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SYNTHESIS AND CHARACTERISATION OF POLYMERIC ADDITIFS AND THEIR APPLICATION IN DRILLING MUDS

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Abstract - Acrylamide (AM) was grafted onto starch via a free radical polymerization. The number of grafting sites and the length of the grafted chains were varied by varying initiator and monomer concentration. The copolymers obtained were characterized using FTIR and viscometric methods. The IR spectra of the copolymer confirmed the presence of a band (1670 cm^{-1}) due to the amide group of polyacrylamide. The intrinsic viscosity was found to increase with the increase in monomer concentration and to decrease with the increase in initiator concentration. A concentration of 2.10^{-4} mol of initiator was found to give the highest intrinsic viscosity. The rheological studies of polymer solutions indicated that the viscosity loss of the copolymer with time and salts was very small (less than 8%). Water solubility was found to increase with the increase in the polyacrylamide side chain length. The filtrate volume of the mud was reduced with the increase in the copolymer concentration before or after the thermal aging test. The rheological properties of the mud were not greatly affected by the copolymer concentration, an essential characteristic of filtrate reducers. The comparison between two synthesized copolymers and a commercial one namely polyanionic cellulose (PAC) indicated that the three polymers are very effective filtrate reducers.

Key words: starch, polyacrylamide, mud, graft copolymerization.

1-INTRODUCTION

Drilling fluid (i.e., mud) perform many functions such as cooling the drilling bit effectively, exerting hydrostatic pressure to prevent the well blow down, carrying the drill cuttings up to the surface, and forming a filter cake on the walls of the borehole, which can prevent water leak-off from the drilling fluid into the geologic formation.

Drilling muds are modeled as a suspension of clay particles and high-gravity solids in water or oil. The properties of these fluids depend on pressure and temperature.

Growing concerns over the environmental impact of oil-based drilling fluids in oil fields have lead to an increasing reliance on water-based systems. An important aspect of water-based muds is the design and testing of water-soluble polymers to control the main functions of the muds i.e shale stabilization, rheological characteristics and fluid loss.

The requirements for such a compound for a given application temperature include: good chemical stability for a sufficiently long time, high viscosity with ability to control the fluid loss, and compatibility with all other components involved, especially in alkaline medium, with the occurrence of divalent ions and negatively charged clay particles from the formations.

To date, naturally occurring and synthetic polymers have found extensive applications in water-based muds. Among these additives, partially hydrolyzed polyacrylamide and starch derivatives are widely used. There is no perfect polymer and each polymer suffers from many limitations. Partially hydrolyzed polyacrylamide for example (PHPA) has good viscosity-building, filtration-control properties, good thermal and biological stability, but it suffers from salts sensitivity and mechanical degradation especially at higher molecular weights. On the other hand, low cost, availability, and salt tolerance of starch make it an attractive polymer for such application, but its biodegradation and lower thermal stability limit its application.

2-EXPERIMENTAL

2.1-Materials

Starch, acrylamide; Acetone, hydroquinone, Ceric ammonium sulphate all from E. Merck, Germany and MI-gel (Bentonite) and PAC –L from MI-drilling and Services Company.

All chemicals are reagent grade and are used as received.

2.2-Preparation and Characterization of the copolymer

Numerous methods have been reported in the literature for initiating graft copolymerization of starch [1, 2]. The Ceric ion initiation method has been used extensively when polyol types of polymers such as polysaccharides are the substrate [1, 2, 3].

Acrylamide (AAm) was grafted onto starch backbone by free radical polymerization using cerium ammonium sulphate (CAS) as active sites generator. The polymerization was conducted at room temperature and under inert atmosphere in a four necked batch reactor equipped with Nitrogen inlet, electric heater, thermometer, and mechanical stirrer.

On one hand the number of active sites for grafting was varied by varying the amount of initiator. On the other hand the length of the grafted chains was varied by varying the amount of monomer concentration but keeping the initiator content constant (i.e. fixing the number of active sites).

The effect of CAS initiator and AAm monomer content on the final product properties was studied by varying the initiator and monomer concentration respectively.

