Characterization of a Biodegradable Polymer Used as Additive to Prepare Drilling Fluids

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Poly 2- hydroxyl ethylmethacrylate was synthesized through polymerization in bulk and processed to colloidal granulation in order to be used as additive for water based drilling fluids. The characterization of the product aimed at underlying properties such as thermal stability, swelling capacity, density, molecular mass and surface charge. The measurements done were meant to show its applicability as a filtrate reducer agent.

Keywords: poly 2- hydroxyl ethylmethacrylate, drilling fluids, filtrate reducer

The drilling fluids are dispersed systems used in the process of drilling oil and gas wells by the rotating – hydraulic method. They are introduced in the well by direct circulation and return to the surface through the annular space into the mud conditioners. Their most important functions are: to bring the slurry to the surface and to separate it; to cool and wash the drill bit; to reduce the friction between the drill pipe and the well formation; to maintain the well bore stability; to prevent reservoir fluids influx; to form a filter cake as thin and impermeable as possible; to contaminate not the productive strata; to comply with the regulations concerning environmental and personnel safety [1, 2].

Recent studies and developments [3, 4] have aimed at aligning to the strict environmental regulations imposed internationally concerning mainly the circulation, deposit and maintenance of the drilling fluids [5]. In this respect, there have been designed water based systems whose specific properties can be adjusted by polymeric additives.

Polymers represent a large range of compounds, important studies being made in current research to synthesize and characterize them [6]. Among the polymers that can be used to the preparation of drilling fluids are included natural polymers (starch) or natural modified polymers (carboxymethylcellulose), biodegradable by enzymatic mechanisms, as well as synthetic polymers (partially hydrolyzed polyacrylamide). To this last group belong acrylic and metacrylic polymers, acting as filtrate reducers.

This paper presents the synthesis and the adequate processing of a new additive with optimum properties to reduce the filtrate volume of water-based drilling fluids, as well as laboratory testing of the properties that recommend it.

The polymer poly 2- hydroxyl ethylmethacrylate was synthesized, being a compound with good water absorption capacity, property which offers fluid loss reducing qualities. In addition, it is known as a biocompatible polymer [7] which has sufficient thermo stability for this kind of applications and its swelling capacity is proportional to the pH index [8]. Its pH sensitivity to low basic values of pH represents another argument in favor of using it to prepare drilling fluids.

Experimental part

Polymer synthesis

The materials used were 2- hydroxyl ethylmethacrylate, monomer of technical grade purity provided by Quimidroga Company, and azo-bis-isobutyronitrile from Fluka Company, as an oil soluble thermal initiator. The synthesis was carried out by block polymerization reaction.

The initiator was mixed directly with the monomer, using a 0.2% (weight/weight) concentration of initiator with respect to the monomer.

The monomer – initiator mixture was introduced in tight closed bottles. They were immersed in an electrically thermostatic bath. The bottles containing the reactive were continuously stirred by rotation inside the bath.

The reaction was carried out under the following conditions: reaction temperature of 70°C and reaction time of 8 h.

Processing of the polymer

In order to be used as additive for the preparation of drilling fluids and to be well dispersed in water, the polymer had to have an adequate granulation. This was accomplished by grinding the polymer until obtaining a powder of colloidal dimensions. It was used a S100 Retsch mill with an agate cap of 500 mL and 12 agate balls of 20 mm diameter. The polymer was ground for 240 min.

Analysis methods

The polymer product was analyzed by the following spectral methods:

-FTIR method, in order to identify the product by comparing its spectrum with the fingerprint from the catalogue; a Magna-IR 560 Nicolet spectrophotometer was used;

-the chemical structure was determined and verified from the ^{13}C NMR spectrum with a NMR spectrometer Bruker Avance DSX300 having the spin velocity of 6700 Hz; the measurement was done in two pulses, with high decupling power. The time of relaxation applied between two consecutive scanning was 12 s.

