

Synthesis, Characterization and Aqueous Properties of a Newly Prepared Lignin-based Graft Copolymer as a Drilling Mud Additive

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Abstract: This study involves a free radical graft copolymerization of lignosulfonates (LS) with 2-propenamide (Am), propenoic acid (AA), and methylene-bis-acrylamide (MBAm) in the presence of hydrogen peroxide as the initiator to produce LS-g-p(AA-co-Am-co-MBAm) copolymer. The resulting copolymer was characterized by various techniques such as infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). Viscosity measurements of the copolymer solution, pH values, solid content, gravimetric conversion and mud properties were determined. The effect of various experimental conditions on the characteristics of the developed copolymer was also investigated. Moreover, the performance of the resulting LS-g-p(AA-co-Am-co-MBAm) copolymer as a pH controlling agent for water-base mud was evaluated. The obtained results revealed that the newly synthesized copolymer has a remarkable pH control performance at different temperatures.

Keywords: drilling fluids, water-based mud, multifunctional, pH control, bioresources.

1 Introduction

Nowadays, there are strongly regulation for oil and gas company to move toward use eco-friendly petroleum additives and this achieved by using additives as one renewable energy. Petroleum drilling is the primordial step in the success of oilfield exploration and drilling fluids, which represent (15 to 18%) of the total cost of well petroleum drilling. Drilling mud classified in three families, The Water Base Mud (WBM) family, The Oil Base Mud (OBM) family and Comprises Gas Aerated Mud (classical mud with nitrogen) or aqueous foams [1]. Principal components of drilling fluids are water, oil/gas and chemical additives [2].

The WBM family is the most used (90-95%) which composed of aqueous solutions of polymers and clays in water or brines, with different types of additives [3], these additives are used to lubricate the drill bit and suspend cuttings [4]. The performances of water-base fluid are directly related to optimum physical properties [5] such as viscosity, density and pH, this is achieved by using mud additives [6]. In addition to, the drilling process should be conducted safely least cost and minimum or no damage to the environment [7]. 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 [2,8,9]. The selection of the additive is generally based on the technical and environmental factors such of these additives are lignin [10]. Lignin extracted from mass can be used [11]. Lignin molecules adsorb on the clay surfaces (bentonite) and prevent the platelets from linking by eliminating electrochemical attractive forces between clay particles [12]. Modified lignin has been proposed for use as multifunctional additives for hydrocarbon industries such as thinner [5,6], filtrate loss control, [13,14] over a wide range of temperature and in the presence of contaminants [15,16].

Due to their desirable, low cost, non-toxic and easily biodegradable [17,18], it is used to produce a number of value-added products for specialty markets such as, wood preservatives [19], corrosion inhibitor [20], combination between corrosion and scale inhibitors [21], emulsifiers [22] and concrete additives [23]. Various of vinyl acrylic monomers such as acrylic acid, acrylamide, 2-acrylamido-2-methylpropane sulfonic acid [24-27], mixtures of acrylic acid and acrylonitrile [28] mixture of acrylic acid - acrylamide [29] and vinyl acetate, [30] were polymerized and grafted onto lignin to cover a huge range of other industrial applications, such as hydro soluble agents for

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dispersing agents, thickeners, flocculating and super-absorbent agents, organic synthesis, copolymer emulsion for paints, cosmetics, papers, varnishes and inks. In addition, dispersions for leather, textiles, glues and adhesives, cleaning and waxing products. Besides, plastics, synthetic resins, synthetic rubbers and lattices [31-39], which have excellent weather ability, water and alkaline resistance [40,41].

Vinyl acrylic polymers are synthesized by copolymerization of acrylates with other materials, either monomers via direct polymerization [42] or with natural materials such as lignin via graft copolymerization using different polymerization techniques [26]. These chemically modified lignin improved properties of lignin and increasing importance in industrial application. The key success in drilling may depend on maintaining proper flow and fluids viscosity under certain conditions. The aim of this study was to prepare lignin graft copolymer, namely LS-g-P(AA-co-Am-co-MBAm) as drilling fluid additive. During preparation, some factors which may be effect on physical properties of the polymer obtained were investigated.

