

# POLYMERS AND THEIR USE IN THE OIL FIELD

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## INTRODUCTION

The word "polymer" is used almost every day in discussions concerning the oil field. However, even though polymers are used in almost every phase of the drilling, completion, and production of oil and gas wells, they continue to mystify many oilfield personnel. Few people in the industry understand what constitutes a polymer or the properties exhibited by these polymers.

This paper discusses naturally occurring,<sup>1</sup> modified naturally occurring, and synthetic polymers<sup>2</sup> with application in drilling, lost circulation, cementing, damage removal, stimulation, water and sand control, and secondary and tertiary recovery. Polymer properties defined and discussed include rheology, viscosity, solubility, shear and temperature stability, chemical reactivity, adsorption, solids-suspending characteristics, and salt sensitivity.

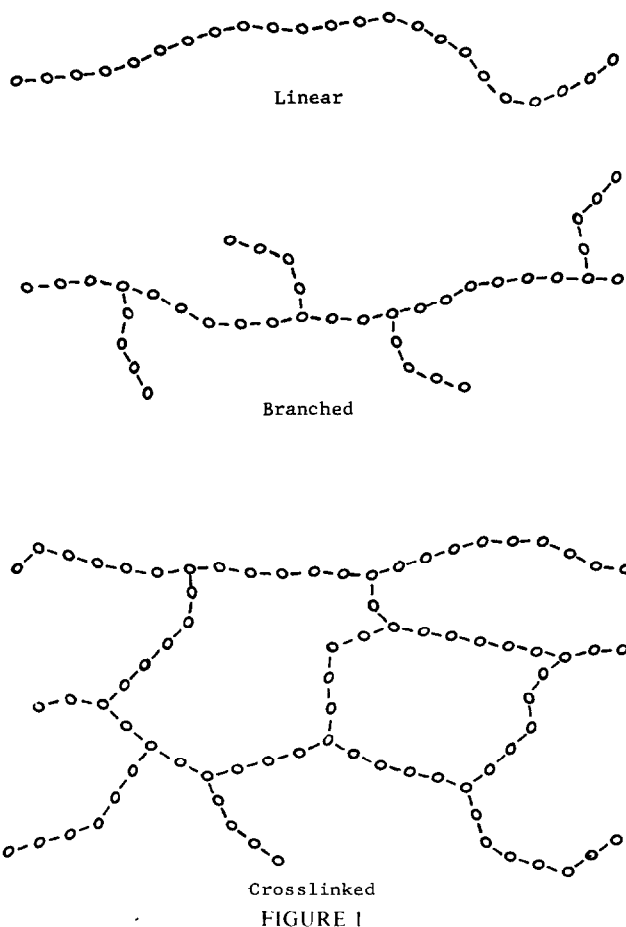
## DEFINITIONS AND CONCEPTS

The word "polymer" is derived from the Greek words "polys", meaning many, and "mere", meaning part. The chemical dictionary defines "polymer" as being a substance, either synthetic or naturally occurring, composed of giant molecules that have been formed by the union of a considerable number of simple molecules.

The starting materials from which polymers are derived are known as monomers and their union is called polymerization. The number of monomer molecules which unite through polymerization varies from two to the millions. The degree of polymerization, in turn, determines the molecular weight of the polymer. The properties and behavior

of the polymer are greatly altered by this degree of polymerization.

The monomer molecules may be all alike, or there may be two or more different monomers involved in forming a single polymer. The units that are repeated throughout the polymer chain are known as repeat units. If each of these repeating units is considered as a link in a chain, then there are three



configurations in which the links can be put together. These configurations as depicted in Fig. 1 are linear, branched, and crosslinked. The configuration, once again, is instrumental in determining many of the polymer properties.

The majority of commercial polymers are composed of organic materials and these polymers are the ones most often found in the oil field. However, it is possible for polymers to be inorganic in composition. An example of this is asbestos which is a naturally occurring inorganic polymer. Other polymers may contain both organic and inorganic components, in which case they are referred to as organometallic polymers. The human body contains many organometallic polymers. Silicone polymers are the only significant synthetic, organometallic polymers.

