

Introduction

Polymers have been used in drilling fluids since the 1930s, when cornstarch was introduced as a fluid-loss-control additive. Since that time, polymers have become more specialized and their acceptance has increased accordingly. Polymers are part of practically every water-base system in use today. Indeed, some systems are totally polymer-dependent and are termed broadly as polymer systems.

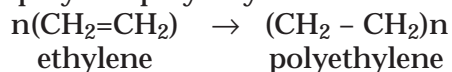
A wide array of polymers is available today. Some polymers — like starch, for instance — originate from natural

sources. Other, more-specialized polymers are modified natural polymers, while still other more-sophisticated polymers are derived from synthetics. The unlimited potential of polymer development makes polymers applicable to virtually every drilling fluid function. With polymer technology, it is possible to analyze a situation on a molecular level and design a polymer with the specific properties to address the situation. For this reason, polymers have an unlimited future in drilling fluids.

Polymer Chemistry and Applications

A polymer is a large molecule comprised of small, identical, repeating units. The small, recurring units are called *monomers*. Polymerization occurs when the monomers are joined together to form the large polymer molecule. Polymers may have molecular weights in the millions or they may consist of only a few repeating units. Polymers that have only a few repeating units are called *oligomers*.

To express the written formula for a polymer, the empirical formula of the simple recurring unit is expressed to the *n*th degree. For instance, the simplest polymer is polyethylene ((C₂H₄)_n). Ethylene is the result of the polymerization of the monomer ethylene (CH₂=CH₂). During the polymerization process, the double bond is lost and the polymer polyethylene is formed.



The resulting polyethylene polymer consists of a long chain of “n” repeating units. The number of times that the monomers are repeated is known as the

degree of polymerization. Polymers typically have a degree of polymerization greater than 1,000.

Polyethylene is an example of a homopolymer. Homopolymers contain only one monomer. Other examples of homopolymers are polypropylene and polystyrene. Copolymers are polymers that are prepared from two or more types of monomers. The monomers can be present in various ratios and in different positions in the chain. Copolymerization offers a great deal more flexibility in designing polymers.

STRUCTURE OF POLYMERS

Polymers' structures are classified as linear, branched or crosslinked. Examples are given below.

Linear



Example:

CMC (Carboxymethylcellulose), PHPA (Partially Hydrolyzed Polyacrylamide) and HEC (Hydroxyethylcellulose).

A polymer is a large molecule comprised of small, identical, repeating units.

Branched



Example: Starch and xanthan gum.

Crosslinked



Example: Crosslinked xanthan gum

There is an infinite possibility of structural variations. Some of the structural possibilities that affect the performance of polymers are listed below.

- Type of monomer or monomers.
- Molecular weight.
- Type and extent of subsequent chemical modification on the polymer.
- Number of branching or crosslinking groups in the polymer chain.

CLASSIFICATION OF POLYMERS

Polymers in drilling fluids can be classified in three ways. They can be classified according to their chemistry, such as anionic or nonionic; they can be classified by their function, such as viscosifier or filtration-control additive; or they can be classified simply by their origin. For this chapter, polymers are classified by their origin. The polymers used in drilling fluids come in three types:

- Naturally occurring.
- Modified naturally occurring.
- Synthetically derived.

NATURAL POLYMERS

Natural polymers are polymers produced in nature, without Man's intervention. These materials are derived from natural sources such as plants,

animals and bacteria fermentation. The final product must go through some processing — at least harvesting, separating, grinding and drying — before bagging. Natural polymers have more complex structures than synthetic polymers, and they typically have higher molecular weights as well. Natural polymers also are less temperature-stable than synthetic polymers and have a lower tolerance to degradation by bacteria.

Natural polymers used in drilling fluids are composed of polymerized sugar molecules and belong to a class of compounds called *polysaccharides*. The monomers are the sugar units and they contain carbon:hydrogen:oxygen in the ratio of 6:12:6 (see Figure 1). Polymerization of the sugar units occurs through a condensation reaction wherein water is removed from the individual sugar units. The resulting polysaccharide consists of the sugar units linked together through common oxygen atoms. Polysaccharides have a C:H:O ratio of 6:10:5 or $C_6(OH)_5$. The backbone linkage of natural polymers is more complicated than that of synthetic polymers. The backbone consists of carbohydrate ring structures and the oxygen atoms that link the rings together. Synthetic polymers have a much simpler carbon-carbon linkage.

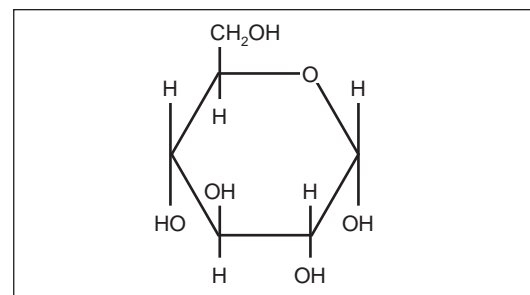


Figure 1: Glucose.

Starch is a natural polymer which comes from a variety of plant and grain sources, with corn and potato starches being the most important

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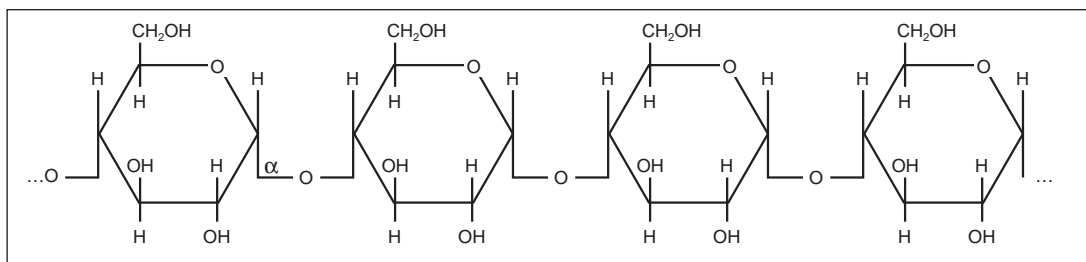


Figure 2: Amylose.

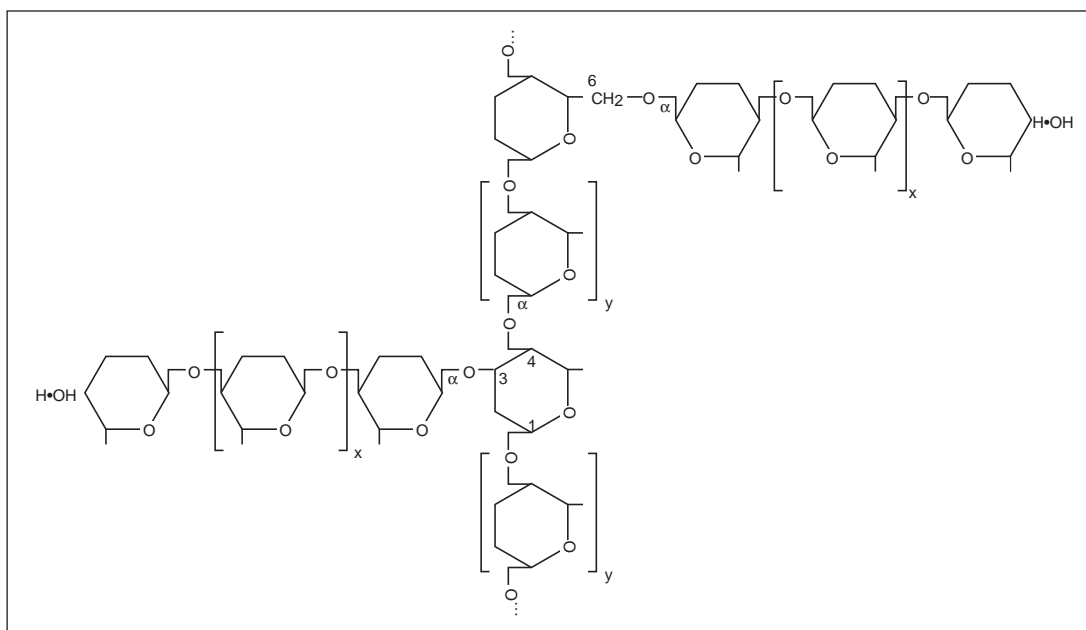


Figure 3: Amylopectin.

source for drilling fluids. Starch consists of two polysaccharides: amylose and amylopectin. Amylose, a chain of carbohydrate rings, makes up the straight chain backbone of the starch molecule. Amylopectin is a highly branched chain of carbohydrate rings that branches off from an amylose backbone. The ratios of the amylose and amylopectin fractions determine the properties of the starch.