2 Experimental

2.1 Material

Acrylic acid was obtained from Elf Chem. Co., ATO, France. Acrylamide product of DSM company and N,N' methylene-bis-acrylamide white powder from Sigma-Aldrich Chemie GmbH Company. Sodium persulfate and ammonium persulfate Product of NBM Chem. Company, England. Carbonate from M.R.P. Inc. of Taxes. The sodium lignosulfonate (LS) and bentonite were obtained from RP Mineral, Egypt. All the chemicals were used as received.

2.2 Preparation of Graft Copolymerization

In order to study the impact of conditions on graft copolymerization, the reaction was carried out in three-necked round-bottomed flask attached to a reflux condenser and equipped with magnetic stirrer, a nitrogen inlet thermometer and heater. 100 g (0.18 mol) of sodium lignosulfonates were dissolved in 120 ml of water to form 45% (mass ratio) solution, then 5 g (0.06 mol) acrylic acid, 3.5 (0.04 mol) acrylamide and 1.5 g (0.008 mol) methylene-bis-acrylamide, which was about 10% of the sodium lignosulfonates solids were added.

After addition of the acrylic monomers the solution was continuously stirred well by magnetic stirrer at 750 rpm, and then, the initiator, sodium persulphate, was prepared by dissolving 3 g of the solid substance in 70 ml of water. The acrylic acid and initiator were metered simultaneously over different time on a hot water bath at 70°C degree for each batch.

2.3 Characterizations

2.3.1 Fourier Transform Infrared (FTIR) spectroscopy

In this study, FTIR spectroscopy was able to differentiate the chemical bonds in the molecular structure of KL and LGC. The un grafted KL and LGC samples were analyzed using KBr pellet technique. In this technique, the KBr thin pellet was prepared by grinding 1% of sample into potassium bromide (KBr). It was then scanned by FT-IR spectrometer in the range from 4000 cm⁻¹ – 400 cm⁻¹

2.3.2 Viscosity of polymer solution

The polymer solution viscosity is measured by using DV-E Brookfield viscometer with spindle 63 and speed 30 at 24°C.

2.3.3 pH measurement

pH measured directly by using MV.temp-PL-700 PV to measure pH of samples.

2.3.4 Solids Content and Gravimetric Conversion

The dispersion polymer was dried to constant mass at a temperature of between 100 and 140 °C (see, for example, ISO 1625) and the solids content is then expressed as the percentage ratio of the dry matter to the total mass of the sample.

$$\text{Theoretical solid content (SC}_{\text{th}}) = \frac{\text{weight of introduced solids (g)}}{\text{sample weight (g)}} \times 100 \quad (1)$$

$$\text{Experimental solid content (SC}_{\text{exp}}) = \frac{\text{weight of dried latex (g)}}{\text{sample weight (g)}} \times 100 \quad (2)$$

$$\text{Gravimetric conversion (GC)} = \frac{\text{SC}_{\text{exp}}}{\text{SC}_{\text{th}}} \%$$

2.3.5 Mud properties test

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 of water before aging it for more than 24 h [12]. For each of the experiment, a fann model 286 viscometer was used at two rotating rates of 300 rpm (θ₃₀₀) and 600 rpm (θ₆₀₀), respectively. Then apparent viscosity (μ_a), plastic viscosity (μ_p) and yield point (τ_y) were calculated as follows (American Petroleum Institute 2003).

$$\mu_a = \theta_{600} / 2 \quad (3)$$

$$\mu_p = \theta_{600} - \theta_{300} \quad (4)$$

$$\tau_y = 0.511 (\theta_{300} - \mu_p) \tag{5}$$

Where θ_{300} and θ_{600} are viscometer shear stress readings at 300 and 600 rpm. Two sets of water-based mud property tests, named Experiments I and III, were designed and evaluated according to the American petroleum Institute Recommended Practice 13B-1 specifications.

3 Results and Discussion

3.1 Studying effect of reaction conditions on graft copolymerization

The graft co-polymerization reaction was conducted in numerous batches with the aim of discovering for the optimum conditions for the reaction. The effects of the dosages of hydrogen peroxide, monomers concentration, reaction temperature and time studied, 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, such that the optimum reaction conditions could be estimated on polymerization process [30].

3.1.1 Effect of initiator dosage

The data are given in table (1) and fig. (1) show that, the viscosity of the obtained polymer solution increase with the concentration of the initiator increase, this may be due to increasing the molecular weight of the polymer obtained, graft copolymerization of crude lignosulfonates with acrylic acid process was carried out via a free radical reaction, the range of initiator concentration studied from 1.5 to 6.5%.