#### *Viscosity of Polymer Solutions*

Most applications of polymers in the oil field involve placing the polymer in solution. There are certain terms applied to these solutions that describe their behavior and properties which we need to understand. Most polymer solutions can be described as non-Newtonian, pseudoplastic, and viscoelastic.

Fluids have been classified into two general categories, Newtonian and non-Newtonian. Newtonian fluids are those whose shear stress is directly proportional to the shear rate. Examples of Newtonian fluids are gases, water, brines, oils, and acid solutions. For non-Newtonian fluids, the ratio of shear stress to shear rate is not constant but varies with shear rate. A more simplified way of stating this is that a Newtonian fluid has uniform viscosity at a constant pressure and temperature for any shear rate, while the viscosity of a non-Newtonian fluid is shear-rate dependent. Because of this, the thickness of a non-Newtonian fluid is described as apparent viscosity instead of viscosity. Apparent viscosity is defined to be the viscosity of a Newtonian fluid that would produce the same pressure drop at the same shear rate. The failure to state the shear rate at which the apparent viscosity of a non-Newtonian fluid was obtained is one of the more common errors prevalent in the industry. Examples of non-Newtonian fluids are polymer solutions, drilling muds, paints, foams and quicksand.

Non-Newtonian fluids have been subdivided

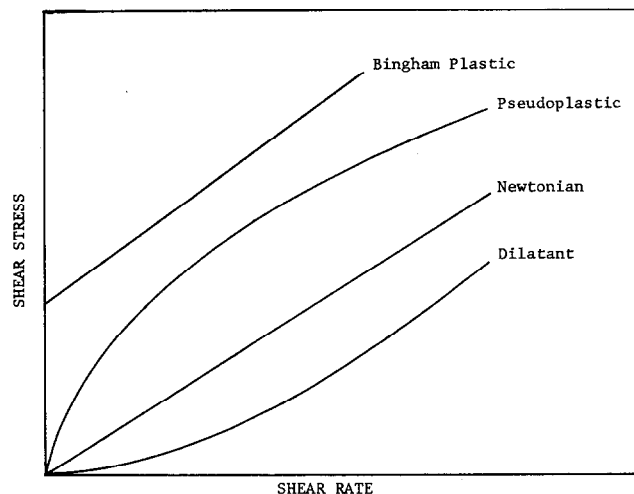


FIGURE 2

further into Bingham plastic, pseudoplastic, dilatant, thixotropic, and rheopectic fluids. The relation of shear stress versus shear rate for these different types of fluids is shown in Fig. 2. However, since most polymer solutions are pseudoplastic in nature this discussion will be limited to this class. Definitions and examples of the other types of fluids may be found in the Appendix.

Pseudoplastic fluids are those fluids which decrease in apparent viscosity with increased shear rate. When a plot of shear stress versus shear rate of such a fluid is made on logarithmic scale, a straight line is obtained. The slope of this straight line,  $n'$ , is a measure of the non-Newtonian behavior of the fluid. For  $n'=1$ , the fluid is Newtonian. The intercept of the line at shear rate of  $1 \text{ sec}^{-1}$ ,  $K'$ , is a measure of the fluid consistency. The larger the value of  $K'$ , the

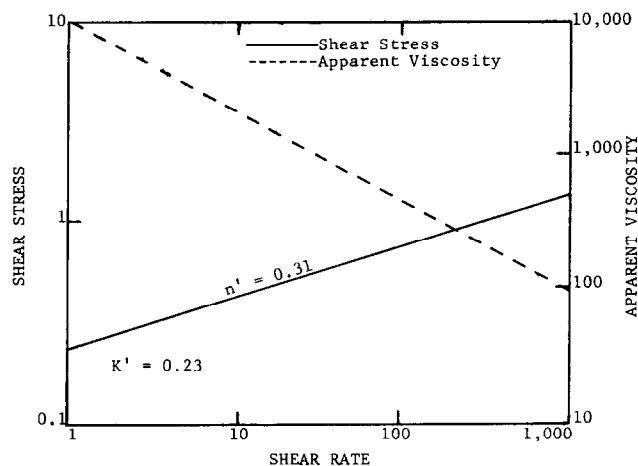


FIG. 3 SHEAR RATE VS. SHEAR STRESS AND APPARENT VISCOSITY FOR A PSEUDOPLASTIC, POLYMER SOLUTION

more viscous is the fluid.