According to some authors [4], homopolymerization of polyacrylamide can be initiated by this synthesis procedure if the monomer and initiator concentrations are greater than 2M and 0.05 M respectively. Thus the monomer and initiator concentration were kept under this range of concentration. In addition, and in order to confirm the absence of free homopolymer in the final product, control reactions were carried out in the absence of starch and keeping the initiator and monomer concentrations the same. No homopolymer was formed in these reactions.

The copolymer obtained was characterized by infrared spectra, viscometric studies, selective solvent, and thermal analysis.

2.3- Copolymer behaviour in solution

In order to imitate the oil-well conditions, such as temperature gradient, injection and flow rates, long time of use (one day to one week), presence of monovalent and divalent ions, the behavior of the copolymer was followed in aqueous solution as a function of temperature, time, shear rate and salts.

The effect of salts concentration (0 to 2000ppm NaCl and $CaCl_2$), and time on the polymer properties was studied by following the viscosity loss of polymer solutions (one gram in 100 ml of double distilled water) with a low-shear viscometer (Contraves LS 40, shear rate range from 1 to 5 s^{-1}).

Results were generally expressed as the relative viscosity RV. ($RV = \eta_{sp} / \eta_{sp0}$)

(h_{sp0}) is the starting solution viscosity (salt-free solution), (h_{sp}) is the solution viscosity measured after a time period (t) or salt concentration (C), and η_{brine} is brine viscosity

The shear effect was studied using a RHEOTEST type viscometer (shear rate range from 0 to 1000 s^{-1}).

2.4-Mud properties tests

A low-solid base mud, 4.3 % pre-hydrated bentonite, was made up by maintaining the ratio of the clay to water at 4.3:100 by weight. Prior to use, the base mud was aged for 24 h at room temperature to hydrate the bentonite. The required quantity of the polymer was added to the base mud and stirred at moderate speed for 10 min. Aging experiments of bentonite–polymer muds were carried out in a rolling oven through hot rolling at 80°C for 16 h. Mud property tests measurements were performed before and after hot rolling and in the absence and presence of two types of salts (NaCl and $CaCl_2$) according to the American Petroleum Institute (API) specifications

Rheological measurements were achieved with a six-speed Fann 35A viscometer. The filtration properties of drilling fluids are generally determined by means of a standard filter press. The test requires 100 psi pressure for 30 min according to the API standardized procedure. The volume of collected liquid VAPI is an indication of the fluid loss properties.

3- RESULTS AND DISCUSSION

3.1- Proof of formation of starch-graft-polyacrylamide

Figure 1 shows the IR spectra of the product and of the starch. The spectrum of the product possesses the characteristic absorption bands of starch at 1020 cm^{-1}, 1080 cm^{-1} and 1150 cm^{-1}, which are due to C-O stretching vibrations. Other characteristic absorption bands of the product at 1620 cm^{-1} and 1670 cm^{-1} result from N-H and C=O stretching vibrations in the $CONH_2$ group which are absent in the starch spectrum[4]. These results prove that the polymer is Starch grafted with Polyacrylamide (S-g-PAAm).

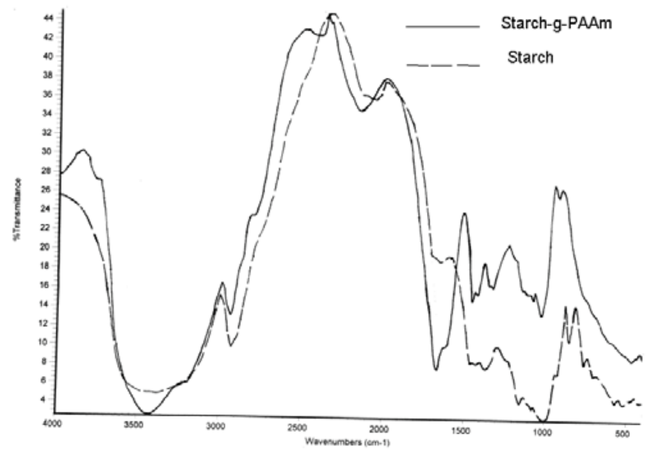

Figure 1: Infrared spectra of starch and C_2 (S-g-PAAm).