The initiator concentration of 4.5% was preferred where it gave maximum grafting ratio, when the initiator dosage exceeded 4.5 %, the viscosity became decrease due to decrease molecular weight this may be due to increasing free radicals formed leading to shorter molecules, which lead to decrease the molecular weight, constant, thus 4.5% initiator concentration is preferred and used as optimum percentage in the next experiment.

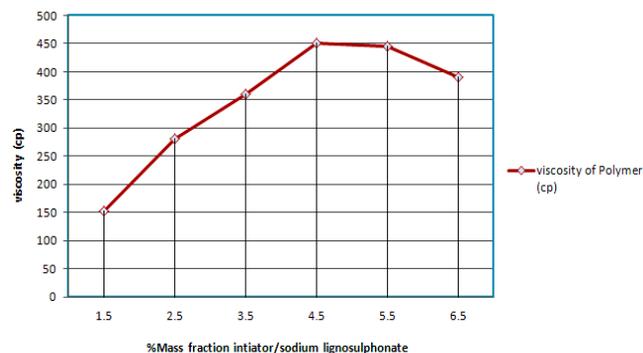


Fig. 1. Effect of initiator concentration on solution viscosity of polymer obtained.

Table 1. Effect of initiator concentration on viscosity of products.

polymer	Initiator	viscosity (cp)
LS-m1	1.5	152
LS-m2	2.5	280
LS-m3	3.5	360
LS-m4	4.5	450
LS-m5	5.5	445
LS-m6	6.5	391

3.1.2 Effect of reaction time

The effect of reaction time on the graft copolymer was studied under predetermined condition, the copolymerization was conducted for a variety of reaction time ranging from 2 to 7 h, table (2) and figure (2) represents the effect of reaction time on the viscosity of the graft polymer. Between the reaction times of 2 and 7 h, the viscosity increases gradually, due to the increase of graft ratio, which leads to increase molecular weight.

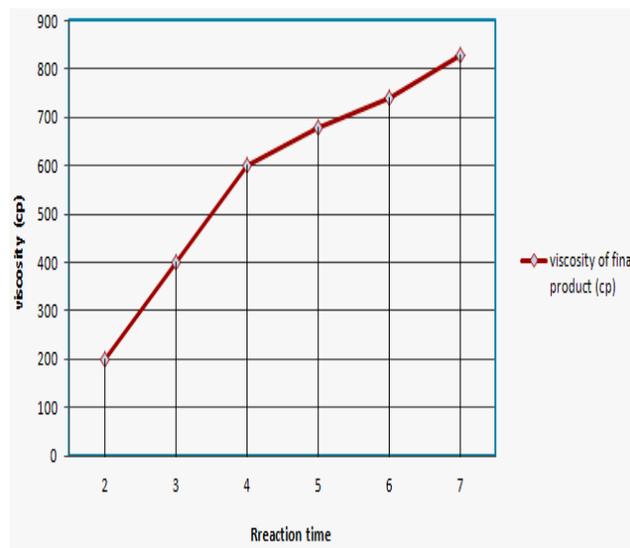


Fig. 2. Effect of reaction time on viscosity of products.

Table 2.Effect of reaction time on viscosity of polymer

Polymer code	Time (h)	viscosity of final product (cp)
LS-m1	2	200
LS-m2	3	400
LS-m3	4	600
LS-m4	5	680
LS-m5	6	740
LS-m6	7	830

3.1.3 Effect of temperature

The data are given in table (3), Fig. (3) show that, with the same amount of monomers the viscosity increase with increase of reaction temperature, due to the increase molecular weight of the polymer, increase temperature accelerate the production of radical groups, and increase the conversion rate of monomers, at high-temperature 80° C the viscosity decrease due to the reaction temperature was high [29], the decomposition of initiator would be too fast [43] so the optimum temperature for polymerization was 70° C, and thus all the next experiment was performed at this temperature.

