

STUDY ON LIGNIN GRAFT COPOLYMER AS ADDITIVE AGENT FOR THE HYDROCARBON DRILLING INDUSTRY

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Abstract:

Crude lignosulfonates was refluxed with acrylic acid at 70°C in the presence of nitrogen atmosphere to form lignosulphonate acrylic acid graft copolymer (LS-g-P(AA)). The modified Lignosulphonate deflocculant was made by graft of Lignosulphonate and acrylic monomer using the hydrogen peroxide as initiator. The impact of experimental conditions (the dose of initiator, reaction temperature, reaction time, stirring rate and the mass ratio of Acrylic Acid and effect concentration of MBAm, cross-linker) on the physical properties, efficiency of the product was investigated and the optimal conditions were obtained: the dose of initiator was 3.5%, reaction temperature was 70°C, reaction time needed 4 h, and the mass ratio of AA was (10:15%) at stirring rate 750 rpm. The application LS-g-P(AA) and LS-g-p(AA-co-MBAm) as an alternative a commercial thinner lignosulphonate in water base mud was investigated.

Keywords: Graft copolymer, Lignosulphonate, Lignin, acrylic acid and drilling fluid/mud.

1. Introduction

Lignin (and/or lignosulphonate) is a waste discharged from paper mills in large quantities and poses huge disposal problem. At the same time, lignin is the second most abundant natural raw material, it is the second most abundant renewable organic material on planet immediately after cellulose, in wood, straw and other plant tissues, represents a vastly underutilized natural polymer, Lignosulfonates are water soluble anionic surface-active derivatives of lignin it is very interesting to use lignosulfonates as chemical reactants or to chemical modify them in order to improve their properties [1,2,3] Lignosulfonates are also used to produce a number of value-added products for specialty markets[4].

In the past years, there had been some reports on direct utilization of lignosulfonates as a category of polymer surfactant for dyestuff, concrete, bitumen, etc. They were also used as binder for producing Plywood, today scientists are still trying to find other applications of crude lignosulfonates [5] The sulfur content (5 wt %) of sulfite lignins is one of the major factors restricting its use in specialty applications, and so most of its lignin is currently used on co-generation [4] and in Oil well drilling muds[6] Lignosulphonate acrylic acid have been proposed for use as gels for conformance improvement in Hydrocarbon Bearing Underground Strata[7]

Lignin isolated from OPEFB black liquor is highly promising and has great potential for us as raw material in industrial applications such as epoxy, biodispersants, foams and phenolic powder resins.as it is abundant and low-cost Due to its significant thermal stability, lignin has the potential to be used as an additive for drilling fluid [8] Drilling fluids, which represent till one fifth (15 to 18%) of the total cost of well petroleum drilling, must generally comply with three important requirements: they should be, i) easy to use, ii) not too

expensive and iii) environmentally friendly. Numerous additives are added to the formulation in order to reach optimized specific purposes which are sometimes contradictory. For example, mud has to be viscous enough in order to be able to lift the cuttings to the surface, but at the same time, viscosity must not be too high in order to minimize friction pressure loss [9]

The WBM family, in which fresh-, salt-, or sea-water is the continuous phase, is the most used (90-95%). The WBM are mainly composed of aqueous solutions of polymers and clays in water or brines, with different types of additives incorporated to the aqueous solution [10]

Drilling process should be conducted safely least cost and minimum or no damage to the environment [11] So the future of research in drilling fluid development should be directed towards the formulation of an environmentally friendly drilling fluid with zero impact on the environment [12] The selection of the additive is generally based on the technical and environmental factors of the well bores unfortunately, most of these types of additives are not resistant to high temperature and pressure conditions [13]. Lignosulphonates obtained from any source may be used for the polymerization with acrylic compound can be used, it used as dispersing agent in water base drilling fluid [14]

Lignin graft copolymer compounds are extensively used as additive agent for the Hydrocarbon Drilling industry, the key success in drilling may depend on maintaining proper flow and fluids viscosity under certain conditions in addition to it is desirable, inexpensive and also be more environmentally compatible or friendlier than chrome or other similar heavy metal containing fluids. The aim of this study was to prepare some lignin graft copolymer, namely SLS-g-p (AA) as water -base drilling mud additive. During

preparation the factors which may be effect on physical properties and efficiency of polymer obtained were investigated.

2. Experimental:

Materials:

Acrylic acid was obtained from Elf Chem. Co., ATO, France. N,N' Methylene-Bis Acrylamide White powder from Sigma Aldrich Chemie GmbH Company. Hydrogen Peroxide, Aqueous solution, conc. (50%) was obtained from OCI Company, Korea. sodium carbonate from M.R.P. Inc. of Taxes. India. The lignosulfonate (LS), Commercial Chromo-lignosulphonate and bentonite clay used in this study were obtained from RP Mineral (Egypt). All the chemicals were used as received.

