.120023.

Lin, L., Luo, P., 2015. Amphoteric hydrolyzed poly(acrylamide/dimethyl diallyl ammonium chloride) as a filtration reducer under high temperatures and high salinities. J. Appl. Polym. Sci. 132. https://doi.org/10.1002/APP.41581.

Lin, X., Sheng, Z., He, J., He, X., Wang, C., Gu, X., Wang, Y., 2021. Preparation of isotropic spinnable pitch with high-spinnability by co-carbonization of coal tar pitch and bio-asphalt. Fuel 295, 120627. https://doi.org/10.1016/J.FUEL.2021.120627.

Lithner, D., Larsson, A., Dave, G., 2011. Environmental and health hazard ranking and assessment of plastic polymers based on chemical composition. Sci. Total Environ. 409, 3309–3324. https://doi.org/10.1016/J.SCITOTENV.2011.04.038.

Liu, P.S., Chen, G.F., 2014. Fabricating Porous Ceramics, Porous Materials. Butterworth-Heinemann. https://doi.org/10.1016/B978-0-12-407788-1.00005-8.

Liu, J., Dai, Z., Xu, K., Yang, Y., Lv, K., Huang, X., Sun, J., 2020. Water-based drilling fluid containing bentonite/poly(sodium 4-styrenesulfonate) composite for ultrahigh-temperature ultradeep drilling and its field performance. SPE J. 25, 1193–1203. https://doi.org/10.2118/199362-PA.

Liu, T., Leusheva, E.L., Morenov, V.A., Li, L., Jiang, G., Fang, C., Zhang, L., Zheng, S., Yu, Y., 2020. Influence of polymer reagents in the drilling fluids on the efficiency of deviated and horizontal wells drilling. Energies 13 (18), 4704. https://doi.org/10.3390/EN13184704.

Luo, Z., Wang, L., Pei, J., Yu, P., Xia, B., 2018. A novel star-shaped copolymer as a rheology modifier in water-based drilling fluids. J. Pet. Sci. Eng. 168, 98–106. https://doi.org/10.1016/j.petrol.2018.05.003.

Luqman Hasan, M., Afiqah Zainol Abidin, N., Singh, A., 2018. The rheological performance of guar gum and castor oil as additives in water-based drilling fluid. Mater. Today Proc. 5, 21810–21817. https://doi.org/10.1016/J.MATPR.2018.07.036.

Luz, S.M., Del Tio, J., Rocha, G.J.M., Gonçalves, A.R., Del'Arco, A.P., 2008. Cellulose and

cellulignin from sugarcane bagasse reinforced polypropylene composites: effect of acetylation on mechanical and thermal properties. Composer Part A Appl. Sci. Manuf. 39, 1362–1369. https://doi.org/10.1016/J.COMPOSITESA.2008.04.014.

M–I SWACO, 2009. Drilling Fluids Guide for Process Engineers.

Ma, F., Pu, X., Wang, B., Li, J., Cao, C., 2017. Preparation and evaluation of poly-ampholyte inhibitor DAM. RSC Adv. 7, 49320–49328. https://doi.org/10.1039/C7RA08385H.

Ma, X., Zhou, T., Zou, Y., 2017. Experimental and numerical study of hydraulic fracture geometry in shale formations with complex geologic conditions. J. Struct. Geol. 98, 53–66. https://doi.org/10.1016/J.JSG.2017.02.004.

Ma, X., Zhou, Z., Shi, W., Hu, Y., 2017. Synthesis and application of a novel betaine-type copolymer as fluid loss additive for water-based drilling fluid. Colloid Polym. Sci. 295, 53–66. https://doi.org/10.1007/S00396-016-3980-X/METRICS.

Ma, C., Li, L., Yang, Y.P., Hao, W.W., Zhang, Q., Lv, J., 2018. Study on the effect of polymeric rheology modifier on the rheological properties of oil-based drilling fluids. IOP Conf. Ser. Mater. Sci. Eng. 292, 12106. https://doi.org/10.1088/1757-899X/292/1/012106.

Ma, J., Pang, S., Zhang, Z., Xia, B., An, Y., 2021a. Experimental study on the polymer/graphene oxide composite as a fluid loss agent for water-based drilling fluids. ACS Omega 6 (14), 9750–9763. https://doi.org/10.1021/acsomega.1c00374.