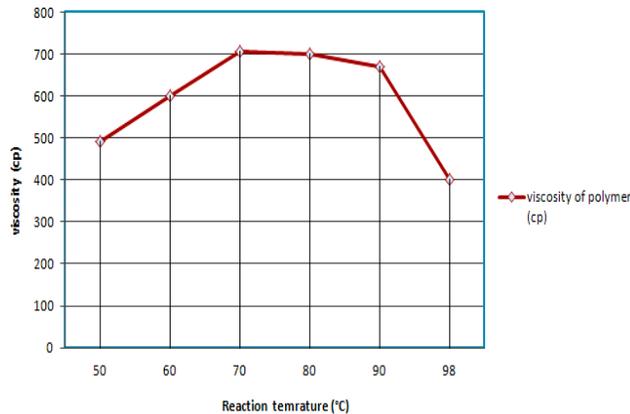


Fig. 3. Effect of polymerization temperature on solution viscosity.

Table 3: Effect of polymerization temperature on the viscosity of the products

polymer code	Temperature (°C)	viscosity of polymer (cp)
LS-m1	50	493
LS-m2	60	600
LS-m3	70	705
LS-m4	80	700
LS-m5	90	670
LS-m6	98	400

3.1.4 Effect of acrylic monomers

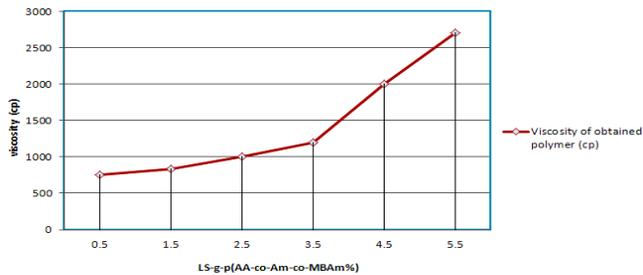


Fig. 4. Effect of cross-linker concentration on viscosity of polymers obtained.

The data listed in a table (4) and show in fig. (4) indicate that, the viscosity increase with the increase concentration of the acrylic monomers, due to the increase molecular weight of the polymer obtained [29,43]. For drilling fluids which may be subjected to normal temperature, from 5 to 10 percent of acrylic acid will result in an effective thinner [29]. and at a high concentration of acrylic monomer about more than 30 %, the polymer obtained act as a thickener for water drilling mud at low temperature [43].

Table 4. Effect of cross-linker concentration on viscosity of the product.

Polymer code	LS-g-p(AA %)	LS-g-p(AA-co-Am-co-MBA m%)	Viscosity of obtained polymer (cp)
LS-m1	9.5	0.5	750
LS-m2	8.5	1.5	830
LS-m3	7.5	2.5	1000
LS-m4	6.5	3.5	1200
LS-m5	5.5	4.5	2000
LS-m6	5.5	5.5	2700

3.2 Application of LS-g-P (AA -co- Am -co- MBA m)

3.2.1 Effect of LS-g-P (AA -co- Am -co- MBA m) on water base drilling mud

The data listed in table (5) show the addition two dosage (0.3% of PLA and 0.5%) under the aging process at two temperatures, ambient temperature of 27°C and high temperature of 90°C and their effect on rheological properties of water base mud formation , to study the effect of addition newly formulated for deep well drilling process ,this table showed that the either dosage(0.3% of PLA and 0.5%) decrease the yield point of mud at both room temperature 27°C and at high temperature 90°C. This experiment was designed to highlight the importance of using correct dosage of treatment to ensure optimum the performance of thinner as well as to reduce unnecessary cost. Besides, the use of excessive or insufficient dosage might bring negative impact to the mud properties [6].

Table.5 Effect of LS-g-P (AA -co- Am -co- MBA m) on water base drilling mud at room and high temperature

Mud formation	Temp.(°C)	μ_a (mpa.s)	μ_p (mpa.s)	Ty(pa)
Water Base Mud+ 0.3%	27	23.85	13.16	10.99
Water Base Mud + 0.5%	27	24.83	14	11.14
Water Base Mud+ 0.3%	90	18.20	6	12.50
Water Base Mud+ 0.5%	90	19.86	5.5	13.82

Table 6: Effect of LS-g-P (AA -co- Am -co- MBAm) on ph. properties of water base mud at different temperature and dosage