Starch in its raw form is not water-soluble; it simply floats around as starch particles. To make starch effective in drilling fluids, it is necessary to rupture the protective shell coating of amylopectin to release the inner amylose. The starch granules are heated until the cells rupture, which allows the amylose to disperse. This process is known as

pregelatination. Once dispersed, the starch hydrates water. It is subsequently dried and bagged as the final product. It is non-ionic and soluble in saturated saltwater as well as freshwater.

MY-LO-JEL™ is a cornstarch consisting of an average of about 25% amylose and 75% amylopectin. POLY-SAL™ is a potato starch which is slightly different from cornstarch. Potato starch has a slightly higher molecular weight than cornstarch and also has a higher concentration of amylose to amylopectin. For these reasons, it functions somewhat differently. POLY-SAL has greater tolerance to hardness and a slightly higher temperature stability than MY-LO-JEL. It also produces slightly more viscosity.

The biggest drawback to the use of starches is their tendency to ferment.

Starch in its raw form is not water-soluble...

They are natural biodegrading materials that must be preserved with a biocide when used in drilling fluids. POLY-SAL contains a biocide in the product. A second limitation of starch is its low thermal stability. Starch degrades rapidly when exposed to prolonged temperatures exceeding 225°F (102°C).

Some environments are more conducive to bacterial degradation than others. The worst environments center around bioactive makeup water. Stagnant pond water is the worst source, although any water sourced through rivers or streams should be considered suspect. Higher temperatures, neutral pH conditions and fresher waters accelerate bacterial growth. Bacterial problems in high-salt systems and high-pH environments are less likely; however, they do occur after time.

Xanthan gum is classified as a natural polymer although it is actually obtained in its bacterially produced form rather than in its natural form. The bacteria *Xanthomonas campestris* produces the gum during its normal life cycle via a complex enzymatic

process. Xanthan is water-soluble, slightly anionic and highly branched. It has a molecular weight in the 2 to 3 million range, which is relatively high for drilling fluids.

Xanthan is a five-ring, repeating structure consisting of a two-ring backbone and a three-ring side chain. The backbone consists of glucose residues identical in structure to cellulose. Branching off the backbone are three-ring side chains of additional sugar residue. Attached to the side chains are various functional groups (carbonyl, carboxyl, hydroxyl and others) which give xanthan its unique viscosifying properties.

The long branching structure of the polymer, coupled with the relatively weak hydrogen bonding among the side groups, imparts unique viscosifying properties to xanthan. When a certain concentration of the polymer is reached, hydrogen bonding develops among the polymer branches and the result is a complex, tangled network of weakly bound molecules. The electrostatic interactions are weak, however, and when shear is applied to the system, the

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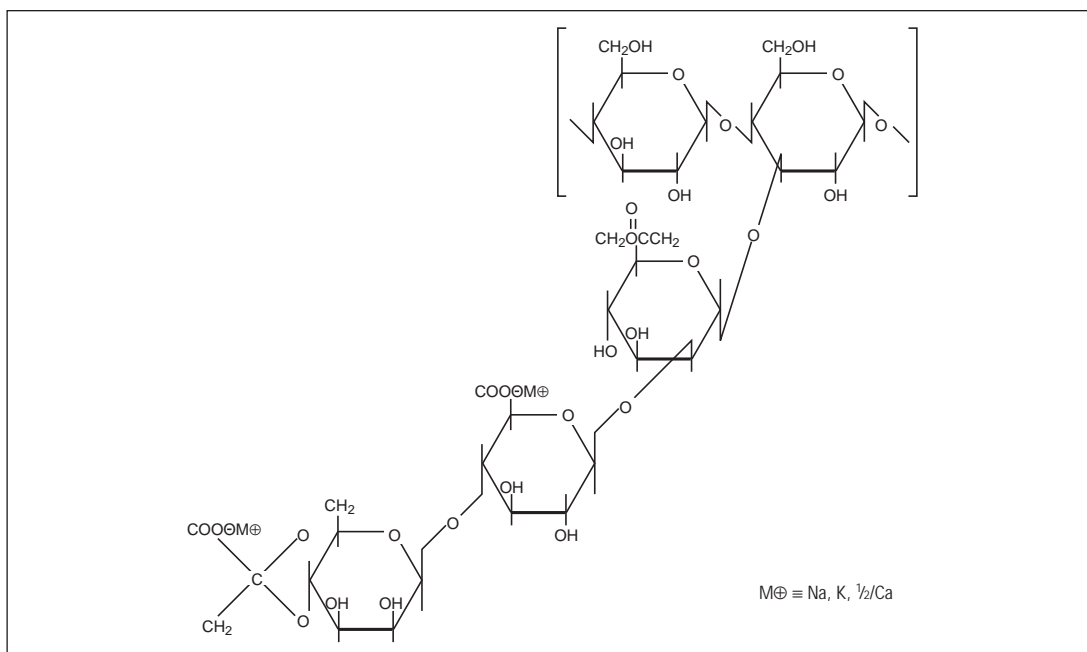


Figure 4: Structure of xanthan gum.

attractive forces holding the polymers together are pulled apart. As the hydrogen bonding breaks, the viscosity of the fluid thins. When the shear is removed, the polymer chains resume their intermolecular hydrogen bonding and their original viscosified state returns.

Xanthan polymer produces pseudoplastic or shear-thinning fluids and gel structures. As the shear is increased, viscosity is progressively decreased. When the shear is removed, the original viscosity of the fluid is completely recovered. Under high-shear-rate conditions — in the drillstring, for instance — the viscosity of the mud system decreases. Under the very high shear rates experienced in the drill bit nozzles, the fluid thins dramatically until it behaves almost like water. Under lower-shear-rate conditions — in the annulus, for instance — hydrogen bonding forms again and viscosity increases. Under static conditions, xanthan fluids display thixotropic characteristics providing gels. Xanthan gum and a similar biopolymer called *welan gum* are two of only a few commercial polymers that produce thixotropic properties (gels) in water-base fluids.

The concentration of xanthan necessary to develop thixotropic properties depends on the makeup water. Only 0.5 lb/bbl may be sufficient for a highly weighted freshwater system while it may take 2 to 3 lb/bbl in a KCl or a high-salinity NaCl system. In high-salinity brines, xanthan polymer — like other water-base polymers — does not hydrate easily and, to some extent, remains coiled. In freshwater, the polymer expands and the polymer branches come in contact, allowing hydrogen bonding and the resulting thixotropy to develop more easily.

Xanthan gum (such as DUO-VIS® and FLO-VIS®) is added to drilling fluids for a number of applications. Most often, it is used as a clay substitute to impart thixotropic properties. Xanthan gum is

used instead of loading a fluid with clay solids to obtain viscosity and suspension. This is beneficial in many ways, most notably by maintaining optimum suspension and carrying capacity in fluids without increasing solids loading. This property makes xanthan gum the polymer of choice for increasing viscosity in extended-reach and horizontal wells, especially when the wells involve low annular velocities.

Xanthan has several properties that make it an ideal polymer for clay-free “drill-in” and workover/completion fluid applications. It viscosifies brines, including seawater, NaCl, KCl, CaCl₂, NaBr and, to some extent, even CaBr₂. It is degradable with oxidizers (bleach) or enzymes, and is acid-soluble for easy clean-up. It develops gel strengths and easily suspends acid-soluble materials like CaCO₃. FLO-VIS is a special, clarified version of xanthan. The clarified version has been processed to remove any bacterial residue for clean fluid applications.

MODIFIED NATURAL POLYMERS

Modified natural polymers are very common in drilling fluids. Cellulose and starch are two natural polymers that frequently are used to produce modified natural polymers. The modified versions can have substantially different properties than the original, natural polymers. For drilling fluids, nonionic natural polymers — such as cellulose and starch — are modified to polyelectrolytes.