The apparent viscosity,  $\mu$ , of pseudoplastic fluids can be calculated at any shear rate, SR, if the  $n'$  and  $K'$  are known from the equation:

$$\mu = 47,917 K' (SR)^{n'-1}, \text{ cp.}$$

Figure 3 shows a typical logarithmic plot of shear stress versus shear rate and viscosity for a polymer solution.

### Drag Reduction

The decrease in apparent viscosity with increased shear rate of pseudoplastic fluids is commonly called shear thinning. This should not be confused with shear degradation which will be discussed later. The ability of a polymer solution to shear thin becomes very important in certain applications. When pumping polymer fluids, as the movement of fluid begins, the fluid structure starts to break down, resulting in a lowering of the viscous resistance. When this happens, the friction pressure between the fluid and the pipe wall decreases and the flow rate increases at constant pressure. When the shear rate decreases, as in the annulus with drilling muds or in the fracture with stimulation fluids or lost circulation fluids, the apparent viscosity increases, enabling solids to be suspended in the fluid.

Another important property of most polymeric solutions is viscoelasticity. These solutions exhibit both viscous and elastic deformation flow properties. Drag reduction under turbulent flow is usually attributed to viscoelasticity. Numerous publications<sup>3-5</sup> have been written concerning this subject, but the drag reduction mechanisms have not been clearly defined. However, it is not uncommon for polymer solutions to exhibit a friction reduction over the base fluid of 80 percent. This drag reduction can exist over a wide range of polymer concentrations and fluid velocities.

### Polymer Solubility

Water-soluble polymers must be highly polar in nature as with any other water-soluble material while oil-soluble polymers are highly nonpolar. Other properties which affect solubility are inter and intramolecular hydrogen bonding of the polymer molecules; temperature, pH, and salt content of the solvent; molecular weight, structure, and ionic nature of the polymer.

In the solid state, the polar polymers are capable of undergoing hydrogen bonding. This bonding may be either inter or intramolecular. For linear polymers, this hydrogen bonding may be complete, which results in the polymer being insoluble. For nonlinear polymers, there are regions where the molecules do not fit together and the hydrogen bonding is only partially satisfied. When a soluble polymer is placed in water, the water molecules quickly penetrate and bind to available sites. This, in turn, releases other sites for hydration. Some polymers undergo complete hydration while others may stop along the way to remain as incomplete dispersed molecules forming gels. These polymers, because they are not totally soluble in aqueous systems, are often used to control fluid leak-off in drilling, cementing and stimulation fluids. Extensive hydration of the polymer leads to improved solution stability and increased solution viscosity. Figure 4 illustrates the attachment of water molecules, hydration, to guar polymer.

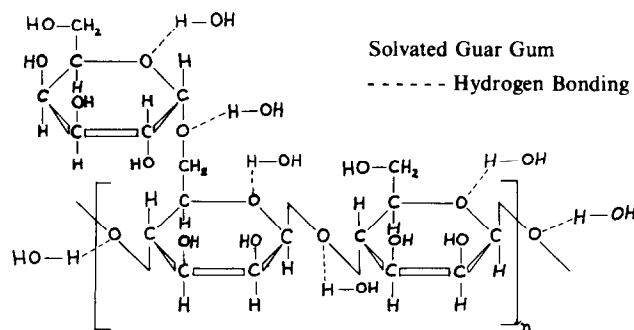


FIG. 4 SOLVATED GUAR GUM - HYDROGEN BONDING

Linear polymers may be modified so that the polymer molecules no longer fit together and thus may become hydratable. Increasing the solvent temperature of these polymers may also increase solvation.

Nonionic polymers are usually stable in moderately high concentrations of salt, unless complexing occurs. However, as the salt concentration increases, the salt's affinity for the water pulls it away from the polymer thereby reducing its solubility, sometimes to the extent that precipitation may occur.

Anionic, negatively charged, polymers are not compatible with salts and will undergo precipitation at relatively low concentrations.