Preparation of SLS-g-P(AA):

In two liter three-necked round-bottomed flask attached to a reflux condenser and equipped with magnetic stirrer, a nitrogen inlet thermometer and heater, 100 grams of sodium lignosulfonates were dissolved in 120 grams water to form 45% (mass ratio) solution then 10 grams acrylic monomer which was about 10% of the sodium lignosulfonates solids were added. After addition of the acrylic acid the solution was continuously stirred well by magnetic stirrer at 750 rpm, and then 3.5 grams of 50% hydrogen peroxide were added and the sample was heated for about 4 hours on a hot water bath at 70°C degree. The pH of the reaction mixture was 3.4.

Mud preparation:

Each batch of base mud used in each experiment was prepared by adding 80 g bentonite together with 4 g of sodium carbonate into 1000 mL water before aging it for more than 24 hours. Evaluate the thinning performance at room temrature and at different aging temperature for 30 minutes, this

experiment was designed to observe the influence of temperature towards the performance of each thinner, when 0.3% thinner were added to the mud. [8,13,15,16]

Equipment:

The equipments that were used in this study are the following:

- 1) ATGO Hand-held refractometer to measure the solid content of samples
- 2) BROOK FIELD DV-E Viscometer to measure the viscosity of samples.
- 4) FT-IR spectra of samples of Lignosulphonate Graft copolymers were recorded on Broker IFS 66 FT-IR spectrophotometer. The film of the polymer was obtained by blending the sample with KBr to obtain transparent discs.

3. Result and discussion:

I-Effect of reaction conditions on graft copolymerization:

The optimum conditions for preparing lignosulphonates Acrylic compounds graft copolymers by studying the effect of different factors, such as stirring rate , reaction time of reaction , monomer concentration and N, N'-Methylene-BisAcrylamide ratio, The effect of each factor on the viscosity of the obtained product was studied separately while the other factors being kept constant. The obtained optimum condition of each factor was applied in next series of experiments.

1-Studying the effect of stirring rate (rpm) on the viscosity of the final products

The data given in table (1) and fig.(1),(fig.(2) show that the viscosity of the obtained polymer solution decreases with stirring rate. and there is not apparent change on viscosity of final products at small change in stirring rate. stirring rate at blow 500 rpm and above at 1250 rpm. gave low thinning

efficiency for drilling fluid mud, The reasons might be that , at low stirring rate is not enough to make good mixing of monomer and initiator with each other [17] The preferred stirring rate which gives high thinner effect is at 750 rpm and thus stirring rate at 750 rpm is stabilized in the following experiments.

Table 1. Effect of stirring Rate (rpm) on the viscosity solution obtained polymer

Polymer code	rpm.	viscosity of final product (cp)	viscosity of mud (cp)
H1	250	1239	287
H2	500	1125	234
H3	750	810	170
H4	1000	628	207
H5	1250	541	255
H6	1400	467	352