Polyelectrolytes. Many polymers are not water-soluble and therefore are not applicable to water-base drilling fluids — unless they are modified. To obtain water solubility, polymers are sometimes modified to polyelectrolytes. This modification involves an alteration of the repeating unit of the polymer. A polyelectrolyte is a polymer that dissolves into water, forming polyions and counter ions of the opposite charge. A polyion has charges that repeat along

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Polymer solubility is affected by pH.

the polymer chain. The charges can be positive, as in a cationic polymer, or negative, as in an anionic polymer. A few examples of cationic polymers exist, but most often polymers in drilling fluids are negatively charged.

The effectiveness of a polyelectrolyte depends on the number of available sites on the polymer which, in turn, depends on the following factors:

- The concentration of the polymer.
- The concentration and distribution of the ionizable groups.
- The salinity and hardness of the fluid.
- The pH of the fluid.

With an increasing number of ionized sites on the polymer, it tends to extend and uncoil. This is due to mutual charge repulsion that elongates and stretches the polymer into a configuration that gives the maximum distance between like charges. In spreading out, the polymer exposes the maximum number of charged sites. Spreading out allows the polymer to attach to clay particles and to viscosify the fluid phase.

CONCENTRATION EFFECTS

As discussed, polymers assume a stretched or elongated configuration when dissolved in the water phase of a drilling fluid. This configuration is not rod-like but twisted and curled to obtain the maximum distance between like charges on the polymer. In dilute concentrations, the polymer hydrates a thick envelope of water (about 3 or 4 water molecules). There is an electrostatic repulsion between these envelopes, whose surfaces are large when the fully extended shape is assumed. This large surface area contributes to the viscosity effects of the polymer.

As the polymer concentration increases, the envelopes of water surrounding the polymers decrease. As more polymer vies for less water, the effect is an increase in viscosity. This

As the polymer hydrates water... viscosity increases.

occurs when polymers become entangled with one another by clinging to a limited amount of water.

pH EFFECTS

Polymer solubility is affected by pH. The pH often determines the extent of the ionization of the functional groups along the polymer chain. For instance, the most common functional group found in water-base polymers is the carboxyl group. The ionized carboxyl group is a distinguishing feature in most anionic polymers including CMCs, PHPAs and xanthan gums, to name a few.

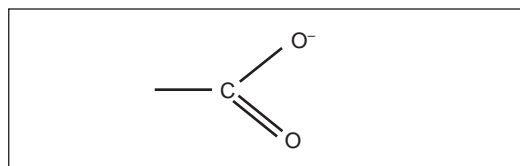


Figure 5: Ionized carboxyl group.

As seen in Figure 5, the ionized carboxyl group has a double-bonded oxygen and a single-bonded oxygen on the terminal carbon. Ionization is accomplished by reacting the carboxyl group with an alkali material such as caustic soda. By ionizing the previous insoluble carboxyl group, solubility of the polymer occurs (see Figure 6).

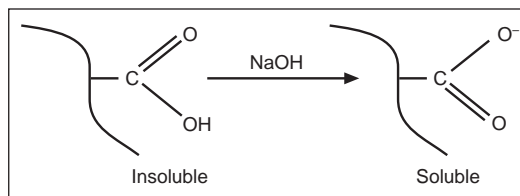


Figure 6: Polymer solubility.

The sodium carboxylate group draws water to it through its anionic charged site. When the polymer is added to water, the sodium ion releases from the polymer chain and leaves behind a negatively charged site. The polymer is now anionic and free to hydrate water. As the polymer hydrates water, the envelope

...calcium and magnesium ions hydrate even more water than the sodium ion.

Salt limits the availability of water in which a polymer can hydrate and expand.

surrounding the polymer increases in size, and viscosity increases.

The optimum solubility of the carboxyl group occurs from 8.5 to 9.5 pH. Enough caustic to reach 8.5 pH is necessary to ionize and make the polymer soluble. If greater amounts of caustic soda are added, the viscosifying characteristics are suppressed slightly. If a pH reversal occurs — i.e., the solution pH drops to acid conditions (less than 7) — then the carboxylate group returns to its original carboxyl form and the polymer loses its solubility.

SALINE EFFECTS

Salinity plays a very big role in determining the effectiveness of a polymer. Salt inhibits the unwinding, elongating effect that occurs when a water-soluble polymer is added to water. Rather than uncoiling and expanding, the polymer takes a comparatively smaller, balled shape and its solubility is likewise reduced. This results from the greater competition for water. Salt limits the availability of water in which a polymer can hydrate and expand. As salinity increases, polymers neither hydrate as much water nor increase viscosity as readily.

When salt is added to a freshwater system in which polymers are fully extended, the addition usually triggers a viscosity hump. As salt hydrates water and strips it from the polymers, the system may be at least temporarily destabilized, and an increase in viscosity occurs. Polymers become entangled with drill solids and other polymers while shrinking back to their balled state. Once the polymers assume their balled state, viscosity is greatly reduced.

Typically, the effectiveness of polymers in saline environments is reduced, but this can be overcome with additional treatment. For instance, PAC

(Polyanionic Cellulose) or xanthan gum may require twice their normal concentration, or even more, to perform in a saline environment.

DIVALENT CATION EFFECTS

When divalent ions such as calcium and magnesium are present in a drilling fluid, their effect on the system can be dramatic. Like the sodium ion, which also hydrates water and limits overall water availability, calcium and magnesium ions hydrate even more water than the sodium ion. This makes polymer hydration in their presence very inefficient.

Anionic polymers have an additional problem with calcium in that calcium reacts with the anionic group on the polymer. In doing so, the polymer becomes flocculated and can be dropped from the system. For this reason, soda ash is often recommended to treat calcium from the system. Polymers that are only slightly anionic, such as xanthan gum, and polymers that are nonionic, such as starch, are not precipitated by calcium. They are affected, however, by the strong hydration characteristic of calcium and their efficiencies are diminished in its presence.

CELLULOSE DERIVATIVES

Cellulose is a natural polymer that is insoluble in water. To become a useful additive in drilling fluids, it is modified to Carboxymethylcellulose (CMC). CMC is an example of a polyelectrolyte. Figures 7 and 8 show how the repeating ring structure for cellulose is modified by introducing the anionic carboxymethyl group. Now the modified polymer, through the anionic group, has an affinity for water and is water-soluble.

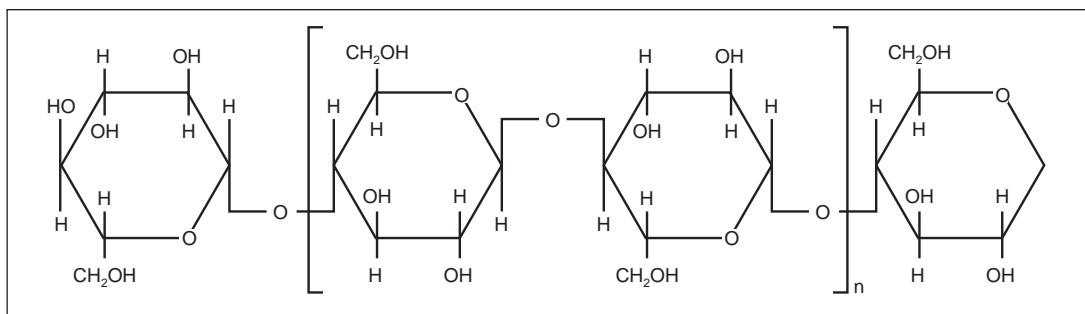


Figure 7: Cellulose.

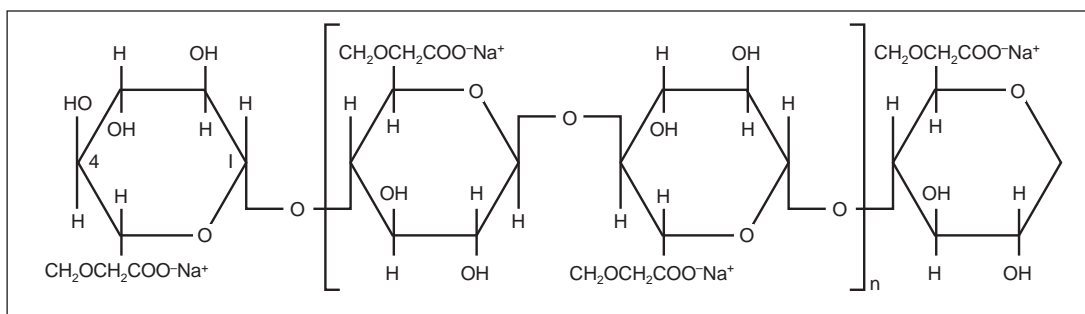


Figure 8: Sodium carboxymethylcellulose, D.S. = 1.0.