Types of Mud / (ph.)	Temperature (°C)						
	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C
0.3%w/w (LS-g-p(AA-co-Am-co-MBAm) + water base mud	10.73	10.85	10.81	10.80	10.80	10.73	10.67
0.5%w/w(LS-g-p(AA-co-Am-co-MBAm) + water base mud	10.64	10.43	10.35	10.32	10.30	10.30	10.30
0.7 %w/w(LS-g-p(AA-co-Am-co- MBAm) + water base mud	10.53	10.14	10.03	10.00	10.99	10.03	10.20
1.2%w/w(LS-g-p(AA-co-Am-co-MBAm) + water base mud	9.50	9.53	9.54	9.64	9.77	9.95	10.10
1.5%w/w(LS-g-p(AA-co-Am-co-MBAm) + water base mud	9.38	9.44	9.50	9.64	9.64	9.73	10.10
1.7%w/w(LS-g-p(AA-co-Am-co-MBAm) + water base mud	9.34	9.38	9.10	9.20	9.26	9.49	10.00

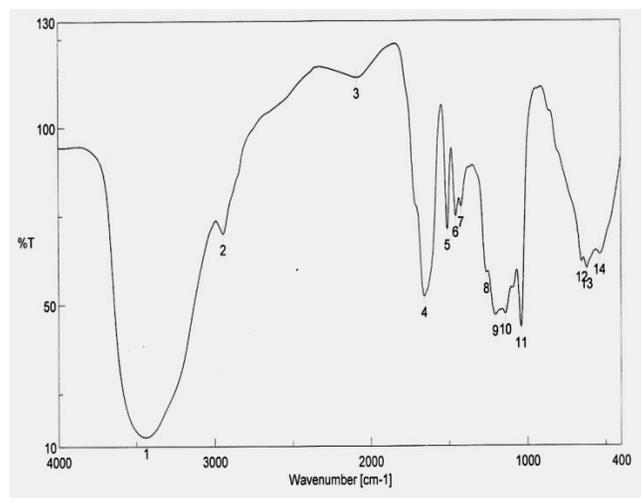
3.2.2 Effect of LGC concentration on the drilling mud pH

The data listed in table (6) shows the addition different dosage base mud, under the aging process at different temperatures from (30 to 90 °C), the results showed that the newly formulated has multifunctional properties , it is may be employed as pH controlling for water base drilling mud at low and high-temperature degree without further additives which added to control pH of the water base drilling mud . The data listed in a table (6) shows the new formulated LS-g-p(AA-co-Am-co-MBAm%) maintained the pH of the drilling mud within the desired drilling pH range and showed that, the pH value was slightly deviated after the aging at high temperature. This also reveals the thermal stability of the polymers. The thermal stability may describe to the chemical structure of LS-g-p (AA-co-Am-co-MBAm%) which comprised different functional groups [10] such as amines , carboxyls, ketones, aromatic rings and sulfate groups.

3.3 IR spectra of LS-g-P (AA -co- Am -co- MBAm)

IR spectra of the film of the Sodium Lignosulphonate acrylic acid graft copolymer sample shown in fig. (5) 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 an absorption band at 3436 cm^{-1} for (OH stretching vibration), the absorption band at 1657 cm^{-1} is attributed to the aromatic ring , absorption at 1462 cm^{-1} is assigned to either CH stretching of methyl or CH stretching of a methylene group. The bands at 2500 cm^{-1} and 3200 cm^{-1}

that is characteristic of carboxyl (OH) group of LS-AA. The carbonyl group C=O stretching vibration at 1723 cm^{-1} .A very broad band having a medium value at 3427 cm^{-1} characteristics for CH aliphatic methylene and methine coupled with that of OH of carboxylic group and that of H₂O [44]. IR spectrum of the Sodium Lignosulphonate acrylamide graft copolymer SLS-AM shows that a characteristic band C=O stretching vibration at 1657 cm^{-1} and a very broad band having a medium value at 3428 cm^{-1} characteristics for CH aliphatic coupling with NH and H₂O.

**Fig. 5.** IR spectra LS-g-P (AA -co- Am -co- MBAm)

4 Conclusion

Determine the optimum conditions for the graft copolymerization of acrylic acid into lignosulfonates such as stirring rate , the 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 4.5 h. The viscosity became relatively constant, and decrease with increase stirring rate, the optimum condition obtained at acrylic acid ratio 10:15%, using initiator concentration 4.5% at temperature 70°C at stirring rate 750 rpm for 7h of reaction time. This must be considered in choosing the optimum conditions for graft polymerization of these monomers as a thinner for water base drilling mud.

The results showed that the newly formulated has multifunctional properties, it may be employed as pH controlling for water base drilling mud at low and high-temperature degree without further additives which added to control pH of the water base drilling mud. In addition to their properties as a rheology modifier.

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