Cationic, positively charged, polymers are compatible with salts to an equal or greater extent than nonionic polymers.

In general, as the molecular weight of the polymer is increased, the solubility decreases but the solution viscosity increases.

### *Polymer Crosslinking and Complexing*

Polymer solutions at low concentrations are classed as sols while solutions at high concentrations are gels. The point usually taken for a sol becoming a gel is when the solution viscosity becomes high enough that air bubbles will no longer rise to the surface. In the oil field, any polymer solution which possesses viscosity is usually called a gel.

It is possible to make a gel from a sol by connecting the polymer molecules in the solution so that a network is formed and the polymer loses its freedom of movement in the solution. This tying together of polymer molecules can be accomplished either through crosslinking or complexing.

Crosslinking is brought about by reacting the polymer with a chemical, which results in the connection of one polymer molecule to another. The bonds formed by this chemical reaction are usually as strong as the bonds within the polymer. Crosslinking is usually accomplished by using another organic molecule.

Complexing is brought about by reacting the polymer with a metal ion. These bonds are usually much weaker than crosslink bonds. They are more easily broken by shear and temperature.

A large degree of complexing or crosslinking can result in the polymer becoming insoluble in the solution.

The conditions for the crosslinking or complexing reactions to take place depend upon the polymer and crosslinking or complexing agent being used. Numerous papers<sup>6-9</sup> have been written on these subjects.

### *Polymer Degradation*

Polymer degradation can occur both physically and chemically. Physical degradation usually involves shear. As the polymer solution is being pumped, a large amount of energy is exerted on the polymer. This shearing energy is capable of physically breaking the polymer molecules apart, resulting in polymers of lower molecular weight. All

polymers are capable of undergoing this shear degradation; however, the high molecular weight, straight chain polymers are usually more easily shear degraded.

Chemical degradation usually involves the reaction of another chemical on the polymer to break the polymer chains. Chemicals capable of polymer degradation are acids and bases, oxidizing agents, and enzymes. Temperature and ultraviolet light are also capable of degrading polymers. Most common polymers thermally decompose at temperatures in excess of 450°F in an inert atmosphere at neutral pH. Increasing the temperature enhances all of the chemical reactions mentioned above.

Increasing the temperature usually results in reducing the viscosity of polymer solutions due to the loss of hydrogen bonding. This is commonly called temperature thinning. The rate at which temperature thinning occurs is dependent upon the polymer and solution conditions. It should be noted that hydrogen bonding is reversible, and a polymer solution which has a low viscosity at an elevated temperature will regain its viscosity upon cooling unless polymer degradation by one of the above-mentioned mechanisms has occurred.

### *Polymer Adsorption*

Polar polymers may be chemically adsorbed from solution on the walls of the formation pores because of the electrical charges associated with the matrix materials. This can result in a reduction in permeability. This property is very useful in controlling fluid loss and in polymer flooding operations.

The polymer may also be physically removed from solution. High molecular weight polymers are large and may be screened out by a small constriction between pore spaces in the same manner as rocks are screened from sand. This can also result in a loss of permeability.

Some polymers are capable of greatly reducing the permeability to water of porous media while only small reductions in permeability to oil are observed. These polymers are often used in mobility control operations.

Mobility is a measure of the ease with which a fluid moves through porous media. It decreases with increased viscosity and increases with increased

permeability to the fluid. Flood fluids become more efficient in their sweep efficiency as their mobility increases with respect to the mobility of the crude.

## COMMON OILFIELD POLYMERS AND THEIR USES

To discuss all of the different polymers used in the oil field is beyond the scope of this paper, and many are probably not known by the author due to their proprietary use. However, some of the more common, widely used polymers, their descriptions, and uses are given below.

### *Guar Gum*<sup>1</sup>

Guar gum is obtained by grinding the endosperm of the bean produced by the guar plant. Most of the guar beans are produced in India and Pakistan but some are produced domestically in North Central Texas and southwestern Oklahoma.

Guar gum is a nonionic, branched chain polymer of the polysaccharide class. Its structure is shown in Fig. 4. It forms viscous solutions when hydrated in water. The time required for hydration is determined by the particle size, pH, temperature, and salt content.