The polymer that has been synthesized and processed was characterized by dynamic light scattering (DLS) to obtain the dimensional distribution of the particles. The

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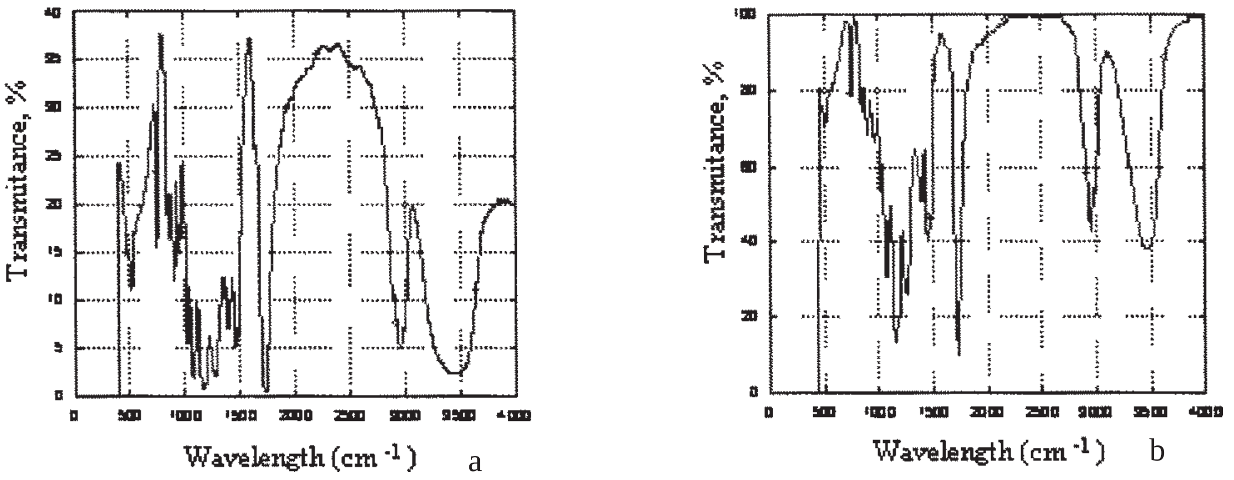


Fig. 1. FTIR spectra: a. polymer sample; b. catalogue spectrum [9]

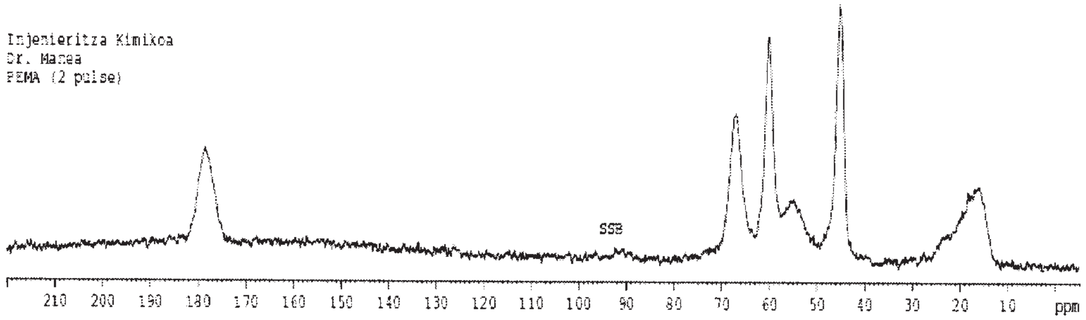


Fig. 2. ^{13}C NMR spectrum of the synthesized polymer

equipment used was a MASTERSIZER Hydro2000SM(A) from Malvern® Instruments, with a measurement range of particles diameter from 0.020 to 2000μm.

Considering the demand of thermal stability for the materials used to prepare drilling fluids, the synthesized polymer was thermally analyzed with the thermogravimetric method (TG) in dynamic heating regime; the equipment used was a TGA Q500, at high resolution.