3.2- Effect of monomer and initiator content on grafting

The effect of CAS and AAm on the intrinsic viscosity is shown in Figures 2 and 3 respectively. The intrinsic viscosity increases with the increase in CAS mole number till it reaches a maximum value of 7.5 dl/g at 2.10-4 moles; this can be explained by the fact that the created active sites are not enough for acrylamide molecules to totally react, and as we go on more active sites were formed and more acrylamide molecules were reacted. However, a further rise of CAS content led to a decrease in the intrinsic viscosity. This decrease is due to a reduction of the side chain length. The AAm are distributed over the higher number of active sites made available leading to shorter thus lower molecular weight side chains **[4]**. It may be also due to the initiator taking part in termination reactions of growing grafted chains **[5]**.

When the amount of starch and CAS was kept constant (the number of active sites was kept constant) and the amount of AAm was varied (varied chain length); the intrinsic viscosity showed an increasing pattern because as the amount of AAm increases the grafted chain length increased **[6]**.

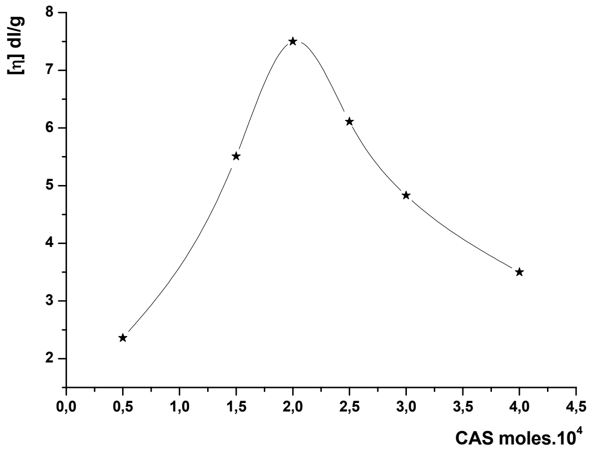

Figure 2: Effect of CAS on intrinsic viscosity: Potato starch 2.381×10^5 moles; acrylamide 8.4424×102moles; CAS 1 to 4×10^4 moles

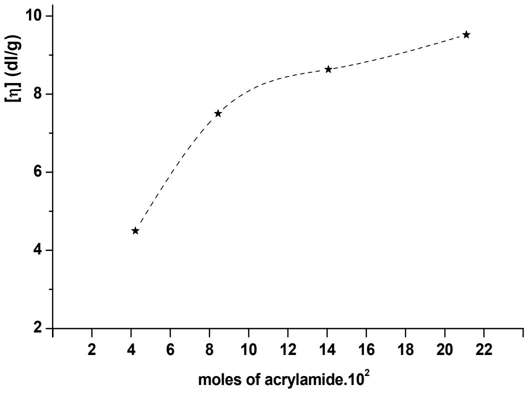

Figure 3: Effect of AAm on intrinsic viscosity: Potato starch 2.381×10^5 moles; acrylamide 4.226 to 21.103×10^2 moles; CAS 2×10^4 moles.

4-POLYMER BEHAVIOUR IN SOLUTION

4.1-Water solubility determination:

In order to determine the water-solubility of starch and the synthesized products, the insoluble matter was separated by filtration. The insoluble matter was recovered, dried, and weighed, and the percent water-solubility was determined as follows:

Water-solubility % = $(W_0-W_{ins})/W_0$.

W_0: initial weight = 1gram W_{ins}: weight of the insoluble matter.

Figures 4 and 5 represent the variation of water solubility of the synthesized copolymers as function of CAS and AAm content in the reaction medium respectively. It is clear from the above graphs that water solubility decreases as the mole number of CAS decreases and increases with the increase in AAm content. This can be explained by the fact that as the CAS content increases this leads to copolymers with higher number of grafting sites but shorter side chains of polyacrylamide responsible for water solubility, these short side chains can not overcome the hydrogen bond of starch. On the other hand increasing AAm content leads to copolymers with fewer but longer PAAm side chains (responsible for water solubility).

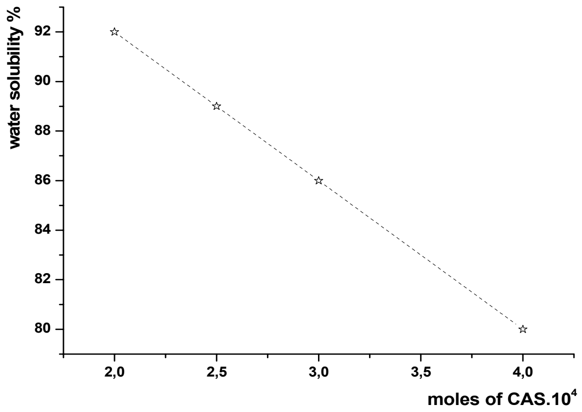

Figure 4: Effect of CAS content on water solubility of polymers A3; A4; A5 and A6.