Because guar gum is nonionic, it is highly compatible with salts such as sodium and potassium chloride and moderately compatible with divalent salts such as calcium and magnesium chloride. It produces high viscosity gels by complexing with many multivalent ions such as borate, chromium, and aluminum under controlled pH conditions. Guar gum will not hydrate if added to water containing these ions if the pH is such that a complex is formed.

Guar gum contains natural enzymes which may cause polymer degradation, and its sols are easily broken by bacteria. To prevent bacteria degradation, bactericides may be added to the sol.

Thermal degradation of guar gum sols is fairly rapid above 175°F. It acts as a very good friction reducer under turbulent flow conditions at concentrations in excess of 0.05%. Guar gum, depending upon its grade and method of separation from the guar bean, contains from 5-10% insoluble material.

Guar gum is used as a viscosifier and drag reducer for hydraulic fracturing and drilling fluids. It is also effective as a fluid loss additive in many instances.

High viscosity, complexed guar gels are sometimes used to temporarily block permeable zones during workover operations.

### *Guar Derivatives*

Recently, hydroxyalkyl derivatives of guar have become available commercially. By controlling the amount and type of derivitization, the properties of the polymer may be greatly modified. The guar derivative most commonly in use now is hydroxypropyl guar. Its viscosity development is similar to that of guar; however, it has several advantages over guar. It is faster hydrating and hydrates at colder temperatures. It has less residue, in the order of one percent, and more temperature stability. Its solutions are less biodegradable and it will gel water containing high concentrations of methanol.

The uses of hydroxypropyl guar are similar to that of guar. New uses of guar derivatives will undoubtedly arise as new modifications become available.

### *Cellulose Derivatives*<sup>1</sup>

Like guar, cellulose is a nonionic, polysaccharide; but unlike guar, cellulose is a straight chain polymer which is insoluble in water. It has been found that by adding side chains to the cellulose polymer it becomes water soluble and can hydrate to form viscous solutions with little or no residue. These side chains determine the properties of the cellulose derivative. The number of different modified cellulose polymers which can be made by altering the number of side chains or by using different side chains approaches infinity. In addition, the molecular weight of the cellulose polymer can vary and this also alters the properties of the modified cellulose.

Cellulose derivatives used in the oil field are both nonionic and anionic. The nonionic derivatives are not easily complexed with metal ions; therefore, they are highly compatible with almost all salts. The anionic derivatives are easily complexed and can become insoluble in salt solutions.<sup>10</sup>

Cellulose derivatives are less biodegradable than either guar or guar derivatives. They are highly shear-stable and are good friction reducers. However, they will not reduce friction to the same extent as guar. The viscosity of cellulose derivative

sols decreases with increased temperature, but some derivatives do not undergo thermal degradation at temperatures in excess of 300°F.

The cellulose derivatives most often found in the oil field and their abbreviated names are hydroxyethylcellulose (HEC), sodium carboxymethylcellulose (CMC), methylcellulose (MC), hydroxypropylcellulose (HPC), and sodium carboxymethylhydroxyethylcellulose (CMHEC).

Cellulose derivatives are used as viscosifiers and drag reducers for hydraulic fracturing, drilling, and sand pack fluids, as fluid loss additives in fracturing, drilling, and cementing fluids; and as retarders for cements. High-viscosity solutions have been used to plug lost circulation zones and to temporarily block permeable intervals in workover and drilling operations. They have been used to shut off water from producing wells and to change mobility ratios in waterflood projects.<sup>11</sup>

The ability to modify cellulose polymers to meet various conditions means that new uses for these polymers are constantly being investigated.

#### *Polyacrylamides<sup>2</sup>*

These polymers, unlike guar and cellulose polymers, are not naturally occurring and must be synthesized. However, because of this, the polymerization conditions can be controlled so that the polymer properties are altered to meet a wide range of applications. For example, the molecular weights of the natural polymers are changed only slightly by their raw source or growing conditions, while the molecular weights of synthetic polymers can be varied from the hundreds into the tens of millions.