To determine the density of the polymer, as a powder, the chosen method was the picnometer with fixed volume (STAS – 1077-67 Romania). The picnometer had special perforated stopper and the weightings were performed with an analytical balance *Mettler Toledo*.

The swelling capacity of the polymer was determined gravimetrically. The experiment consisted in observing the weight gain for a known quantity of material kept for 24 h immersed in a certain volume of water. The weightings were performed with an analytical balance *Mettler Toledo* and were repeated three times. Each probe had 0.25 g polymer in 10 cm^3 of water.

The molecular mass of the polymer was determined by gel permeation chromatography (GPC). The analysis was done with GPC equipment *Waters Model* 510, with Waters 2410 Refractive Index Detector. The polymer probe was dissolved in tetra hydro furan (THF), mobile phase, toluene being added as standard. For the data analysis, a universal calibration was used.

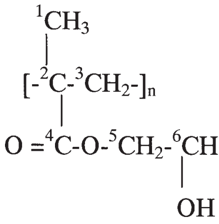
The electrical charge of the polymer surface was studied comparing the zeta potential, the mobility and conductivity of a polymer probe, a clay probe and a mixed probe of polymer and clay. The measurements were done with an apparatus ZetaSizer Nano ZS from Malvern Instruments, using the dynamic light scattering method. The solid probes were introduced in aqueous solutions 0,02mM $NaNO_3$, to insure a medium of enough ionic strength as to allow detecting the mobility of the present ionic species. Special cells with electrodes were used.

Results and discussions

Figure 1 shows the FTIR spectrum, in transmittance coordinates, of a polymer sample, figure 1.a., and the catalogue [9] spectrum of the compound, poly 2- hydroxyl ethylmethacrylate, in figure 1.b.

From the superposition of the two spectra, the similitude degree was found to be of 93%, enough to identify properly the product and to consider it of high purity.

The chemical structure of the synthesized polymer was composed and verified using the ^{13}C NMR spectrum (fig. 2).



$$\begin{array}{l} \quad {}^{1}CH_3 \\ \quad | \\ [-{}^{2}C-{}^{3}CH_2-]_n \\ \quad | \\ O={}^{4}C-O-{}^{5}CH_2-{}^{6}CH_2 \\ \qquad\qquad\qquad | \\ \qquad\qquad\qquad OH \end{array}$$

Fig. 3. Chemical structure of poly 2- hydroxyl ethylmethacrylate

To help interpret the spectrum from figure 2, figure 3 presents the chemical structure of poly 2- hydroxyl ethylmethacrylate, having numbered the carbon atoms.

The six peaks of the spectrum correspond to the six types of carbon atoms of the chemical structure; see figure 4. Thus, it is possible to identify two quaternary carbon atoms, ^{2}C and ^{4}C, at chemical shifts of 176.1 ppm and at 66.5 ppm, respectively [10]. Three secondary atoms, ^{3}C, ^{5}C and ^{6}C, appear consecutively at the following shifts: 60.5 ppm, 54 ppm, 44.7 ppm. Finally, the only primary carbon atom, ^{1}C, is identified at the minimal chemical shift, 18.1 ppm.

In figure 4 there are represented, together, the particle size distributions of two probes: one of a commercial mixture polymer and clay, as reference, and one of polymer, processed and synthesized. The purpose was to verify if the polymer granulation, obtained by processing, corresponds to the second peak in the reference probe distribution, knowing that the first peak corresponds to the clay material from the composition of commercial clay minerals [11].