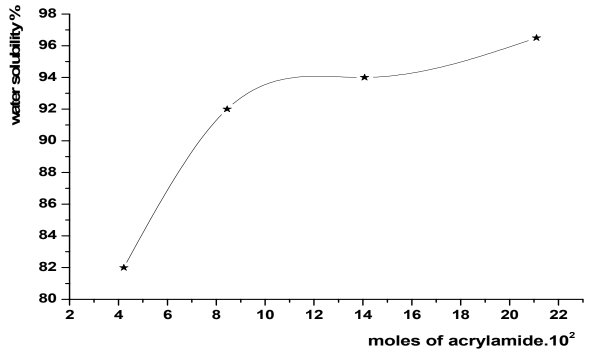

Figure 5: Effect acrylamide content on water solubility of polymers A3; B1; B2 and B3.

4.2-Effect of temperature, time, salts and shear

The effects of temperature, time, shear and salts are shown in figures 6 to 9 respectively. From these figures, the copolymer viscosity decreases as temperature increases due to decrease of inter-chain distance leading to a decrease in attractive forces, the copolymer viscosity remains constant for more then one week; this reflects its viscosity stability with time. The presence of salts (monovalent and divalent) has no effect on the polymer viscosity; this can be explained by the absence of anionic sites on the polymer chains.

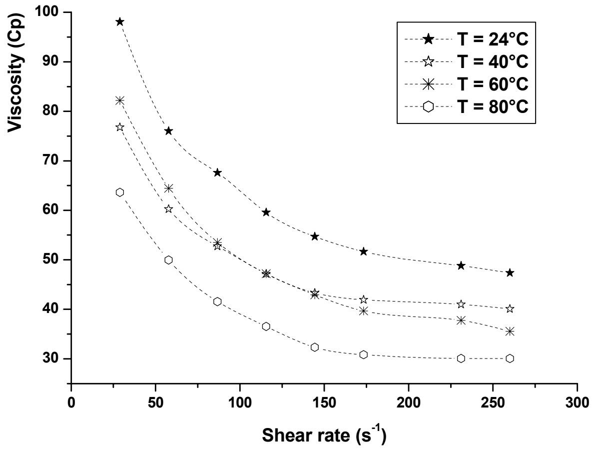

Figure 6: solution viscosity as function of temperature.

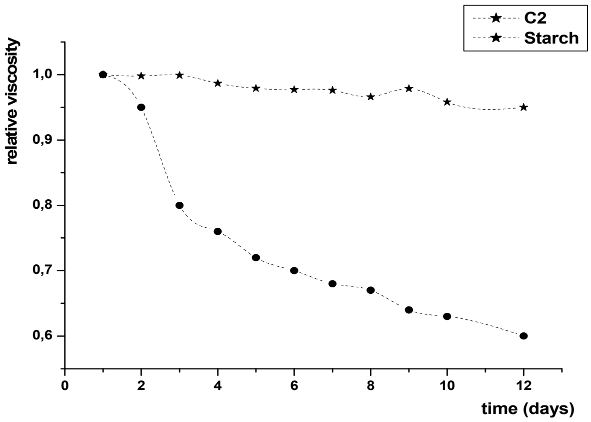

Figure 7: solution viscosity as function of time

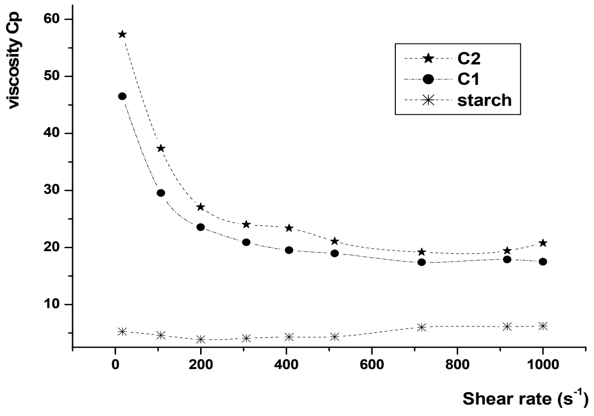

Figure 8: solution viscosity as function of shear rate. Copolymers C1, C2, and starch (1% w/v) in double distilled water.