Ma, J., Xu, J., Pang, S., Zhou, W., Xia, B., An, Y., 2021b. Novel Environmentally friendly lubricants for drilling fluids applied in shale formation. Energy Fuel. 35, 8153–8162. https://doi.org/10.1021/ACS.ENERGYFUELS.1C00495/ASSET/IMAGES/MEDIUM/EF1C00495_0014 (GIF).

Ma, J.Y., Xia, B.R., An, Y.X., 2022. Advanced developments in low-toxic and environmentally friendly shale inhibitor: a review. J. Pet. Sci. Eng. 208, 109578. https://doi.org/10.1016/J.PETROL.2021.109578.

Madani, M., Hosny, S., Alshangiti, D.M., Nady, N., Alkhursani, S.A., Alkhaldi, H., Al-Gahtany, S.A., Ghobashy, M.M., Gaber, G.A., 2022. Green synthesis of nano-particles for varied applications: green renewable resources and energy-efficient synthetic routes. Nanotechnol. Rev. 11, 731–759. https://doi.org/10.1515/NTREV-2022-0034/ASSET/GRAPHIC/J_NTREV-2022-0034_FIG_005.JPG.

Madkour, T.M., Fadl, S., Dardir, M.M., Mekewi, M.A., 2016. High performance nature of biodegradable polymeric nanocomposites for oil-well drilling fluids. Egypt. J. Pet. 25, 281–291. https://doi.org/10.1016/J.EJPE.2015.09.004.

Manjare, S.D., Dhingra, K., 2019. Supercritical fluids in separation and purification: a review. Mater. Sci. Energy Technol. 2, 463–484. https://doi.org/10.1016/J.MSET.2019.04.005.

Mao, H., Wang, W., Ma, Y., Huang, Y., 2021. Synthesis, characterization and properties of an anionic polymer for water-based drilling fluid as an anti-high temperature and anti-salt contamination fluid loss control additive. Polym. Bull. 78, 2483–2503. https://doi.org/10.1007/S00289-020-03227-Y/FIGURES/12.

McKeen, L., 2012. Film properties of plastics and elastomers. Film Prop. Plast. Elastomers. https://doi.org/10.1016/C2011-0-05606-5.

Metwally, M., Nguyen, T., Wiggins, H., Saasen, A., Gipson, M., 2022. Experimental lab approach for water based drilling fluid using polyacrylamide friction reducers to drill extended horizontal wells. J. Pet. Sci. Eng. 212. https://doi.org/10.1016/j.petrol.2022.110132.

Mirabbasi, S.M., Ameri, M.J., Alsaba, M., Karami, M., Zargarbashi, A., 2022. The evolution of lost circulation prevention and mitigation based on wellbore strengthening theory: a review on experimental issues. J. Pet. Sci. Eng. 211, 110149. https://doi.org/10.1016/J.PETROL.2022.110149.

Mohamadian, N., Ghorbani, H., Wood, D.A., Khoshmardan, M.A., 2019. A hybrid nanocomposite of poly(styrene-methyl methacrylate- acrylic acid)/clay as a novel rheology-improvement additive for drilling fluids. J. Polym. Res. 26. https://doi.org/10.1007/s10965-019-1696-6.

Morariu, S., Teodorescu, M., Bercea, M., 2022. Rheological investigation of polymer/clay dispersions as potential drilling fluids. J. Pet. Sci. Eng. 210, 110015. https://doi.org/10.1016/J.PETROL.2021.110015.

Moslemizadeh, A., Khezerloo-ye Aghdam, S., Shahbazi, K., Zendehboudi, S., 2017. A triterpenoid saponin as an environmental friendly and biodegradable clay swelling inhibitor. J. Mol. Liq. 247, 269–280. https://doi.org/10.1016/J.MOLLIQ.2017.10.003.

Murtaza, M., Tariq, Z., Zhou, X., Al-Shehri, D., Mahmoud, M., Kamal, M.S., 2021. Okra as an environment-friendly fluid loss control additive for drilling fluids: experimental & modeling studies. J. Pet. Sci. Eng. 204, 108743. https://doi.org/10.1016/J.PETROL.2021.108743.

Nagre, R.D., Owusu, P.A., Tchameni, A.P., Kyei, S.K., Azanu, D., 2021. Synthesis and assessment of a hydrophobically associating heteropolymer in water-based mud. Chem. Pap. 75, 1197–1209. https://doi.org/10.1007/S11696-020-01379-9/FIGURES/10.