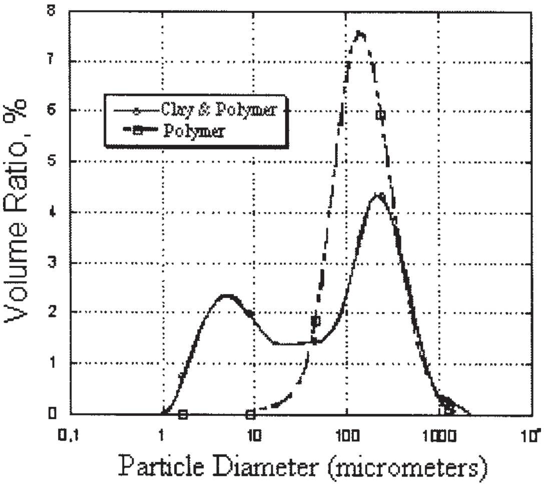


Fig. 4. Particle size distribution of a commercial probe of clay and polymer and of a synthesized and processed polymer probe

This analysis allowed us to determine a series of parameters that influence directly the rheological behavior of the dispersed systems, drilling fluids respectively, prepared with this polymeric powder material. Thus, the specific surface of poly 2- hydroxyl ethylmethacrylate particles is 0.0586 m^2/g, the surface average diameter is 102.630 µm. The volume average diameter is 183.565µm. A fraction of 10% of the particle number has a diameter below 55.171µm, 50% of them have a size up to 138.736 µm diameter, and most of the particles, 90%, are not bigger than 364.596 µm.

All the granulometric characteristics foresee an adequate behavior of poly 2- hydroxyl ethylmethacrylate, regarding its capacity to disperse well in water. So, it can be used to prepare water based drilling fluids.

In order to see if the synthesized product can be used in real working conditions, meaning exposure to high temperatures, a polymer sample was analyzed by thermogravimetry (fig. 5).

It can be noticed that, up to 153.2°C, the polymer probe maintains its integrity in a proportion of 97.33%. The weight loss registered till this point represents the evaporating water accumulated by this highly hydrophilic compound. Starting from this temperature on, till 246.8°C, the first stage of decomposition takes place. A total 13.42% of the probe mass is lost. The second decomposition stage means the loss of 78.32 % of probe mass, so that, at around 400°C only 5.6% weight of organic mass is left. This last quantity of probe is totally disintegrated in the next increment of temperature.

The results regarding the polymer capacity to absorb water are given in table 1.

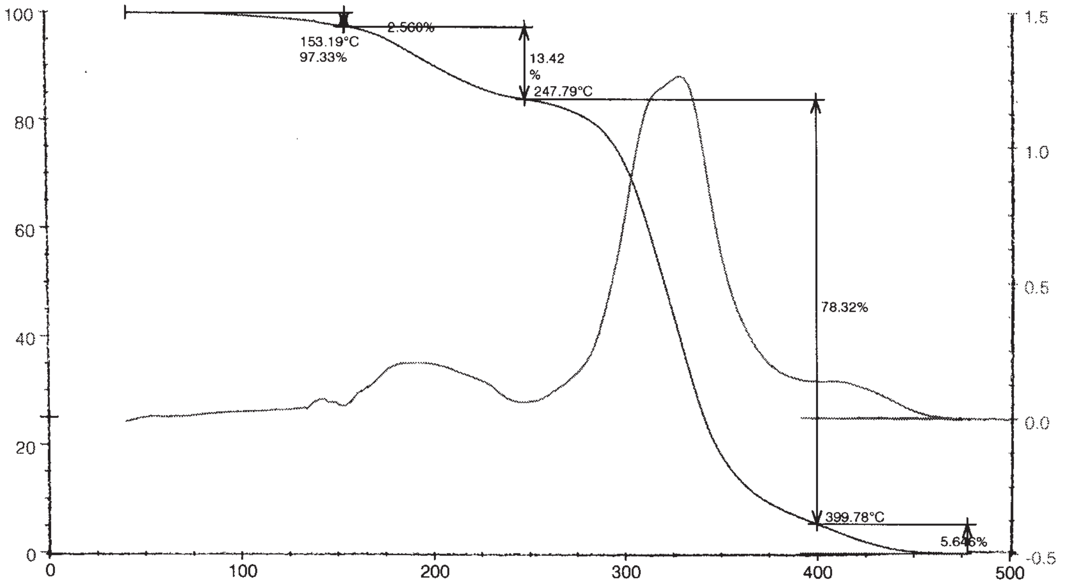


Fig. 5. Weight loss (%) vs. temperature (°C) curve for a sample of the synthesized polymer