Fig. 5. Effect of stirring rate (rpm) on the thickening effect of the product

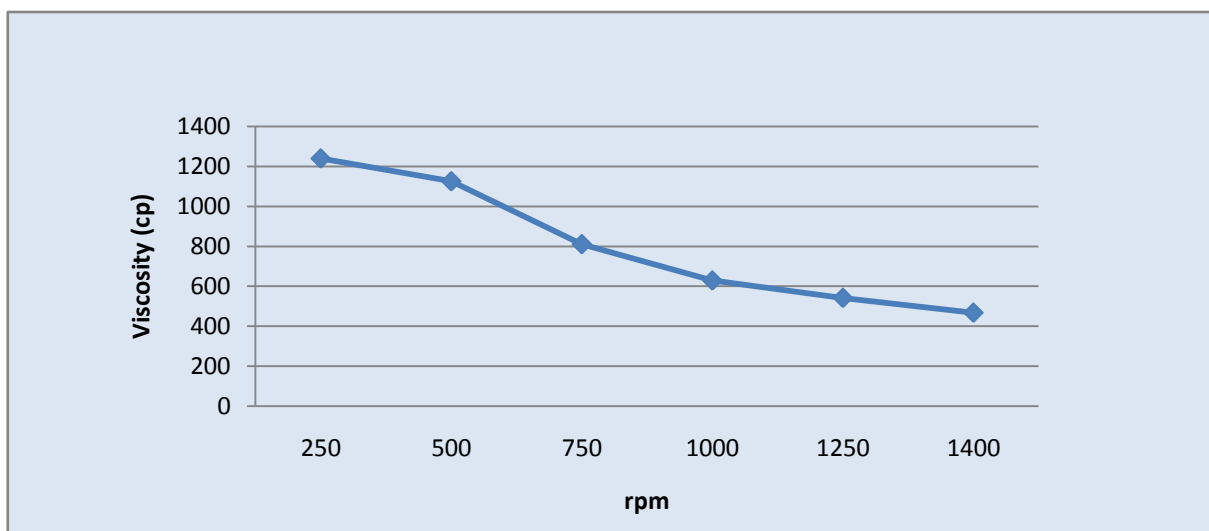
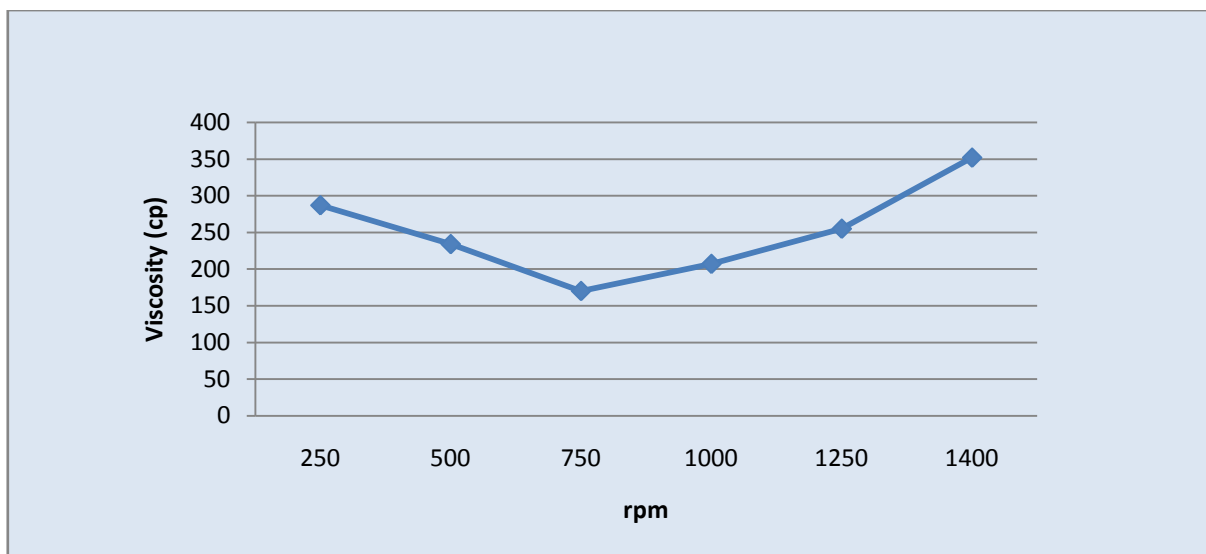


Fig. 2. Effect of stirring rate (rpm) on the viscosity of the mud



2- Studying the effect of reaction time(hrs) on the viscosity of the obtained polymer and mud:

The effect of reaction time on the graft copolymer were studied under predetermined condition, the copolymerization was conducted for a variety of reaction time ranging from 1 to 6 h, table (2) and figure (3),(4) represents the effect of reaction time on viscosity of the graft polymer. Between the reaction times of 1 and 4 h, the viscosity increased gradually. When the reaction time exceeded 4 h, the Viscosity became relatively constant.

Table (2): Influence of Time on viscosity of Products

Polymer code	Time (hrs.)	viscosity of final product (cp)	Viscosity of mud (cp)
I1	1	197	310
I2	2	375	240
I3	3	590	116
I4	4	823	130
I5	5	831	170
I6	6	827	200

Fig. 3. Influence of reaction time on viscosity of Products.