Neshat, J., Shadizadeh, S.R., 2016. Evaluation of a naturally-derived deflocculant (Terminalia chebula) in bentonite dispersions. Iran. J. Oil Gas Sci. Technol. 5, 21–44. https://doi.org/10.22050/ijogst.2016.15788.

Nuyken, O., Pask, S.D., 2013. Ring-opening polymerization-an introductory review. Polymers 5, 361–403. https://doi.org/10.3390/POLYM5020361.

OCED 117, 2004. Test No. 117: partition coefficient (n-octanol/water), HPLC method. OECD iLibrary, OECD guidelines for the testing of chemicals. Section 1. https://doi.org/10.1787/9789264069824-EN.

OCED 301, 1992. Test No. 301: Ready biodegradability. OECD iLibrary, OECD guidelines for the testing of chemicals. Section 3. https://doi.org/10.1787/9789264070349-EN.

OCED305, 2012. Test No. 305: Bioaccumulation in Fish: Aqueous and Dietary Exposure. OECD iLibrary, OECD Guidelines for the Testing of Chemicals. Section 3. https://doi.org/10.1787/9789264185296-EN.

Ogunkunle, T.F., Oni, B.A., Afolabi, R.O., Fadairo, A.S., Ojo, T., Adesina, O., 2022. Comparative analysis of the performance of hydrophobically associating polymer, xanthan and guar gum as mobility control agent, in enhanced oil recovery application. J. King Saud Univ. - Eng. Sci. https://doi.org/10.1016/J.JKSUES.2022.01.003.

Oncsik, T., Trefalt, G., Borkovec, M., Szilagyi, I., 2015. Specific ion effects on particle aggregation induced by monovalent salts within the Hofmeister series. Langmuir 31, 3799–3807. https://doi.org/10.1021/ACS.LANGMUIR.5B00225/SUPPL_FILE/LA5B00225_SI_001.PDF.

Oseh, J.O., Mohd Norddin, M.N.A., Ismail, I., Gbadamosi, A.O., Agi, A., Mohammed, H.N., 2019. A novel approach to enhance rheological and filtration properties of water−based mud using polypropylene−silica nanocomposite. J. Pet. Sci. Eng. 181, 106264. https://doi.org/10.1016/J.PETROL.2019.106264.

Oseh, J.O., Mohd, N.M.N.A., Gbadamosi, A.O., Agi, A., Blkoor, S.O., Ismail, I., Igwilo, K.C., Igbafe, A.I., 2023. Polymer nanocomposites application in drilling fluids: a review. Geoenergy Sci. Eng. 222, 211416. https://doi.org/10.1016/J.GEOEN.2023.211416.

Osipov, M., Wang, J., Chen, M., Li, X., Yin, X., Zheng, W., 2022. Effect of synthetic quadripolymer on rheological and filtration properties of bentonite-free drilling fluid at high temperature. Crystals 12, 257. https://doi.org/10.3390/CRYST12020257.

OSPAR, 2006. Part A: a Sediment Bioassay Using an Amphipod Corophium Sp.

Ouaer, H., Gareche, M., 2018. The rheological behaviour of a water-soluble polymer (HEC) used in drilling fluids. J. Brazilian Soc. Mech. Sci. Eng. 40, 1–8. https://doi.org/10.1007/S40430-018-1301-7/FIGURES/7.

Patel, A., Stamatakis, E., Young, S., Friedheim, J., 2007. Advances in inhibitive water-based drilling fluids—can they replace oil-based muds? Proc. - SPE Int. Sysposium Oilfield Chem. 614–621. https://doi.org/10.2118/106476-MS.

Pereira, L.B., Sad, C.M.S., Castro, E.V.R., Filgueiras, P.R., Lacerda, V., 2022. Environmental impacts related to drilling fluid waste and treatment methods: a critical review. Fuel 310, 122301. https://doi.org/10.1016/J.FUEL.2021.122301.

Pham, M., Pakrasi, A., 2019. Air pollution control technologies. Proc. Air Waste Manag. Assoc. Annu. Conf. Exhib. AWMA 377–428. https://doi.org/10.1016/B978-0-12-814934-8.00013-2.

Pinho De Aguiar, K.L.N., Frias De Oliveira, P., Elias Mansur, C.R., 2020. A comprehensive review of in situ polymer hydrogels for conformance control of oil reservoirs. Oil Gas Sci. Technol. − Rev. d'IFP Energies Nouv. 75, 8. https://doi.org/10.2516/OGST/2019067.