Table 1
POLYMER SWELLING CAPACITY

Probe	Dry polymer mass, g	Hydrated polymer mass, g	Swelling capacity, %
1	0.25	0.47	88
2	0.25	0.44	76
3	0.25	0.46	84

Table 2
ELECTROKINETIC PARAMETERS

Probe	Zeta potential, ζ (mV)	Electrical mobility, U_E (*10^{-8} m^2/V*s)	Electrical conductivity, λ (mS/cm)
Polymer	-20.6	1.62	2.14
Clay	-37.4	2.93	3.20
Clay and polymer	-55.3	4.34	2.53

The average value of the swelling capacity experimental measurements is 82.7%. So, this material has a great swelling capacity, absorbing a quantity of water almost equal to its own mass.

This property is very important because it explains the mechanism through which this polymer can work as a fluid loss reducer in water based systems.

Considering the fact that drilling fluids are dispersed systems, in this case referring to the ones having water as continuous phase, their stability depends on the electric charge on the surface of dispersed particles (clay, polymer). Table 2 presents the electro kinetic parameters of a polymer dispersion sample, clay dispersion and a dispersion containing both components (clay and polymer).

The zeta potentials, both for clay and polymer, are negative. This aspect proves the anionic nature of these species, indicating the attraction towards cationic species coming from contaminating electrolytes. In the presence of clay, the polymer particles will undertake part of the contaminating positive ions and will reduce the ionic change process on the clay plates. The polymer does not undergo ionic change process with the counter ions, but it will fix them on its surface. The polymer properties as fluid loss reducer will not suffer.

In addition, the zeta potential values of clay and polymer are close. In the case of combining the two compounds, the zeta potential is cumulative, being equal to the sum of the individual potentials. The effect of such behavior is the increase of stability when adding the polymer particles in the clay – water dispersion.

Depending on the molecular mass and the ionic nature, the polymers can encapsulate the clay colloids. This type of compounds is called flocculants.

The molecular mass, weight average, was determined 6500 g/mol and the number average molecular mass was 5800 g/mol. The synthesized polymer is considered to be a low molecular mass polymer, according to literature classifications [12]. Anionic polymers with relatively short chain length are likely to be the kind of flocculants that encapsulate by attaching on the edges of clay colloids.

The relative density of the polymer was determined experimentally as 1.35 g/cm^3. This property allows to estimate the degree in which this polymer additive will contribute to the overall density of the system.

Conclusions

Poly 2- hydroxyl ethylmethacrylate was synthesized by in bulk polymerization, processed and brought to an adequate granulation for using it as additive in aqueous dispersed systems.

After measuring the specific properties of the synthesized polymer, a series of conclusions can be drawn, as follows:

-by spectral analysis, using methods like FTIR and ^{13}C NMR, the synthesized product was identified as poly 2-hydroxyl ethylmethacrylate; its structure and quality were verified, as well;

-the thermal resistance of the polymer assures an adequate functioning up to over 150°C, temperature rarely exceeded during drilling operations, therefore the product is perfectly useful to such purposes;

-a sample of the polymer proves to completely decompose thermally, certifying the non-polluting feature of the material; the ecological risk is reduced, without existing residues that need treatment and depositing;

-due to its considerable swelling capacity in aqueous medium, this polymer takes the free water from the system and can become a fluid loss reducing agent for the water based drilling fluids;

-with an electric charge similar to that of the clay plates and acting in synergism with them, the synthesized polymer can increase the stability of the clay – water dispersions and can reduce the effect of the electrolyte contamination;

-the synthesized product has an encapsulating function by adherence to the clay plate's edges; thus, protective polymer films are created on the clay surface which inhibit the hydration of the clay.

Polymer poly 2- hydroxyl ethylmethacrylate has a series of specific properties determined in this study that recommend it as fluid loss reducer additive for water based drilling fluids.

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