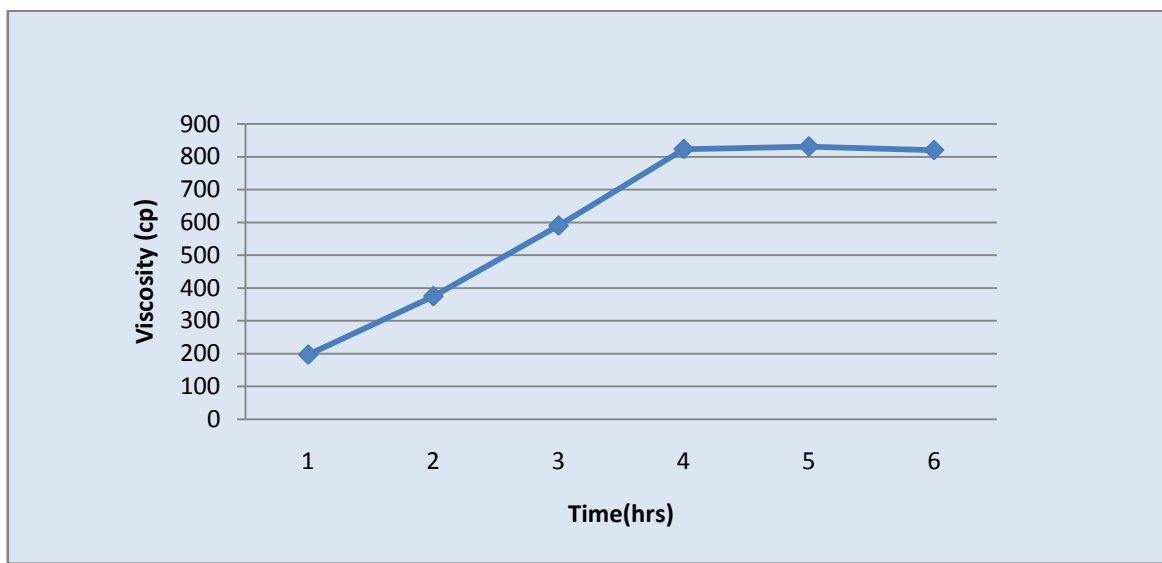
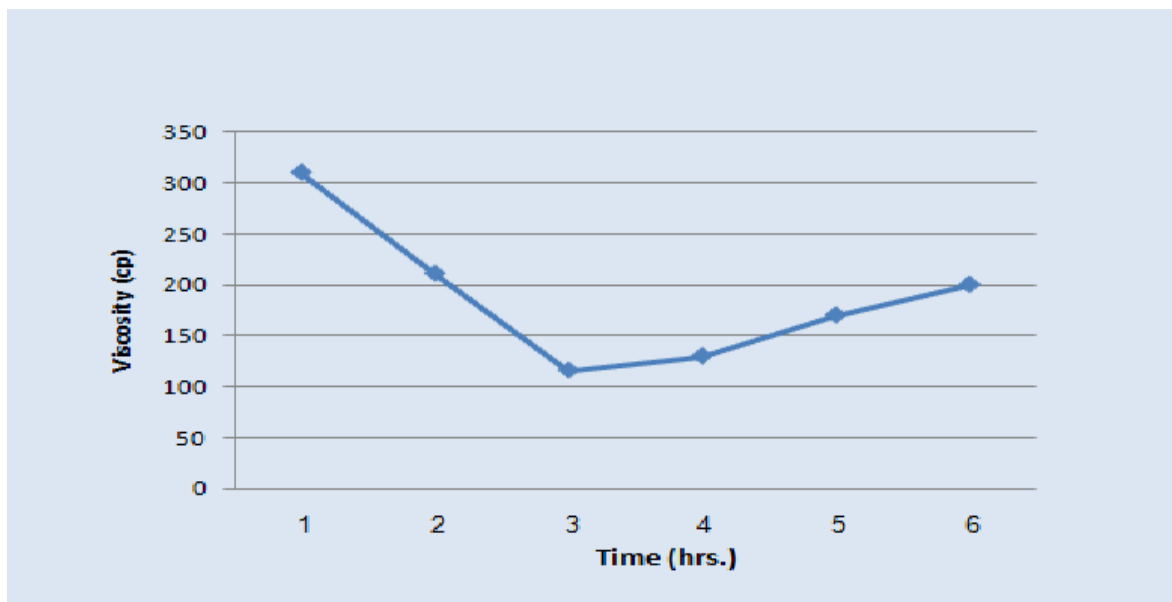


Fig. 3. Influence of reaction time on viscosity of Products.



3- Studying the effect of different Acrylic Acid ratio LS-g-p(AA%) on viscosity of the obtained polymer and mud:

The data given in table (3), Figure (5) and figure (6) show that the viscosity increases with the increase concentration of the Acrylic acid, due to the increased molecular weight of the polymer. Increase molecular weight generally increases solution viscosity [18]. viscosity increases with the

concentration of the added monomer, due to the increased molecular weight of the polymer [19]. For drilling fluids which may be subjected to normal temperatures, from 5 to 10 percent of acrylic acid will result in an effective thinner, where the thinning effect change from (217 cp) at (SLS-AA 20) to (450 cp) and at (SLS-AA 30) to (933cp). Largely increasing of The AA concentration about certain concentration (20%) give lower thinning efficiency.