Qi, L., 2014. The application of polymer mud system in drilling engineering. Procedia Eng. 73, 230–236. https://doi.org/10.1016/J.PROENG.2014.06.192.

Rajak, V.K., Gautam, S., Ajit, K.P., Kiran, R., Madhumaya, A., 2022. Rheological property measurement and application of formate-based drilling fluids at elevated temperatures: a Review. MAPAN 1–17. https://doi.org/10.1007/S12647-022-00546-5.

Rana, A., Arfaj, M.K., Saleh, T.A., 2019. Advanced developments in shale inhibitors for oil production with low environmental footprints-A review. Fuel 247, 237–249. https://doi.org/10.1016/J.FUEL.2019.03.006.

Riding, J.B., 2021. A guide to preparation protocols in palynology. Palynology 45, 1–110. https://doi.org/10.1080/01916122.2021.1878305/SUPPL_FILE/TPAL_A_1878305_SM0124.DOC.

Riley, A., 2012. Basics of polymer chemistry for packaging materials. Packag. Technol. 262–286. https://doi.org/10.1533/9780857095701.2.262.

Rokhade, A.P., Patil, S.A., Aminabhavi, T.M., 2007. Synthesis and characterization of semi-interpenetrating polymer network microspheres of acrylamide grafted dextran and chitosan for controlled release of acyclovir. Carbohydr. Polym. 67, 605–613. https://doi.org/10.1016/J.CARBPOL.2006.07.001.

Saboorian-Jooybari, H., Dejam, M., Chen, Z., 2016. Heavy oil polymer flooding from laboratory core floods to pilot tests and field applications: half-century studies. J. Pet. Sci. Eng. 142, 85–100. https://doi.org/10.1016/J.PETROL.2016.01.023.

Safi, B., Zarouri, S., Chabane-Chaouache, R., Saidi, M., Benmounah, A., 2016. Physico-chemical and rheological characterization of water-based mud in the presence of polymers. J. Pet. Explor. Prod. Technol. 6, 185–190. https://doi.org/10.1007/S13202-015-0182-X/FIGURES/9.

Saleh, T.A., Ibrahim, M.A., 2021. Synthesis of amyl ester grafted on carbon-nanopolymer composite as an inhibitor for cleaner shale drilling. Petroleum 8 (4), 529–537. https://doi.org/10.1016/J.PETLM.2021.07.002.

Saleh, T.A., Rana, A., Arfaj, M.K., Ibrahim, M.A., 2022. Hydrophobic polymer-modified nanosilica as effective shale inhibitor for water-based drilling mud. J. Pet. Sci. Eng. 209, 109868. https://doi.org/10.1016/J.PETROL.2021.109868.

Sepehri, S., Soleyman, R., Varamesh, A., Valizadeh, M., Nasiri, A., 2018. Effect of synthetic water-soluble polymers on the properties of the heavy water-based drilling fluid at high pressure-high temperature (HPHT) conditions. J. Pet. Sci. Eng. 166, 850–856. https://doi.org/10.1016/j.petrol.2018.03.055.

Singh, T., Singhal, R., 2013. Kinetics and thermodynamics of cationic dye adsorption onto dry and swollen hydrogels poly(acrylic acid-sodium acrylate-acrylamide) sodium humate. New pub Balaban 53, 3668–3680. https://doi.org/10.1080/19443994.2013.871342.

Steube, M., Johann, T., Barent, R.D., Müller, A.H.E., Frey, H., 2022. Rational design of tapered multiblock copolymers for thermoplastic elastomers. Prog. Polym. Sci. 124, 101488. https://doi.org/10.1016/J.PROGPOLYMSCI.2021.101488.

Sun, X., Bai, B., 2023. Chemical enhanced oil recovery. In: Recovery Improvement Gulf Professional Publishing, pp. 185–279. https://doi.org/10.1016/B978-0-12-823363-4.00003-0.

Sun, J., Chang, X., Lv, K., Wang, J., Zhang, F., Jin, J., Zhou, X., Dai, Z., 2021. Environmentally friendly and salt-responsive polymer brush based on lignin nanoparticle as fluid-loss additive in water-based drilling fluids. Colloids Surfaces A Physicochem. Eng. Asp. 621, 126482. https://doi.org/10.1016/J.COLSURFA.2021.126482.