Polyacrylamides are probably the most widely used polymers in the oil field. These polymers usually have molecular weights in the range of one million to thirty million. This molecular weight is 10-100 times larger than that of guar or cellulose polymers. They are straight chain polymers that can be prepared as cationic, nonionic, or anionic. These polymers can be both complexed and crosslinked, and the acrylamide monomer can undergo copolymerization with other monomers in varying ratios to further change the polymer properties.

Concentrations of certain polyacrylamides as low as 0.05 lb/ bbl are capable of reducing friction in pipe under turbulent flow conditions by as much as 80%.

Some of these polymers are stable in high concentrations of hydrochloric acid and salts. Therefore, these polymers are commonly used to reduce pipe friction in hydraulic fracturing and acidizing treatments and in drilling and workover fluids.

Some polyacrylamide polymers are effective in reducing the relative permeability of a formation to water without greatly affecting its permeability to oil.<sup>11-13</sup> This, combined with the increase in viscosity of the polymer solution over that of water, greatly reduces the mobility of water in water injection projects. For this reason, these polymers are widely used in polymer flood operations and in establishing improved water injection profiles. Because these polymers can be synthesized and/or crosslinked in situ,<sup>14</sup> are highly stable to bacteria and oxidation, contain no insoluble residue and undergo less temperature thinning than many other polymers, they are even more suited for these applications.

Polyacrylamides have been used as viscosifiers for hydraulic fracturing and drilling fluids. They have been shown to be effective in controlling clay swelling and migration and in reducing shale sloughing and heaving, especially when used in combination with potassium or calcium chloride.<sup>15</sup>

Because of the wide range of properties exhibited by these polymers, new and improved applications are continually being developed.

#### *Other Polymers*

Numerous other polymers are used in the oil field but not to the extent of the three classes discussed previously. Some of these polymers, their unique properties and more common uses are discussed here.

Xanthan gum<sup>1</sup> is a polysaccharide-type, biopolymer. It is grown from a culture of carbohydrates and microorganisms. It is highly stable to bacteria, undergoes very little temperature thinning, and forms high viscosity solutions at low concentrations. It is used primarily in drilling fluids and polymer floods.

Starch is another natural polymer belonging to the polysaccharide class.<sup>1</sup> It does not form a true solution but is a colloidal dispersion. It is sometimes used as a viscosifier but its primary use is as a fluid control additive. The naturally occurring polymers, karaya, arabic, ghatti, locust bean, and batu, have

all been used at one time or another as fluid loss additives, flocculating or deflocculating agents, or emulsifiers, in drilling, cementing, or stimulation fluids.<sup>1</sup> All of these polymers are polysaccharides.

Some low molecular weight polymers can be used as scale inhibitors. These function by adsorbing onto the sites where scale crystals are growing, thereby resulting in poisoning the site for future crystal growth.

The only hydrocarbon-soluble polymers of any significant use in the oil field today are synthetic polymers of the polymethylmethacrylate type.<sup>16</sup> These polymers are used to reduce friction in pumping crudes through pipe under turbulent conditions.

## CONCLUSIONS

The more common polymers, their properties, and applications in the oil field have been presented. The terms used in discussing the everyday use of polymers have been defined and explained. These definitions and others may be found in the Appendix of this paper.

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## APPENDIX

### *Polymeric Terms Most Often Heard in the Oil Field*

**adsorption** - The process whereby a solid takes up a gas, vapor, liquid, or dissolved material on its surface.

**amphoteric polymer** - A polymer which can be either anionic, cationic, or neutrally charged depending upon the conditions.

**anionic** - Possessing a negative charge.

**apparent viscosity** - The viscosity at a given shear rate of non-Newtonian fluid which produces the same pressure drop as a Newtonian fluid with equivalent viscosity.

**Bingham plastic** - Fluids which yield a straight line relationship between shear rate and shear stress that does not go through the origin.

**biopolymers** - Polymers produced by the action of microorganisms on carbohydrates.

**cationic** - Possessing a positive charge.

**centipoise** - Unit of viscosity.

**colloidal** - Condition in which finely divided particles are suspended in a liquid.

**complex** - The tying together of polymer molecules with metal ions. These bonds are weaker than the interpolymer bonds. These bonds are called coordinated covalent bonds.