Table (3): Effect of different Acrylic Acid ratio on viscosity of the obtained products

Polymer code	Acrylic Acid (%)	viscosity of final product (cp)	viscosity of mud (cp)
J1	5	357	124
J2	10	750	129
J3	15	1120	217
J4	20	1680	318
J5	25	2744	450
J6	30	3300	933

Fig. 5. Effect of acrylic acid concentration on solution viscosity

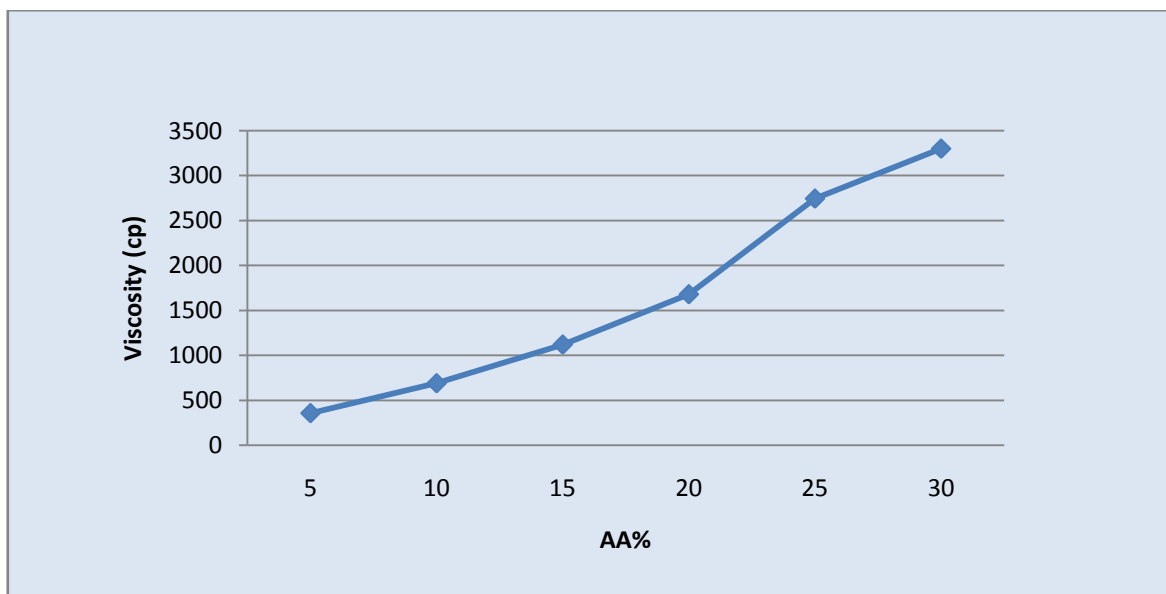
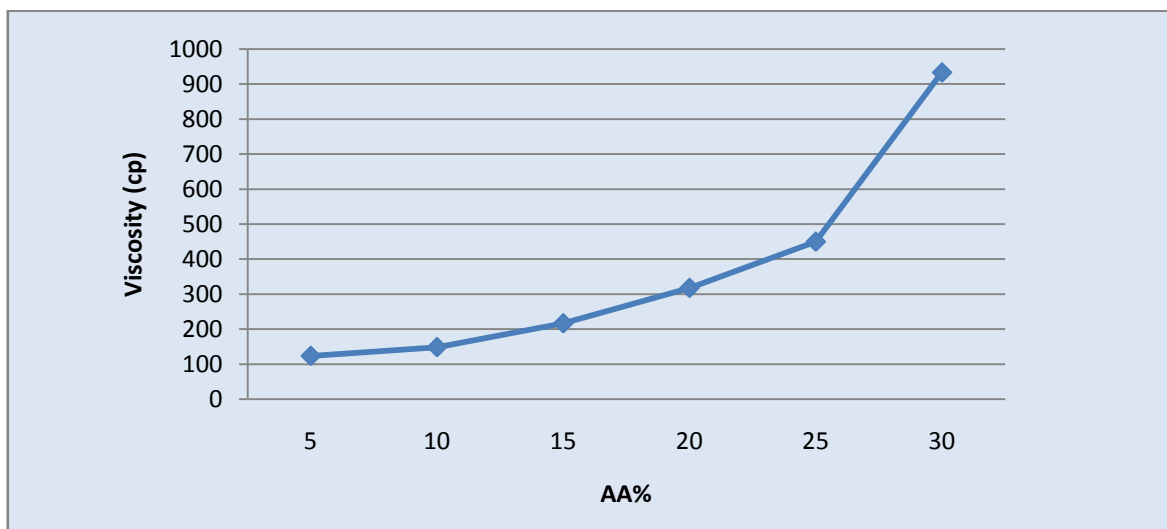


Fig. 6. Effect of Acrylic Acid Concentration on viscosity of mud



4-Effect of cross linker and its concentration on solution viscosity lignosulphonate acrylic acid graft copolymer LS-g-p(AA-co- MBAm).