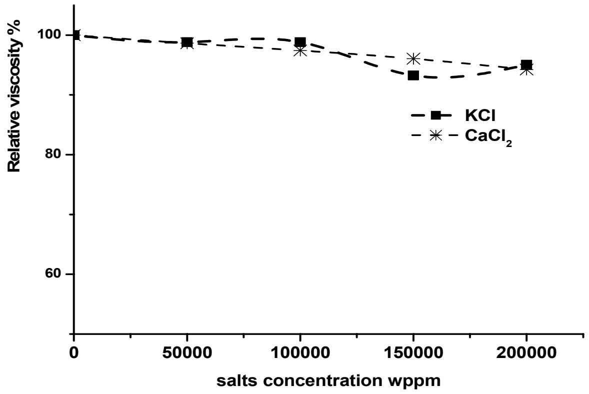

Figure 9: Relative viscosity as function of salts. Copolymer C2 (1% w/v) in double distilled water.

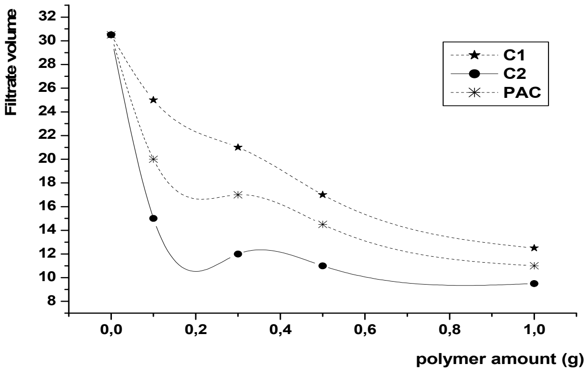

Figure 11: Effect of C1, C2 and PAC concentrations on the filtrate volume of fresh water mud (after hot rolling).

4.3-Drilling mud application

The polymers effect on the filtration and rheological properties of the fresh water mud is shown in figures 10 to 13 respectively (before and after hot rolling). It can be seen that the filtrate volume decreased with the increase of the three polymers concentration before or after the thermal aging test. The filtrate volume after the aging test was larger than that before the aging test, meaning that the elevated temperature could raise permeability of the filter cake and spoil a part of the mud gel structure [7]. The polymers effect can be classified as follows C1>PAC>C2. The three polymers do not affect the rheological properties of the mud (represented by Pv), an essential requirement for filtrate reducers [7]; this indicates that the three polymers are good filtrate reducers.

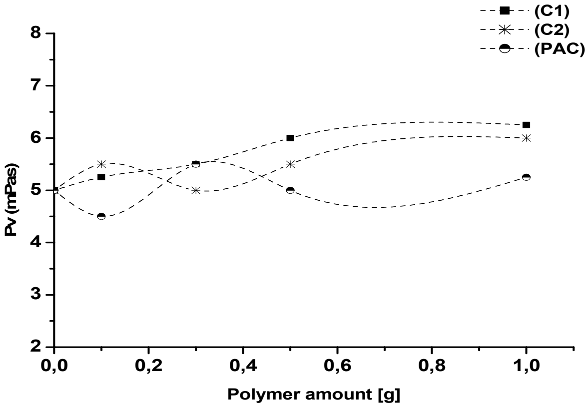

Figure 12: effect of C1, C2 and PAC concentrations on the Pv of fresh water mud (after hot rolling).

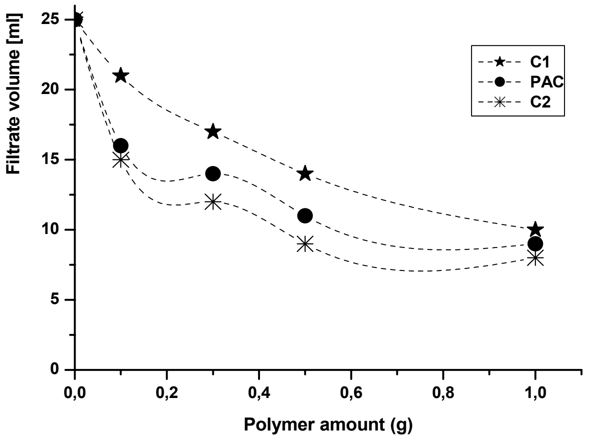

Figure 10: Effect of C1, C2 and PAC concentrations on the filtrate volume of fresh water mud (before hot rolling).