Carboxymethylcellulose is formed by the reaction of the sodium salt of monochloroacetic acid (ClCH₂COONa) with cellulose. A substitution occurs most often at the (-CH₂OH) group to form a soluble polyelectrolyte.

The properties of sodium carboxymethylcellulose are dependent on several factors:

- The Degree of Substitution (D.S.).
- The Degree of Polymerization (D.P.).
- The uniformity of the substitution.
- The purity of the final product.

The degree of polymerization refers to the number of times the ring structure is repeated. The ring structure is the repeating structure that defines the polymer. The higher the D.P., the higher the molecular weight. Viscosity increases as the D.P. for CMC increases. High-viscosity CMC has a higher molecular weight than low-viscosity CMC.

The degree of substitution refers to the number of substitutions that occur on a single repeating ring structure. In the sodium carboxymethylcellulose

figure above, there is exactly one substitution on each ring structure. That means the D.S. is 1.

In the example above, the substitution occurred only on the methyl hydroxy (-CH₂OH) group. Substitution also could have occurred at either of the two hydroxyl (-OH) groups, giving a potential D.S. of 3. Water solubility is achieved when the D.S. reaches 0.45. The typical D.S. range for CMC is 0.7 to 0.8. High-viscosity CMC has the same D.S. as medium- or low-viscosity CMC. The only difference is their respective D.P. Relatively higher substituted CMC often is called *Polyanionic Cellulose (PAC)*. PAC has the same chemical structure and the same D.P. as CMC; only the D.S. for the two polymers is different. The typical D.S. range for PAC is 0.9 to 1.0.

The higher D.S. produces a polymer that is more soluble than CMC. This makes the performance of PAC generally better than that of CMC. Both materials perform about the same in

The degree of polymerization refers to the number of times the ring structure is repeated.

POLYPAC[®] is a high-quality polyanionic cellulose.

freshwater, but in saline and hard waters, PAC outperforms CMC.

Sometimes CMC and PAC — with identical D.P., D.S and purity — perform differently. This is due to the uniformity (or lack of uniformity) of the substitution along the chain. A good-quality CMC or PAC has uniform substitution along the polymer. A poorly performing CMC or PAC may have substitution occurring at only one end or in the middle of the polymer. This results in a polymer with limited solubility and, therefore, poor performance.

POLYPAC[®] is a high-quality polyanionic cellulose. It provides fluid-loss control in freshwater, seawater, NaCl and KCl systems. It forms a thin, tough, pliable filter cake which limits the loss of filtrate to permeable formations. It also produces excellent viscosity in both saltwater and freshwater. POLYPAC is recommended over CMC for use in seawater, saltwater and waters with soluble calcium levels above 400 mg/l. A table with the technical specifications and limitations of CMC and PAC is found below.

Product	Mol. Wt	D.P.	D.S.
PAC LV	140-170	850-1,000	0.9-1.0
PAC HV	200-225	1,130-1,280	0.9-1.0
CMC LV	40-170	850-1,000	0.7-0.8
CMC HV	200-225	1,130-1,280	0.7-0.8

Table 1: CMC and PAC.

HEC (Hydroxyethylcellulose) is another type of modified cellulose polymer. It is produced by soaking cellulose in a caustic soda solution, then reacting the alkali cellulose with ethylene oxide. The result is a substitution of hydroxyethyl groups on the hydroxymethyl and hydroxyl sites. Even though the polymer is non-ionic, the hydroxyethyl groups have sufficient affinity with water to make the polymer water-soluble. In addition to the D.S., the structure of the polymer is affected also by the D.P. of the ethoxylated side chains. The D.P. of the side chains is called the Molar Substitution (M.S.), or the average number of ethylene oxide molecules that have reacted with each cellulose unit. Once a hydroxyethyl group is attached to each unit, it can further react with additional groups in an end-to-end formation. As long as ethylene oxide is available, this reaction can continue. The greater the M.S., the greater the water solubility of the polymer and, therefore, the greater the tolerance to salt and hardness. Typically, M.S. values range from 1.5 to 2.5 for HEC.

HEC is used primarily for viscosity and fluid-loss-control in workover and completion fluids. It is compatible with most brines including seawater, KCl, NaCl, CaCl₂ and CaBr₂. It is a very clean polymer and is acid-soluble,

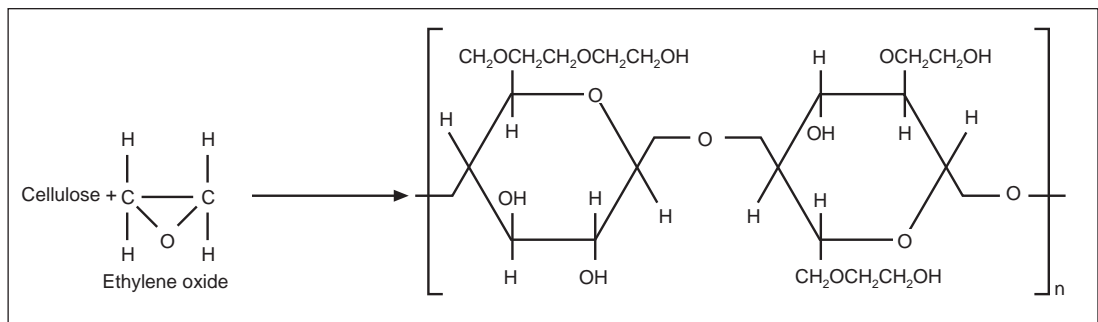


Figure 9: Hydroxyethylcellulose.

...HEC...does not react as strongly with charged surfaces as do ionic polymers.

which makes it ideally suited for gravel-packing and other operations where the completion fluid contacts the production interval. Since HEC is non-ionic, it does not react as strongly with charged surfaces as do ionic polymers. This further enhances its role as a completion fluid additive.

HEC has a temperature limitation of 250°F (121°C). It is not affected greatly by pH (above 10 pH, there may be a minor loss of viscosity) and it is resistant to bacteria. It is not a thixotropic polymer (does not generate gel structures for suspension) and, in fact, provides little if any Low-Shear-Rate Viscosity (LSRV), although it produces a great deal of overall viscosity.

Starch derivatives. As stated earlier in this chapter, starch is useful in many applications without chemical modification. But with chemical modification, starch derivatives can be made to have different properties. Starch can be modified in such a way that it no longer is susceptible to bacterial degradation. It also can be made significantly more temperature-stable with simple modifications. A few examples of modified starches are given below.

Carboxymethyl Starch (CMS).

Another example of a modified polymer is carboxymethyl starch. Like CMC, carboxymethyl starch undergoes a carboxylate substitution at either the hydroxymethyl group or at either of the two hydroxyl groups on the ring

structure. Also like CMC, the substitution occurs most readily at the hydroxymethyl group.

THERMPAC® UL, a carboxymethyl starch, controls fluid loss with a minimum increase in viscosity in most water-base drilling fluids. It is an alternative to PAC materials in systems requiring tight filtration control and low rheological properties. THERMPAC UL performs more like a CMC material than a starch. It has a temperature stability similar to CMC and PAC (up to 300°F (149°C)) and does not require a bactericide.

THERMPAC UL is most effective when applied in drilling fluids containing less than 20,000 mg/l Cl⁻ and 800 mg/l Ca²⁺. It performs at any pH level and is compatible with all water-base systems.

Hydroxypropyl starch. Another example of modified starch is Hydroxypropyl (HP) starch. It is produced by reacting starch with propylene oxide. The resulting modified starch is nonionic and is water-soluble. The modification actually adds to the water solubility of the starch. As with CMS and HEC, the substitution occurs at either the hydroxymethyl group or at either of the two available hydroxyl groups on the ring structure. Also like CMC and CMS, the substitution occurs most readily at the hydroxymethyl group.