Sun, J., Zhang, X., Lv, K., Liu, J., Xiu, Z., Wang, Z., Huang, X., Bai, Y., Wang, J., Jin, J., 2022. Synthesis of hydrophobic associative polymers to improve the rheological and filtration performance of drilling fluids under high temperature and high salinity conditions. J. Pet. Sci. Eng. 209. https://doi.org/10.1016/j.petrol.2021.109808.

Takasu, A., Hayashi, T., 2015. Cationic ring-opening polymerization. Encycl. Polym. Nanomater. 324–329. https://doi.org/10.1007/978-3-642-29648-2_176.

Thakur, V.K., 2018. Biopolymer grafting: synthesis and properties. In: Biopolymer Grafting: Synthesis and Properties. Elsevier. https://doi.org/10.1016/C2015-0-06910-6.

Tikadar, D., Gujarathi, A.M., Guria, C., 2021a. Safety, economics, environment and energy based criteria towards multi-objective optimization of natural gas sweetening process: an industrial case study. J. Nat. Gas Sci. Eng. 95, 104207. https://doi.org/10.1016/J.JNGSE.2021.104207.

Tikadar, D., Gujarathi, A.M., Guria, C., Al Toobi, S., 2021b. Retrofitting and simultaneous multi-criteria optimization with enhanced performance of an industrial gas-cleaning plant using economic, process safety, and environmental objectives. J. Clean. Prod. 319, 128652. https://doi.org/10.1016/J.JCLEPRO.2021.128652.

Utracki, L.A., Wilkie, C.A., 2014. Polymer Blends Handbook, Polymer Blends Handbook. Springer Netherlands. https://doi.org/10.1007/978-94-007-6064-6.

van Herk, A.M., 2013. Chemistry and technology of emulsion polymerisation. In: Chem. Technol. Emuls. Polym, second ed. https://doi.org/10.1002/9781118638521

Van Oort, E., Ahmad, M., Spencer, R., Legacy, N., 2015. ROP Enhancement in Shales through Osmotic Processes. SPE/IADC Drill. Conf. Proc, pp. 1795–1819. https://doi.org/10.2118/173138-MS.

Wan, T., Yao, J., Zishun, S., Li, W., Juan, W., 2011. Solution and drilling fluid properties of water soluble AM−AA−SSS copolymers by inverse microemulsion. J. Pet. Sci. Eng. 78, 334–337. https://doi.org/10.1016/J.PETROL.2011.06.027.

Wang, X., Zhang, Y., Lv, F., Shen, B., Zhang, R., Zhou, F., Chu, P.K., 2011. Cross-linked polystyrene microspheres as density-reducing agent in drilling fluid. J. Pet. Sci. Eng. 78, 529–533. https://doi.org/10.1016/J.PETROL.2011.06.016.

Wang, H., Ge, Y., Shi, L., 2017. Technologies in deep and ultra-deep well drilling: present status, challenges and future trend in the 13th Five-Year Plan period (2016−2020). Nat. Gas. Ind. B 4, 319–326. https://doi.org/10.1016/J.NGIB.2017.09.001.

Wang, W., Lu, W., Goodwin, A., Wang, H., Yin, P., Kang, N.G., Hong, K., Mays, J.W., 2019. Recent advances in thermoplastic elastomers from living polymerizations: macromolecular architectures and supramolecular chemistry. Prog. Polym. Sci. 95, 1–31. https://doi.org/10.1016/J.PROGPOLYMSCI.2019.04.002.

Wang, H., Li, M., Wu, J., Yan, P., Liu, G., Sun, K., Mou, Q., Zhang, C., 2022. Nano-SiO2/hydroxyethyl cellulose nanocomposite used for 210 °C sedimentation control of petroleum drilling fluid. J. Polym. Eng. 42, 163–171. https://doi.org/10.1515/POLYENG-2021-0188/MACHINEREADABLECITATION/RIS.

Wang, J., Chen, M., Li, X., Yin, X., Zheng, W., 2022. Effect of synthetic quadripolymer on rheological and filtration properties of bentonite-free drillingfluid at high temperature. Crystals 12, 257. https://doi.org/10.3390/CRYST12020257.