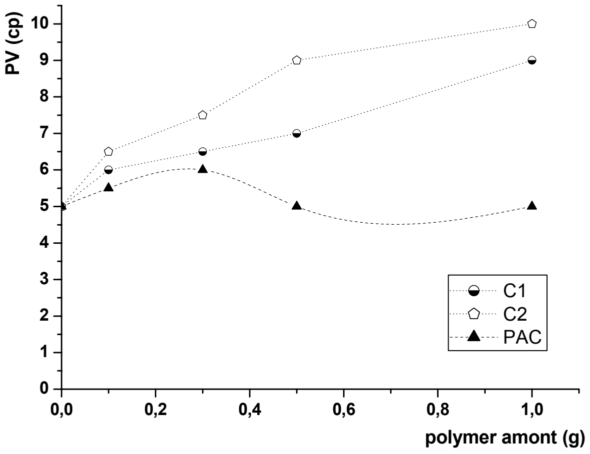

Figure 13: effect of C1, C2 and PAC concentrations on the Pv of fresh water mud (after hot rolling).

5- CONCLUSIONS

- A starch graft polyacrylamide copolymer was synthesized through a free radical polymerization using cerium ammonium sulphate as active sites generator. The IR spectrum of the product confirmed the grafting.
- The monomer and initiator concentrations in the reaction medium have a great effect on the final properties of the copolymer as shown by the viscometric studies.
- Intrinsic viscosity was found to increase with increasing monomer concentration and to decrease with decreasing initiator concentration.
- The copolymer is water soluble with water solubility directly proportional to Polyacrylamide content.
- Grafting Acrylamide onto starch greatly improves starch resistance to biodegradation
- The copolymer is salt resistant with rheological properties stable with time.
- The copolymer had a strong effect on the mud properties. The filtrate volume decreases with the increase in the copolymer concentration before and after the thermal aging test.
- The rheological properties of the mud were not affected by the copolymer.
- The copolymer effectiveness was found to increase with increasing starch and polyacrylamide content.
- The copolymer C2 is more effective filtrate reducer than PAC (a commercial polymer)
- A 'tailor made' starch grafted polyacrylamide copolymer with specific number of grafting sites and appropriate side chain length can be synthesized to achieve specific functions

REFERENCES:

[1] J. Meister,: "Synthesis, characterization, properties, and derivatives of poly (starch-g-(1-amidoethylene: I. synthesis and characterization"; *J.App Poly. Sci*; 26, 1270-1285; 1987.

[2] G.F. Fanta,: "Block and Graft Copolymerization"; Ceresa, R. J., Ed.; John Wiley & Sons: London, 1973; Vol. 1, pp 1-44.

[3] G.F.Fanta,: "Starch graft copolymers" ; *Poly. Mat. Ency. (CD-ROM), CRC Press,*Inc. ; 1996

[4] S.R Deshmukh and R.P. Singh; "Drag reduction effectiveness, shear stability and biodegradation resistance of Guar-gum based graft copolymers"; *J.App Poly. Sci*; 26, 1963-1975; 1987.

[5] L.M Zhang, D-Q Chen; "Grafting of 2-(Dimethylamino)ethyl Methacrylate onto Potato Starch Using Potassium Permanganate/Sulfuric Acid Initiation System"; Starch/Stärke 53, 311–316 ; 2001.

[6] Shaojie Lu Tong Lin, Deyong Cao; "Inverse Emulsion of Starch-graft-Polyacrylamide"; Starch/ Stärke 55, 222-227 ; 2003.

[7] Y.M. Wu, D.J. Sun, B.Q. Zhang, Ch. G. Zhang;"Properties of High Temperature Drilling Fluids Incorporating Disodium Itaconate / Acrylamide / Sodium 2-Acrylamido-2-methylpropanesulfonate Terpolymers as Fluid-Loss Reducers"; *J.App Poly. Sci*; 83 , 3068-3075; 2002.