The data listed in table (4) and shown in figures (7), figure (8) indicate viscosity increased with increase N, N'-Methylene-BisAcrylamide (cross-linker) concentration and making as thickening (viscofier) for water base drilling mud at Rome temperature. If concentration MBAm was too high, the final product was in a gel form (Hydrogel).The reason should be that, formation of H-bond between carboxyl groups and amides which increases the physical cross-linking points of the copolymer, thickening the solution of copolymers. Hydrogel materials are made from water soluble monomers and have been used in many fields [1]. An increasing in viscosity of polymer depend on hydrophobe content, hydrophobe type, molecular weight and degree of hydrolysis, increase hydrophobe content lead to an increase in bulk viscosity and the hydrophobe monomer significantly enhances the viscosity[18].Amide groups in AM polymers are less hydrophilic than carboxylic groups in AA polymers, therefore viscosity of products from AM was higher than that from AA[4].

Table (IV.12): Effect of MBAm concentration on viscosity of product.

Polymer code	SLS-g-p(AA %)	SLS-g-p(AA-MBAm %)	Viscosity polymer (CP)	Viscosity (0,3%) mud
K1	9,5%	0,5	750	315
K2	8,5%	1	830	376
K3	7,5%	1,5	1000	400
K4	6,5	2	1200	500

Fig. Effect of Cross linker concentration on viscosity of polymers obtained

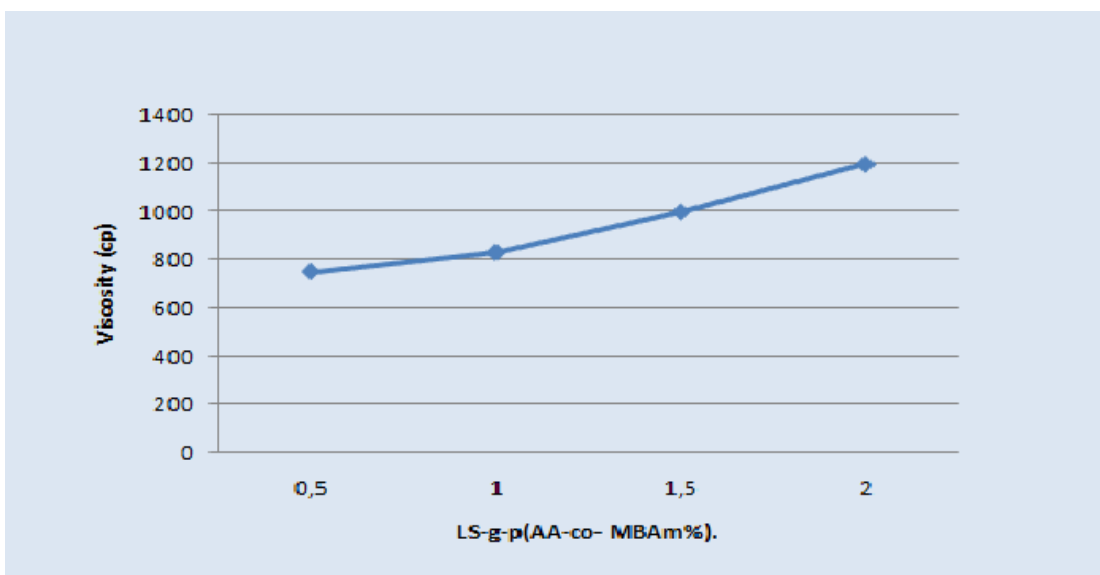
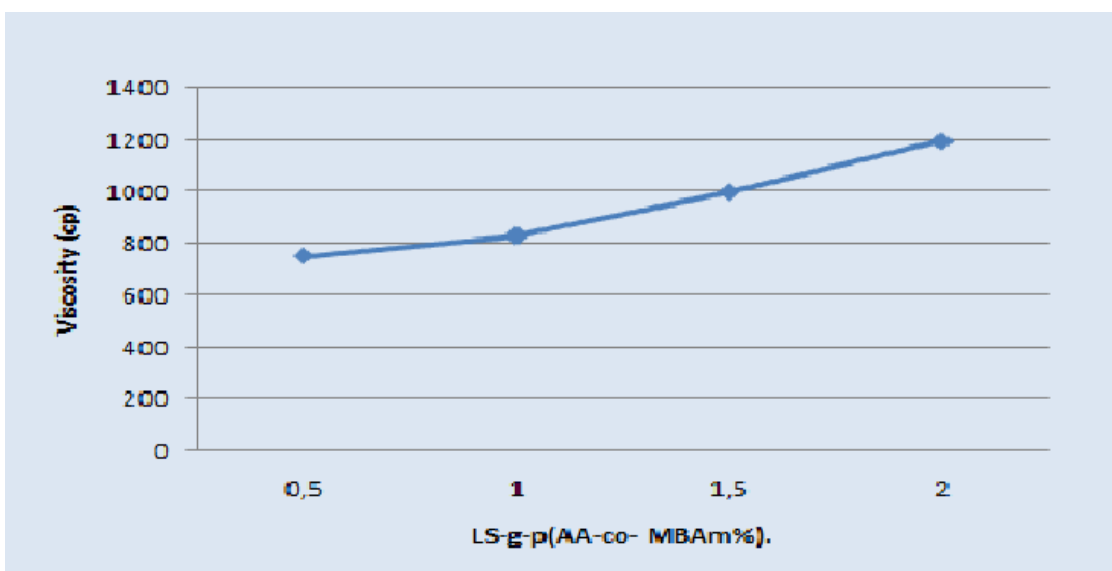


Fig.6. Effect of Cross linker concentration on viscosity of mud.