William, J.K.M., Ponmani, S., Samuel, R., Nagarajan, R., Sangwai, J.S., 2014. Effect of CuO and ZnO nanofluids in xanthan gum on thermal, electrical and high pressure rheology of water-based drilling fluids. J. Pet. Sci. Eng. 117, 15–27. https://doi.org/10.1016/J.PETROL.2014.03.005.

Wypych, G., 2022. Handbook of Rheological Additives, Handbook of Rheological Additives. ChemTec Publishing. https://doi.org/10.1016/C2021-0-00266-2.

Xia, S., Zhang, L., Davletshin, A., Li, Z., You, J., Tan, S., 2020. Application of polysaccharide biopolymer in petroleum recovery. Polymers 12, 1860. https://doi.org/10.3390/POLYM12091860.

Xian, J.L., Oren, A.S., 2012. Polymeric and Self Assembled Hydrogels: from Fundamental Understanding to Applications. Monogr. Supramol. Chem., Monographs in Supramolecular Chemistry. https://doi.org/10.1039/9781849735629.

Xie, G., Luo, P., Deng, M., Su, J., Wang, Z., Gong, R., Xie, J., Deng, S., Duan, Q., 2017. Intercalation behavior of branched polyethyleneimine into sodium bentonite and its effect on rheological properties. Appl. Clay Sci. 141, 95–103. https://doi.org/10.1016/J.CLAY.2017.02.018.

Xie, B., Ting, L., Zhang, Y., Liu, C., 2018. Rheological properties of bentonite-free water-based drilling fluids with novel polymer viscosifier. J. Pet. Sci. Eng. 164, 302–310. https://doi.org/10.1016/J.PETROL.2018.01.074.

Xu, L., Xu, G., Liu, T., Chen, Y., Gong, H., 2013a. The comparison of rheological properties of aqueous welan gum and xanthan gum solutions. Carbohydr. Polym. 92, 516–522. https://doi.org/10.1016/J.CARBPOL.2012.09.082.

Xu, L., Xu, L., Dai, W.S., Tsuboi, T., Xie, H. De, 2013b. Preparation and characterization of a novel fluoro-silicone acrylate copolymer by semi-continuous emulsion polymerization. J. Fluor. Chem. 153, 68–73. https://doi.org/10.1016/J.JFLUCHEM.2013.05.017.

Xu, J., Hu, Y., Chen, Q., Chen, D., Lin, J., Bai, X., 2017a. Preparation of hydrophobic carboxymethyl starches and analysis of their properties as fluid loss additives in drilling fluids. Starch - Stärke 69, 1600153. https://doi.org/10.1002/STAR.201600153.

Xu, J., Qiu, Z., Huang, W., Zhao, X., 2017b. Preparation and performance properties of polymer latex SDNL in water-based drilling fluids for drilling troublesome shale formations. J. Nat. Gas Sci. Eng. 37, 462–470. https://doi.org/10.1016/J.JNGSE.2016.11.064.

Xu, J.G., Qiu, Z., Zhao, X., Zhang, Y., Li, G., Huang, W., 2018. Application of nano-

polymer emulsion for inhibiting shale self-imbibition in water-based drilling fluids. J. Surfactants Deterg. 21, 155–164. https://doi.org/10.1002/JSDE.12019.

Xuan, Y., Jiang, G., Li, Y., Yang, L., Zhang, X., 2015. Biodegradable oligo (poly-L-lysine) as a high-performance hydration inhibitor for shale. RSC Adv. 5, 84947–84958. https://doi.org/10.1039/C5RA16003K.

Yahya, S., Kee, K.E., Puad, M.J.M., Ismail, M.C., 2022. Evaluation on steel corrosion in water-based drilling fluids: inhibitors and scale involvement. J. Pet. Sci. Eng. 211, 110127. https://doi.org/10.1016/J.PETROL.2022.110127.

Yamak, H.B., 2013. Emulsion polymerization: effects of polymerization variables on the properties of vinyl acetate based emulsion polymers. Polym. Sci. https://doi.org/10.5772/51498.

Yang, J., Lei, Z., Dong, B., Ai, Z., Peng, L., Xie, G., 2022. Synthesis and plugging performance of poly (MMA-BA-ST) as a plugging agent in oil-based drilling fluid. Energies 15, 7626. https://doi.org/10.3390/EN15207626.