The result is a substitution of propoxylated groups. The D.P. of the propoxylated groups is known as the

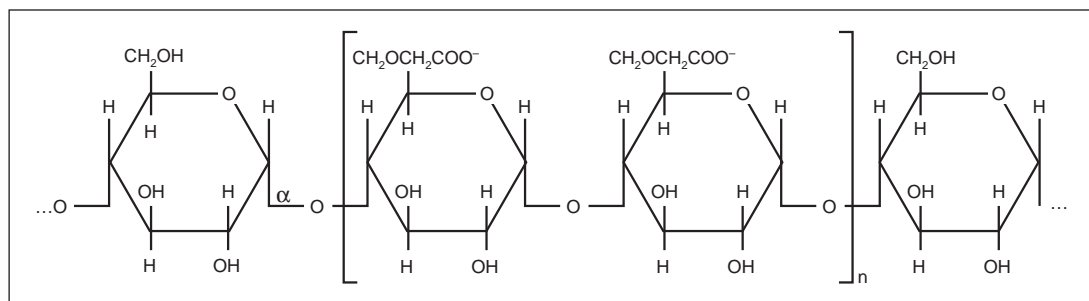


Figure 10: Carboxymethyl starch, D.S. = 1.0.

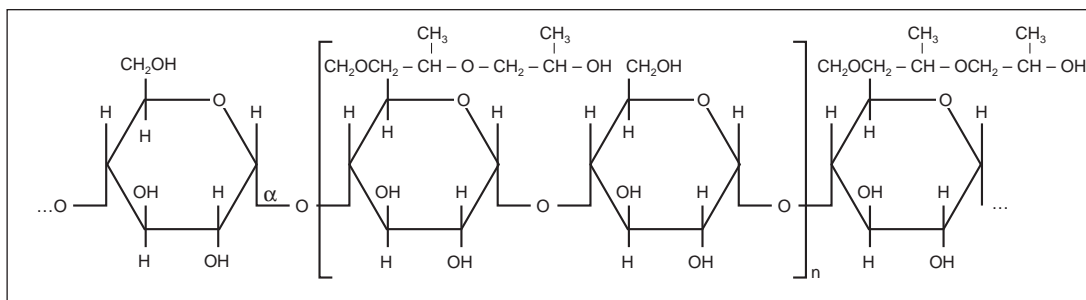


Figure 11: Hydroxypropyl starch, D.S. = 0.5, M.S. = 2.0.

Molar Substitution (M.S.). The M.S. is the average number of propylene oxide molecules that have reacted with each starch unit. Once a hydroxypropyl group is attached to each unit, it can react further with additional groups in an end-to-end formation. The reaction of propylene oxide with starch has similarities to the reaction of cellulose with ethylene oxide. In each case, substitution occurs with a repeating structure that must be defined by its M.S.

Many types of HP starch are available. The properties vary with the D.P., the D.S. and the degree of polymerization of the substituted group (M.S.).

FLO-TROL™ An HP starch used primarily for fluid-loss-control in FLO-PRO® systems. It works in conjunction with calcium carbonate to form an easy-to-remove, acid-soluble filter cake. Like starch, FLO-TROL is compatible with most makeup brines including seawater, NaCl, KCl, CaCl₂, NaBr, CaBr₂ and formate brines. It does not require a bactericide.

FLO-TROL has unique viscosifying characteristics that make it suitable for “drill-in” fluid applications. Unlike PAC products, FLO-TROL contributes to LSRV. It works synergistically with FLO-VIS to increase Low-Shear-Rate Viscosity (LSRV).

Recommended FLO-TROL concentrations are 2 to 4 lb/bbl for most applications, although higher concentrations are used to achieve lower filtration rates. Temperature stability for FLO-TROL is better than most starch materials. It

is thermally stable to 250°F (121°C) in brine applications.

Mor-Rex™ An enzyme-hydrolyzed cornstarch which has been chemically modified to a maltodextrin. The hydrolysis of the starch results in a product that is much lower in molecular weight (less than 5,000) and imparts a slightly anionic character to the polymer.

Mor-Rex has been used in lime-base drilling fluids almost exclusively. This is due primarily to its tendency to increase the calcium solubility in a lime-base fluid environment. In such an environment, the Mor-Rex polymer is further hydrolyzed and Ca²⁺ attaches to the free carboxylate groups formed during hydrolysis. This results in an increased concentration of soluble calcium. In other words, a lime-base system treated with Mor-Rex contains more soluble calcium than the same lime-base system without Mor-Rex. It is thought that the additional Ca²⁺ provides additional inhibition benefits.

Functionally, Mor-Rex acts as a deflocculant, which is consistent with its size and anionic character. Typical concentrations for Mor-Rex in a lime/Mor-Rex system are 2 to 4 lb/bbl. Like traditional starch, it is thermally stable to about a 200°F (93°C) circulating temperature and requires a bactericide.

SYNTHETIC POLYMERS

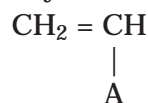
Synthetic polymers are chemically synthesized, usually from petroleum-derived products. Unlike natural and modified natural polymers, synthetic

**...FLO-TROL
contributes
to LSRV.**

Synthetic polymers afford an almost unlimited flexibility in their design.

polymers are “built up” from relatively smaller molecules. Synthetic polymers afford an almost unlimited flexibility in their design. They can be tailor-made to fit almost any application. Their size and chemical composition can be made to produce properties for almost any function.

Frequently, synthetic polymers are prepared from substituted ethylene. The polymerization process occurs through an *addition reaction* wherein the substituted ethylene groups are added to the end of the polymer chain. In the figure below, the substituted group “A” can be any functional group.



Note the carbon-carbon backbone and the unlimited substitution possibilities. The carbon-carbon backbone is a more stable linkage than the carbon-oxygen linkage encountered earlier with starch- and cellulose-base polymers. The carbon-carbon linkage is resistant to bacteria and has temperature stability in excess of 700°F (371°C). The substitution groups most likely will degrade before the carbon-carbon linkage.

Polyacrylate. The polymerization of acrylic acid and the subsequent neutralization with sodium hydroxide yields the polymer Sodium Polyacrylate (SPA). SPA is an anionic polymer that can function either as a deflocculant or a fluid-loss control additive, depending on the molecular weight of the polymer.

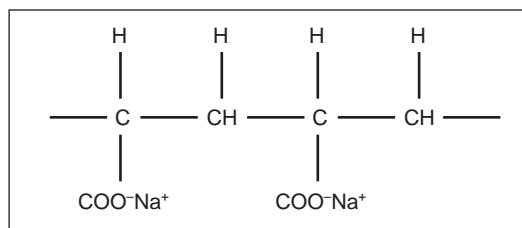


Figure 12: Sodium polyacrylate.

During the drilling of a well, the interaction between the drilled solids has a profound effect on the properties of the mud. There is a natural tendency for flocculation to occur (see Figure 13). Flocculation results in an overall increase in the rheological properties of the drilling fluid.

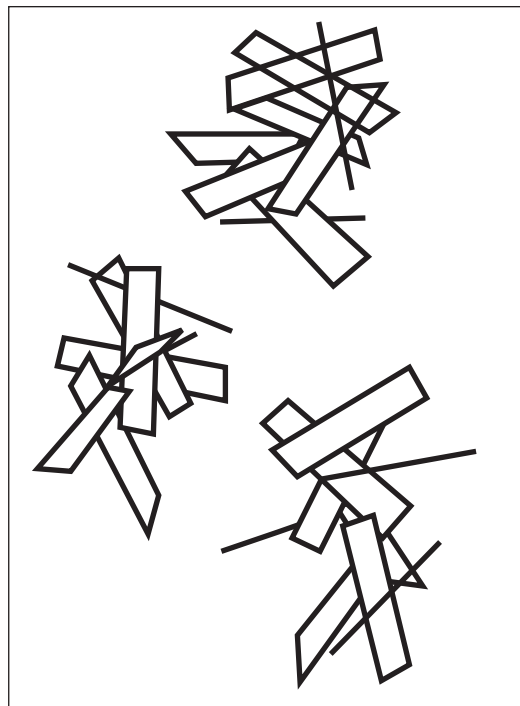


Figure 13: Flocculation of drill solids.