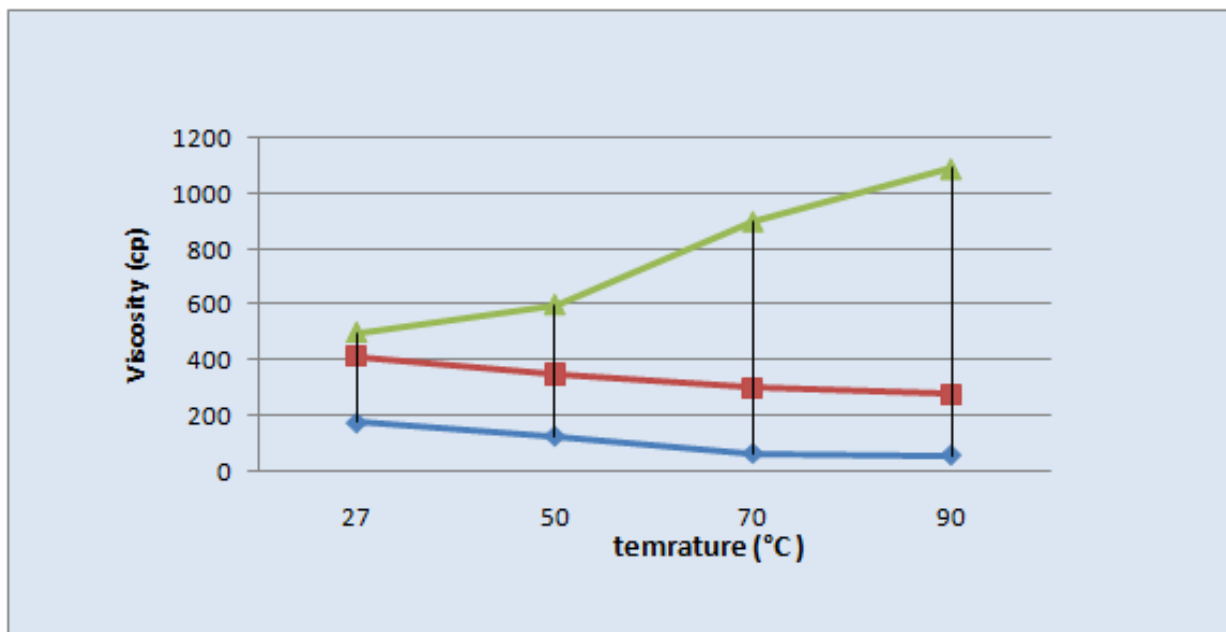
II-Comparative study on thinning Effect of SLS-g-p(AA) , (SLS-g-p(AA-co-MBAm) and Commercial Cr-lignosulphonate (Cr-LS) at different temperature:

Table (6) and figure (10) showed that, Sodium Lignosulphonate acrylic acid graft copolymer is better thinning abilities compared to Cr-Lignosulphonate at different temperature with the same concentration (0.3% thinner). The results showed that (LS-g-p(AA) can improve the viscosity at temperature lower than 50°C and decrease the viscosity at temperature above 70°C. (LS-g-P(AA).This is because at high temperature, the absorption of (SLS-g-AA) on the clay surfaces (bentonite) will be increase and prevent the platelets from linking[4]. addition of cross linker to SLS-g-p(AA) lead to the invert product from Thinner to viscofier for water Base drilling fluid which make increasing of viscosity of drilling fluid at different temperature with the same concentration (0.3% thinner), Because very high molecular weight polymer obtained.

Table (5): Comparison between LS-g-p(AA), LS-g-p(AA-co-MBAm) and Cr-lignosulphonate at different temperature

Sample Temperature (°C)	SLS-g-p(AA)	SLS-g-p(AA-co-MBAm)	Cr-lignosulphonate
27	126	500	480
50	108	600	460
70	66	900	400
90	60	1090	370

Fig. 7: Comparison between LS-g-p(AA) , LS-g-p(AA-co-MBAm) and Cr-lignosulphonate at different temperature.