**copolymer** - A polymer prepared from two different monomers.

**crosslink** - The tying together of polymer molecules such that the bonds formed are of the same order of strength as the bonds within the polymer. These bonds are called covalent bonds.

**dilatant** - Fluids whose apparent viscosity increases with increased shear rate.

**enzyme** - Proteins which act as catalysts for hydrolysis reactions.

**flocculate** - Converting finely divided suspensions of solids into larger particles so that rapid settling occurs.

**gel** - Colloid in which the dispersed phase has combined with the continuous phase to produce a viscosity such that air bubbles will not rise through it.

**graft polymer** - A polymer in which the main chain of atoms has attached to it, side chains which are different to the makeup of the main chain.

**gum** - Plant or microbial polysaccharides that are dispersable in water and produce viscosity.

**hydration** - The process of absorption or combination of water with another substance to form one or more new substances.

**hydrophilic** - Capable of uniting or mixing with water.

**hydrogen bonding** - The weak bond formed between a hydrogen atom already bonded and oxygen, fluorine, or nitrogen.

**inorganic polymer** - Polymer containing no carbon.

**$K'$**  - The consistency index of non-Newtonian fluids. It is derived by taking the intercept at a shear rate of  $1 \text{ sec}^{-1}$  when shear rate is plotted against shear stress on a logarithmic scale.

**laminar flow** - The flow of a material such that all regions of flow are parallel to the direction of flow.

**mobility** - The ease with which fluid flows through a porous medium. It is directly proportional to relative permeability and indirectly proportional to the fluids viscosity.

**molecular weight** - The sum of the atomic weights of atoms in a molecule.

**monomer** - The starting material from which polymers are derived.

**$n'$**  - A measure of the non-Newtonian behavior of a fluid. Obtained by measuring the slope of a shear rate-shear stress plot on logarithmic scale.

**natural polymer** - Those polymers such as polysaccharides which are usually produced by plants.

**Newtonian fluid** - Fluids which exhibit a direct



proportionality between shear rate and shear stress. Viscosity is independent of shear rate.

*nonionic* - Having no charge. Neutral

*non-Newtonian fluid* - Fluids which do not show a direct proportionality between shear rate and shear stress. Viscosity changes with changing shear rate.

*organic polymer* - A polymer which is largely composed of carbon. It may also contain other atoms such as hydrogen, oxygen, nitrogen, sulfur and phosphorus.

*organometallic polymer* - Containing both inorganic and organic segments.

*oxidizing agent* - A material which gains electrons and causes another material to lose electrons. These materials are capable of degrading polymers. Oxygen and peroxides are the most common oxidizing agents.

*polar* - Materials which have positive and negative sites.

*polymer* - Substance composed of giant molecules that have been formed by the union of simple molecules.

*polymerization* - The process whereby monomers are combined to form polymers.

*polysaccharide* - A class of polymers composed of long chains of sugars of which cellulose, starch and guar are examples.

*pseudoplastic* - Fluids which decrease in viscosity with increases in shear rate.

*rheology* - The behavior of materials under flow.

*rheopectic* - Fluids which increase in apparent viscosity at low shear rate but decrease in apparent viscosity at high shear.

*shear rate* - The rate at which a fluid moves under a given pressure. Its units are  $\text{sec}^{-1}$  or inverse time.

*shear stress* - The pressure required to move a fluid at a given rate. Its units are dynes per centimeter or force per unit area.

*sol* - Colloid in which the dispersed phase has combined with the continuous phase to produce a viscosity such that air bubbles will rise through it.

*solvate* - The process of absorption or combination of a solvent with another substance.

*syneresis* - The release of fluid by a gel due to gel contraction.

*synthetic polymer* - Polymers which are not naturally occurring but must be man-made.

*thixotropic* - Fluids which possess a structure. This structure breaks down with shear and time but reforms with reduced shear.

*turbulent flow* - The flow of material such that all fluid does not move parallel to the direction of flow but instead swirls and tumbles in the direction of flow.

*viscoelastic* - Fluids which possess both viscosity and elasticity of shape.

*viscosity* - The internal resistance of flow exhibited by a fluid.