SPA functions as a deflocculant at low molecular weights (less than 10,000). It is highly anionic and adsorbs on the active solids in drilling fluids. The adsorbed polymer neutralizes the positive charges on aggregated particles, which results in mutual repulsion and deflocculation. This is best accomplished with a small polymer. Short-chain polymers create maximum adsorption on the particle surfaces and eliminate the flocculating effect that occurs when one polymer adsorbs to several particles (see Figure 14).

A copolymer contains two or more different types of monomers.

TACKLE is an example of a copolymer.

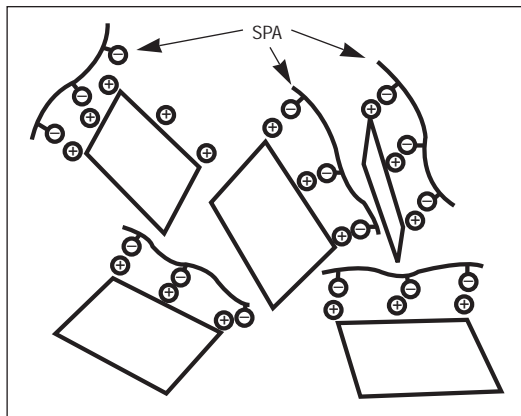


Figure 14: Diagram of SPA and clays.

Many mud companies use low-molecular-weight sodium polyacrylate as their primary deflocculant for low-solids, non-dispersed and other polymer systems. It can be prepared as a dry powder but usually is available in liquid form.

SPA functions at much lower concentrations than lignosulfonates. Typically, concentrations of 0.25 to 1.0 lb/bbl are sufficient to control rheological properties. SPA does not depend on alkaline pH and can tolerate temperatures to 500°F (260°C). It performs best in polymer systems but is sometimes used as a stand-alone product in spud mud and in geothermal applications.

SPA is sensitive to high concentrations of solids. Since it is a surface-active material, it can get overwhelmed in a high-solids environment. It works best when the CEC of the mud is less than

20 lb/bbl bentonite equivalent and the mud weight is less than 12 lb/gal. TACKLE® is also affected by soluble calcium, although it is still effective in seawater applications.

Copolymerization. So far, this chapter has dealt only with homopolymers, i.e., polymers prepared from identical units (or monomers). It is possible to start with more than one type of monomer and undergo polymerization and end up with a copolymer. A copolymer contains two or more different types of monomers.

Through copolymerization, polymers can be made which have different properties than any of the homopolymers alone. Adding more monomers creates a completely new dimension for design possibilities. It is possible to use more than a single monomer to impart specific properties to the finished polymer product. For instance, one monomer can be used to extend temperature stability and a second monomer can be used to inhibit shale.

TACKLE is an example of a copolymer. It is prepared from two monomers: sodium acrylate (as in SPA) and a monomer known in the industry as AMPS (2-acrylamido-2-methyl propane sulfonic acid). The AMPS monomer provides a sulfonate group that imparts greater temperature stability and tolerance to solids, salinity and hardness than the sodium acrylate group alone.

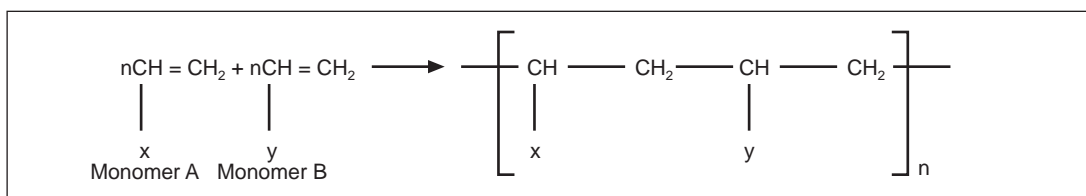


Figure 15: Copolymerization.

...SP-101 has a stabilizing effect on drilled cuttings.

AMPS is a fairly expensive monomer; however, it can give high temperature stability in the presence of contaminants, which is more than PAC and modified starch can give.

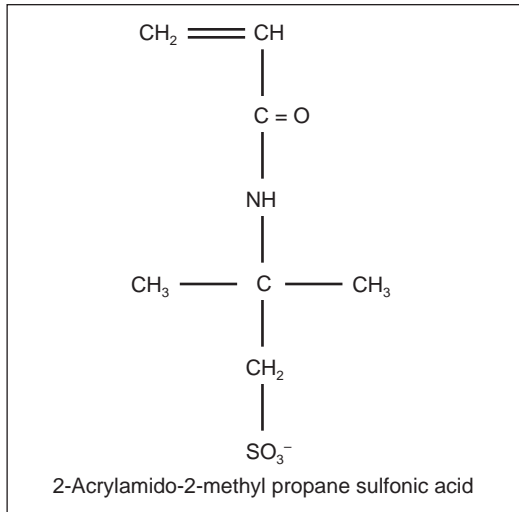


Figure 16: AMPS monomer.

TACKLE...is more functional in seawater than low-molecular-weight SPA.

TACKLE, due to the AMPS monomer, has greater contamination resistance and tolerance to solids than SPA alone. Like SPA, it still is better suited to polymer systems and low-solids, non-dispersed applications. It also has trouble controlling viscosity in a high-solids environment. However, it is more functional in seawater than low-molecular-weight SPA.

SP-101[®] is a medium-molecular-weight ($\pm 300,000$) polyacrylate used primarily for fluid-loss control. It is stable to very high temperatures ($>400^\circ\text{F}$ (204.4°C)) and is often applied in geothermal applications. Like TACKLE, it is not pH-dependent or subject to bacterial degradation, but it is susceptible to soluble calcium contamination. It is recommended that soluble calcium be maintained at a concentration of 300 mg/l or less for optimum performance. It is most effective in freshwater systems.

SP-101 is most often used in low-solids, non-dispersed systems and

other polymer systems like PHPA. In addition to providing fluid-loss control, SP-101 has a stabilizing effect on drilled cuttings. SP-101 attaches to clay particles and provides some encapsulation of the drilled cuttings. Sometimes, a viscosity hump is seen when SP-101 is first added to a system. Once the polymer is worked into the system at a sufficient concentration to encapsulate the solids, the system thins back and stabilizes. Typically, this concentration occurs at about 1 lb/bbl, but it can be slightly more or less, depending on the solids load. SP-101 is an effective defloculant, especially in high-temperature applications and polymer applications.

While SP-101 does not provide the immediate thinning effect that is seen with TACKLE, it provides stabilization of the rheological properties when the concentration exceeds 1 lb/bbl. SP-101 is very effective at stabilizing the rheological properties of many freshwater systems including PHPA; geothermal; and low-solids, non-dispersed systems.

Polyacrylamide/polyacrylate copolymer. Partially Hydrolyzed Poly Acrylamide (PHPA) is often used to identify the copolymer polyacrylamide/polyacrylate. The end product of a PHPA is the same polymer that is formed by a polyacrylamide/polyacrylate copolymerization. Even though the product is frequently referred to as PHPA, it actually is made by the copolymerization of acrylamide and sodium acrylate monomers. For the sake of simplicity, the material will be referred to as PHPA.

The properties of PHPA are affected by the molecular weight and by the ratio of the carboxyl groups to the amide groups. Polyacrylamide by itself is insoluble, so it must be copolymerized with sodium acrylate to obtain water solubility. Copolymerization with sodium acrylate results in an anionic polymer that is water-soluble. The ratio

of sodium polyacrylate to acrylamide at the beginning of the process determines the ratio of the two functional groups on the final copolymer. The two monomers that make up the copolymer are shown below.

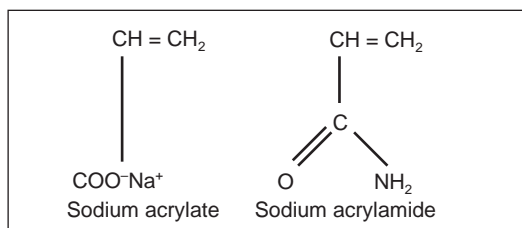


Figure 17: Sodium acrylate/acrylamide.