IR spectra of lignosulphonates acrylic acid graft Copolymer sample SLS-g-p(AA):

IR spectra of the film of the Sodium Lignosulphonate acrylic acid graft copolymer sample shown in figure (8) were recorded on FT-IR spectrometer. The film of the polymer was obtained by blending the sample with KBr to obtain transparent discs. An IR spectrum of lignosulphonate shows absorption band at 3432 cm^{-1} for phenolic or hydroxyl groups, band at 1640 cm^{-1} is attributed to the aromatic ring, absorption at 1458 cm^{-1} is assigned to either CH stretching of methyl or CH stretching of methylene group. The band at 2500 and 3200 cm^{-1} that is characteristic of carboxyl [OH] group of LS-AA. The carbonyl group C = O stretching vibration at 1716 cm^{-1} . A very broad band having a medium value at 3432 cm^{-1} characteristic for CH aliphatic methylene and methine coupled with that of OH of carboxylic group and that of H₂O [21]

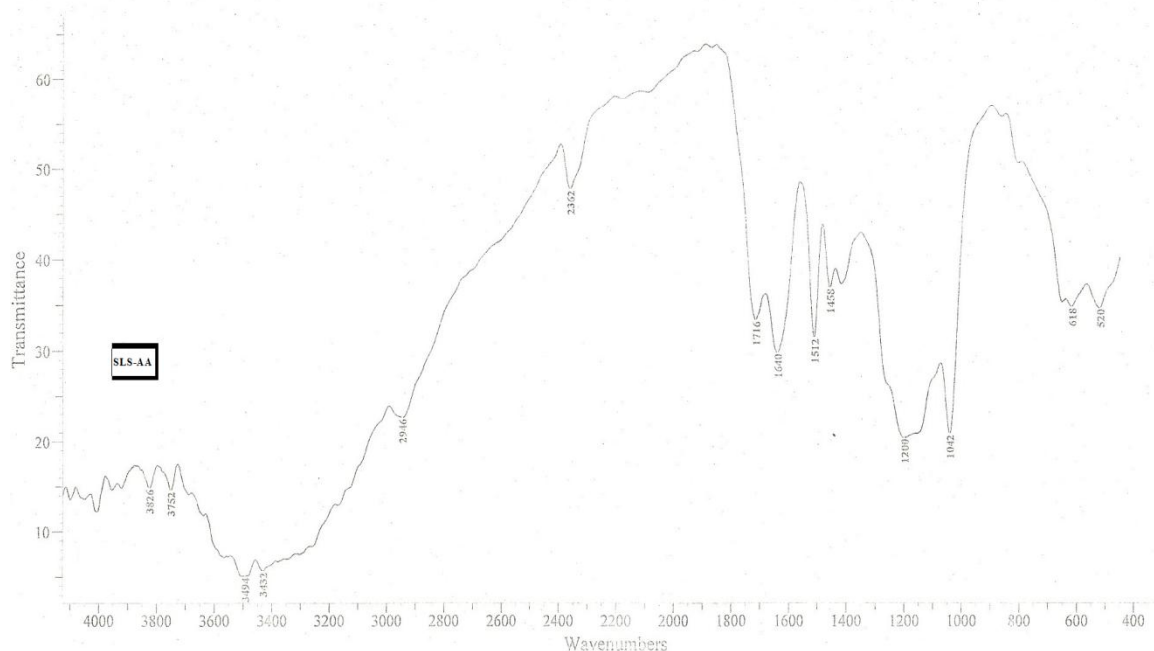


Fig. 11: IR spectra of SLS-g-p(AA) sample.

Conclusion:

(1) determine the optimum conditions for the Graft copolymerization of acrylic acid into lignosulfonates such as stirring rate , reaction time of reaction and monomer concentration .can conclude that viscosity of the polymer solutions and hence their molecular weight increases by increasing monomer concentration, reaction time when the reaction time exceeded 4 h. the Viscosity became relatively constant, and decreases with increase stirring rate, The optimum condition obtained at acrylic acid ratio 10:15%, using initiator concentration 3,5%at temperature 70°C at stirring rate 750 rpm for 4h of reaction time.

This must be considered in choosing the optimum conditions for graft polymerization of these monomers as thinner for water base drilling mud.

(2) LS-g-p(AA) Graft copolymer has more thinning effect in water Base mud than the comparative Cr-lignosulphonate thinner while small amount addition from (MBAM) lead to increase viscosity of water base drilling mud.

(3) Viscosity of products was used to measure the progress of polymerization. Viscosity of final products was increased following the increase of dosage of monomers due to increase molecular weight.

(4) At the same dosage, products modified with MBAm (LS-g-p (AA-co-MBAm)) had higher viscosity than those with AA (LS-g-p (AA)), such difference should be attributed to different hydrophobe content and different hydrophilicity of various groups in polymers. amide groups in MBAm polymers are less hydrophilic than carboxylic group in AA polymers.

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