Zangari, G., 2017. Chemistry, molecular sciences and chemical engineering. In: Chemistry, Molecular Sciences and Chemical Engineering. Elsevier Inc., pp. 1–20

Zevallos, M.A.L., Candler, J., Hooker Wood, J., Reuter, L.M., 1996. Synthetic-based fluids enhance environmental and drilling performance in deepwater locations. Proc. SPE Int. Pet. Conf. Exhib. Mex. 235–242. https://doi.org/10.2118/35329-MS.

Zhang, Y., Dubé, M.A., 2018. Green emulsion polymerization technology. Adv. Polym. Sci. 280, 65–100. https://doi.org/10.1007/12_2017_8/FIGURES/15.

Zhang, X., Jiang, G., Dong, T., Wang, L., Li, X., Wang, G., 2018. An amphoteric polymer as a shale borehole stabilizer in water-based drilling fluids. J. Pet. Sci. Eng. 170, 112–120. https://doi.org/10.1016/J.PETROL.2018.06.051.

Zhang, J.R., Xu, M.D., Christidis, G.E., Zhou, C.H., 2020. Clay minerals in drilling fluids: functions and challenges. Clay Miner. 55, 1–11. https://doi.org/10.1180/CLM.2020.10.

Zhang, Z., Nie, X., Wang, F., Chen, G., Huang, W.Q., Xia, L., Zhang, W.J., Hao, Z.Y., Hong, C.Y., Wang, L.H., You, Y.Z., 2020. Rhodanine-based Knoevenagel reaction and ring-opening polymerization for efficiently constructing multicyclic polymers. Nat. Commun. 11, 3654. https://doi.org/10.1038/s41467-020-17474-0.

Zhang, C., Luo, C., Ye, L., Zhang, H., Xiang, H., Zhang, C., Luo, C., Ye, L., Zhang, H., Xiang, H., 2021. Research and application of anti-collapse lubricant compound polyalcohol for water-based drilling fluid. Open J. Yangtze Oil Gas 7, 1–12. https://doi.org/10.4236/OJOGAS.2022.71001.

Zhao, X., Li, D., Zhu, H., Ma, J., An, Y., 2022. Advanced developments in environmentally friendly lubricants for water-based drilling fluid: a review. RSC Adv. 12, 22853–22868. https://doi.org/10.1039/D2RA03888A.

Zheng, Y., Asif, A., Amiri, A., Polycarpou, A.A., 2021. Graphene-based aqueous drilling muds as efficient, durable, and environmentally friendly alternatives for oil-based muds. ACS Appl. Nano Mater. 4, 1243–1251. https://doi.org/10.1021/ACSANM.0C02852/SUPPL_FILE/AN0C02852_SI_001.PDF.

Zhong, F., Pan, C.Y., 2022. Dispersion polymerization versus emulsifier-free emulsion polymerization for nano-object fabrication: a comprehensive comparison. Macromol. Rapid Commun. 43, 2100566. https://doi.org/10.1002/MARC.202100566.

Zhong, H., Qiu, Z., Huang, W., Cao, J., 2012. Poly (oxypropylene)-amidoamine modified bentonite as potential shale inhibitor in water-based drilling fluids. Appl. Clay Sci. 67 (68), 36–43. https://doi.org/10.1016/J.CLAY.2012.06.002.

Zhong, H., Shen, G., Qiu, Z., Lin, Y., Fan, L., Xing, X., 2018. Mitigation of lost circulation in oil-based drilling fluids using oil absorbent polymers. Materials 11, 2020. https://doi.org/10.3390/MA11102020.

Zhong, H., Shen, G., Qiu, Z., Lin, Y., Fan, L., Xing, X., Li, J., 2019. Minimizing the HTHP filtration loss of oil-based drilling fluid with swellable polymer microspheres. J. Pet. Sci. Eng. 172, 411–424. https://doi.org/10.1016/J.PETROL.2018.09.074.

Zhong, H., Gao, X., Qiu, Z., Sun, B., Huang, W., Li, J., 2020a. Insight into β–cyclodextrin polymer microsphere as a potential filtration reducer in water-based drilling fluids for high temperature application. Carbohydr. Polym. 249, 116833. https://doi.org/10.1016/J.CARBPOL.2020.116833.

Zhong, H., Gao, X., Qiu, Z., Zhao, C., Zhang, X., Guo, B., Li, G., 2020b. Formulation and evaluation of β–cyclodextrin polymer microspheres for improved HTHP filtration control in water-based drilling fluids. J. Mol. Liq. 313, 113549. https://doi.org/10.1016/J.MOLLIQ.2020.113549.