During copolymerization, the two monomers are linked together in a random fashion to form a linear, carbon-carbon backbone. The resulting copolymer has carboxyl groups and amide groups randomly distributed along its backbone. The resulting copolymer is shown in Figure 18.

Note that due to the carbon-carbon linkage, the polymer has exceptional thermal stability and is resistant to bacteria. Also note that the polymer is anionic, meaning it is affected by hardness and cationic surfaces like those found on clays.

POLY-PLUS.® The most commonly used PHPA in drilling fluids is the high-molecular-weight version which is prepared with 65 to 70% acrylamide and the remaining percentage acrylate. Molecular weights range up to 20 million. POLY-PLUS is used as a shale inhibitor and solids-encapsulating polymer in freshwater, seawater, NaCl and KCl systems. In addition to its

shale-inhibiting properties, it also provides drilled cuttings encapsulation and viscosity in freshwater systems.

The shale-inhibition feature of PHPA occurs when the polymer attaches to clays on the wellbore and blocks the hydration and dispersion that normally occurs. **The anionic carboxyl groups attach to the positive charges on the edges of the clay particles.** Since the polymer has a high molecular weight and is relatively long, it combines with several sites along the wellbore. This has the effect of coating the wellbore and restricting water from entering the clay.

The same effect is seen on the drilled cuttings. The polymer helps preserve the integrity of the cuttings, which allows for much easier cuttings removal at the surface.

PHPA also aids in shale stabilization by thickening the water phase. PHPA increases the viscosity of the drilling fluid filtrate, which has the effect of limiting the filtrate depth of invasion. Although water may penetrate far into a shale, a thick polymer filtrate faces much greater resistance due to the rapid buildup of capillary pressures. This has the effect of reducing the amount of filtrate water available for hydration. It also limits the ability of a filtrate to enter a small fissure or fracture plane within a shale.

Shale studies have established that a 70:30 ratio of acrylamide units to acrylate units is optimum for drilling fluids. This often is referred to as 30% hydrolysis. It has also been determined

PHPA also aids in shale stabilization by thickening the water phase.

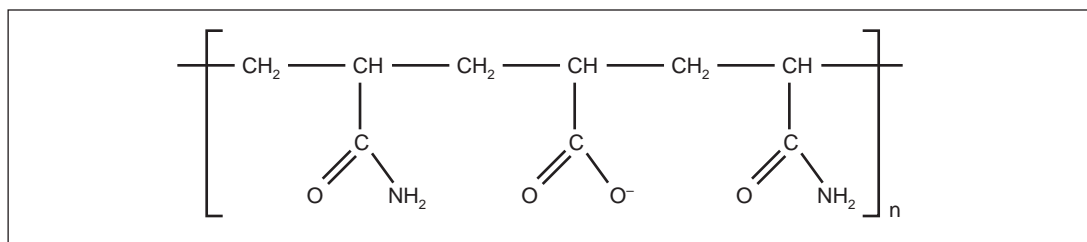


Figure 18: PHPA.

that higher-molecular-weight polymers encapsulate shale better than low-molecular-weight polymers.

As mentioned earlier, it is necessary to copolymerize with sodium acrylate to achieve water solubility; however, a 100% polyacrylate does not provide as much inhibition as the 70:30 ratio. Even at similarly high molecular weights, the 70:30 ratio provides better shale inhibition.

It is thought that a high-molecular-weight polyacrylate has too much affinity with the positive charges on clays. Similar to lignosulfonates, as the polymer remains in the system and attaches to active clay edges both in the fluid system and on the wellbore, strong attractive forces may actually pull the clays apart and cause them to disperse into the system. The amide group helps by providing some distance between the strongly anionic carboxyl groups and the cationic sites on the clay particles. When the amide groups and the carboxyl groups are distributed evenly along the polymer chain, the bulkiness of the amide group prevents the carboxyl group from getting too close to the clay charges and breaking the clays apart.

The acrylamide group also has an affinity with the clay surface, but it is a relatively weak hydrogen bond compared to the strong ionic interaction between the carboxyl group and positively charged edges on clay particles. The acrylamide group is capable of forming hydrogen bonds along the clay surface. While not nearly as strong as the ionic interaction taking place alongside, it serves to hold the polymer/clay interaction in place as well as to provide distance between the free charges.

In a salt environment, PHPA is still very effective in a shale-stabilizing capacity, although its concentration must be increased to obtain a significant effect on filtrate viscosity. As the

salinity of the water increases, the PHPA does not hydrate free water as readily, and the polymer remains somewhat coiled. This leads to a decrease in the viscosifying characteristic of the polymer. The polymer is still anionic, however, and is still adsorbed on the active sites on the wellbore.

Applying PHPA to salt-base drilling fluids simply means that more PHPA polymer must be added to obtain the same encapsulating and filtrate-thickening effects. Since salt muds, particularly KCl muds, impart a great deal of shale stabilization on their own, a salt PHPA mud offers exceptional shale-stabilization characteristics. The salt or KCl provides excellent shale stabilization and the PHPA provides a viscosified filtrate that limits invasion depth.

One of the drawbacks to PHPA is its sensitivity to soluble calcium. Like polyacrylate, the anionic carboxyl site reacts with calcium. This is particularly a problem in freshwater systems, where calcium can precipitate the PHPA polymer as well as whatever solids the polymer is adsorbed on. In some cases, PHPA functions as a flocculant in the presence of calcium, particularly when the solids content of the drilling fluid is low. When the solids content is low and calcium is introduced, flocculation occurs and the solids precipitate and settle out of the mud. In high-solids systems, the introduction of calcium flocculates the system and very high viscosities result.

In a salt mud, the PHPA polymer remains relatively coiled and is not as susceptible to the flocculating effects of soluble calcium. It is still affected by Ca^{2+} , at least to some extent. Since the Ca^{2+} reacts directly on the polymer with an anionic site, that anionic site is no longer available for an active wellbore site. In short, more polymer must be used to overcome the effect of calcium.

It is recommended to treat soluble calcium to below 300 mg/l in PHPA

One of the drawbacks to PHPA is its sensitivity to soluble calcium.

Removing calcium from the system requires adding a carbonate source...

Hydrolysis of the PHPA polymer...is insignificant until a pH of 10 is reached...

systems. This is easier to perform in low-solids, low-density applications, particularly when the solids are not that hydratable. When the solids concentration is relatively high, such as a mud weight over 10 lb/gal and an MBT above 20 lb/bbl bentonite equivalent, then it is more difficult to treat calcium. Removing calcium from the system requires adding a carbonate source, such as soda ash or bicarbonate of soda, which may flocculate the system.

A similar analogy is made with magnesium contamination. Magnesium also is attracted to the anionic carboxyl site. To treat magnesium, it is necessary to increase the pH to the 10.0 to 10.5 level. Since the reaction that occurs at that pH is reversible, the pH must be maintained at that high level to prevent the now-insoluble magnesium from becoming soluble again. PHPA systems are non-dispersed systems and do not tolerate alkaline pH easily. Like any non-dispersed system, the addition of caustic soda has a flocculating effect on PHPA systems. The hydroxide ion (OH⁻) is very reactive and goes straight to the unprotected clays in the system. The result is the same that is seen when caustic soda is added to spud mud, which is flocculation.

Hydrolysis of the PHPA polymer occurs at any pH, but it is insignificant until a pH of 10 is reached, when a more rapid hydrolysis begins. The hydrolysis is nowhere complete at pH 10, but since hydrolysis results in the release of ammonia gas (NH₃), which is very noticeable at low concentrations at the rig site, it is something to avoid. Hydrolysis is actually a fairly slow process at pH 10, taking a very long time for the reaction to proceed through the coiled polymer. The process can be accelerated by high temperatures. At temperatures above 300°F (149°C), hydrolysis occurs at a much higher rate.

PHPA AS A BENTONITE EXTENDER, SELECTIVE FLOCCULANT AND TOTAL FLOCCULANT

Depending on its molecular weight and ratio of acrylamide to acrylate monomers, PHPA can serve several functions in a water-base drilling fluid.

GELEX[®] An example of PHPA used as a bentonite extender. When the conditions are right, very low concentrations of PHPA can extend the viscosity of bentonite. When the total solids of the system are less than 4% by volume, and the total bentonite concentration is less than 20 lb/bbl, PHPA can attach to the positive sites on a bentonite clay particle. With the bentonite particle attached to part of the polymer and the remaining polymer free to hydrate and/or attach to other clay particles, the result is an increase in viscosity. In effect, the PHPA polymer is hydrated and uncoiled and in suspension with colloidal bentonite particles.

For PHPA to extend the yield of bentonite effectively, several conditions other than bentonite and total solids concentrations must be met. First, the system must be a freshwater system and relatively free of calcium (< 200 mg/l) for the bentonite to hydrate properly. Second, the amount of polymer must be in the 0.05 to 0.1 lb/bbl concentration range. Third, no dispersants — or any other additive that adsorbs to the bentonite — can be in the system.

The process of extending bentonite is fragile and limited to low-solids, non-dispersed applications. The addition of only a small amount of PHPA causes an immediate increase in viscosity. As the concentration of PHPA is increased, the viscosity reaches a maximum value and then, as additional polymer is added, breaks back. The effective range of polymer concentration is very narrow. Too little polymer concentration, and the system is little more than a gel slurry with a low concentration of bentonite.

PHPA also can be used as a flocculant.

Overtreat with polymer, and the system thins out too much.

The degree of bentonite extension depends on the following factors:

- The MW and the ratio of acrylamide to acrylate.
- The size and hydration of the particle.
- The salinity and hardness of the makeup water.
- The concentration of the PHPA polymer.

FLOXIT.™ PHPA also can be used as a flocculant. Flocculation is the process by which individual particles are connected in loosely bound, large aggregates by a flocculating polymer. The resulting mass of linked particles increases to the point at which the solids agglomeration falls out of suspension. Settling is most effective when the system is static.

The mechanism involved in flocculation is very much like the mechanism used for bentonite extension. PHPA is also effective in both applications. It should be noted that PHPA is not as effective at flocculating systems that contain bentonite. Since bentonite breaks up into colloidal-size, hydrated solids, bentonite does not settle. The small hydrated particles do not have enough density to settle.

The use of FLOXIT is limited to clear-water drilling applications. Once solids build in the water or the system is weighted, the product is no longer useful. Determining the optimum concentration of FLOXIT must be determined by pilot testing. The effectiveness of the flocculation depends on the interaction of the polymer with the solids, which in turn depends on the following:

- Hydratability of the solids.
- The concentration of the solids.
- Salinity of the water.
- Hardness of the water.
- Chemical characteristics of the polymer.
- Polymer concentration.
- Rheological properties of the system.

- Geometry and size of the settling pit.
- Retention time.
- Temperature.

It is recommended that FLOXIT be mixed in dilution water at a concentration of 1 to 2 lb/bbl before adding it to the system. Again, pilot testing is necessary to determine the optimum concentration.

HIGH-TEMPERATURE SYNTHETIC POLYMERS

Due to the thermally stable carbon-carbon linkage that makes up the backbone of synthetic polymers, high-temperature polymers are synthetically derived. Several high-temperature polymers are available for drilling fluids. A number of them are prepared from the AMPS (2-acrylamido-2-methyl propane sulfonic acid) monomer. AMPS was covered earlier in this chapter in conjunction with TACKLE. AMPS is used in the preparation of TACKLE to improve tolerance to solids, salinity and hardness at high temperatures.

AMPS is also used to improve the high-temperature tolerance to contaminants in fluid-loss-control additives. Examples of copolymers and terpolymers that incorporate the AMPS monomer or other sulfonated monomers are the Hoechst's Hostadrill 2825, Drilling Specialties' Driscal-D and SKW's Polydrill. The manufacturers of these materials claim that their respective polymers withstand salt and hardness at temperatures to 400°F (204°C). Chemical structures for Hostadrill and Polydrill are given in Figures 19 and 20.

An example of a high-temperature polymer that functions to prevent high-temperature gelation is a Sulfonated Styrene Maleic Anhydride (SSMA) copolymer. Generally, it is applied to wells at high temperatures prior to logging runs and at other times when the drilling fluid is not circulated for an extended period of time. It has the effect

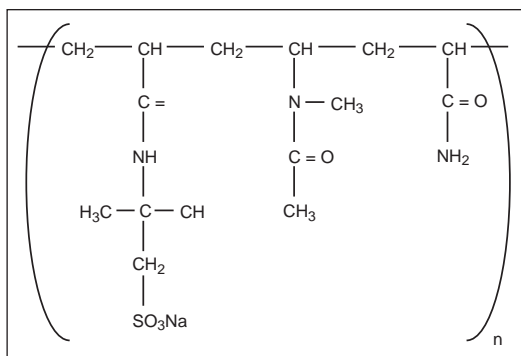


Figure 19: Hostadrill 2825.

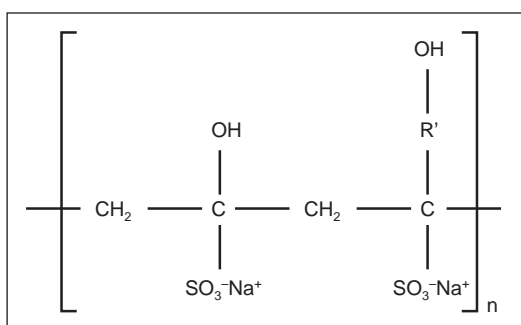


Figure 20: Polydrill.

of maintaining stable gel strengths at high temperatures. It is not a fluid-loss control additive or a deflocculant (see Figure 21).

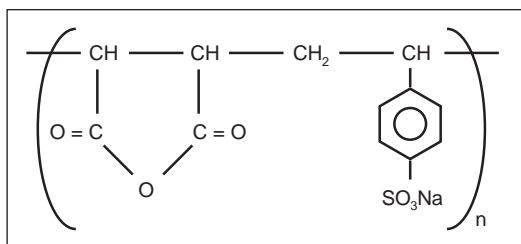


Figure 21: SSMA.

**The M-I
POLYSTAR™ 450
system is
based on
synthetic
polymers.**

The M-I POLYSTAR™ 450 system is based on synthetic polymers. One product, RHEOSTAR™, is used to control high-temperature gelation, high-temperature bentonite flocculation, and to provide thinning or deflocculation. Due to the complex nature of high-temperature, water-base environments, RHEOSTAR is actually a blend of three low-molecular-weight synthetic polymers. These polymers are different from the more traditional AMPS acrylate-base

polymers. RHEOSTAR is a dry powder that is readily functional in seawater and freshwater. It is stable to 450°F (232°C). Typical concentrations vary from 6 to 12 lb/bbl.

DURASTAR.™ DURASTAR provides high-temperature filtration control in the POLYSTAR 450 system. It is a crosslinked copolymer prepared from acrylamide monomer, a sulfonated monomer and a crosslinking monomer. The degree of crosslinking in the polymer structure plays an important role in the polymer's solubility and fluid-loss control characteristics. Too much crosslinking results in a polymer that is rigid and poorly hydrated, while too little crosslinking results in a polymer that has properties similar to PHPA, which is long and linear with little tolerance to contamination.

Due to its crosslinked structure, DURASTAR is compact and globular in structure. It retains a compact, spherical shape compared to the expanded, uncoiled forms of linear polymers (see Figure 22) which uncoil into linear-shaped particles.

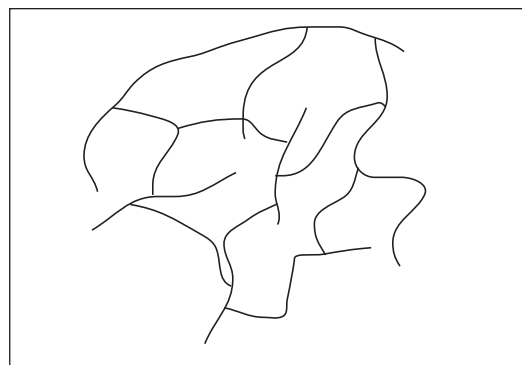


Figure 22: DURASTAR.

An advantage to its compact shape is that DURASTAR is more protected and, therefore, more thermally stable and resistant to solids and hardness. DURASTAR is stable to 450°F (232°C) in both freshwater and seawater applications. Typical concentrations range from 5 to 10 lb/bbl. It is available as a 30% active inverse emulsion.