

Structure-Property Relationship of Polyetheramines as Clay-Swelling Inhibitors in Water-Based Drilling Fluids

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ABSTRACT: The influences of structure parameters of polyetheramines as clay-swelling inhibitors in water-based drilling fluids on the application performances were studied. Interactions of polyetheramines with clays were investigated through elemental analysis (EA), X-ray diffraction (XRD), and thermogravimetric analysis (TGA). The results showed that lower molecular weight, hydrophobic oxypropylene segment, and plentiful amino group of polyetheramines favored improvement of inhibitive properties, enhancement of adsorption abilities, and expelling interlayer bound waters of clays (as confirmed by cutting rolling test, bentonite inhibition test, EA, XRD, and TGA studies). Simultaneously, the polyetheramines did not produce adverse effect to filtration control of the drilling fluids. In addition, XRD patterns revealed that these polyetheramines could intercalate into interlayer spaces of clays and display a monolayer arrangement. The corresponding basal spacing of clays was correlated only with molecular weight of polyetheramines. The dense loading of polyetheramines in the interlayer of clays was beneficial in improving inhibitive properties. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 1074–1079, 2013

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INTRODUCTION

Water-based drilling fluids are increasingly being used for oil and gas exploration, and are usually considered to be more economical and environmentally friendly than oil-based or synthetic-based fluids. Unfortunately, their use can facilitate hydration and swelling of water-sensitive clay-based shale formations, thereby resulting in a series of wellbore instability problems such as hole closure causing tight hole, cave-ins, leading to fill on trips and problems when running casing. Clay swelling can also cause agglomeration of drilled cuttings, leading to reduced hole-cleaning efficiency, build-up of thick cuttings beds, and reduced rates of penetration arising from balling of the drill bit with sticky clay. According to statistics,¹ the reactive shales are found in about 75% of the formations drilled all over the world and are responsible for approximately 90% of the wellbore instability and relative problems.

To minimize the hydration-induced swelling of the reactive shales (clays), various chemicals have been used. One of the earliest and most widely used methods is based on the addition of high concentrations of inorganic salts such as potassium

chloride, sodium chloride, and divalent brines to drilling fluids. These salts act through a variety of mechanisms. Widespread research^{2,3} has shown that clay swelling can occur via two different regimes: (1) crystalline swelling, involving the adsorption of limited amounts of water in the interlayer of clays and (2) osmotic swelling, related to unlimited adsorption of water owing to the difference between ion concentrations close to the clay surface and pore water. It is generally accepted that the crystalline swelling is restricted via the intercalation of chemicals into the interlayer of clays, similar to the mode of action of the potassium chloride, whereas sodium chloride and divalent salts help to prevent osmotic swelling by increasing the ionic concentration of water phase and filtrate viscosities and reducing water activities.^{3–5}

It is well known that potassium cation has not been completely successful in inhibiting the swelling of clay minerals and has various limitations.^{3,4,6–8} Moreover, potassium chloride in large quantities has an adverse impact on chemical and biological ecosystems and flocculates clay minerals, resulting in both high fluid losses and an almost complete loss of thixotropy.^{9–11} To overcome the disadvantages, alternative cation sources have

Table I. Summary of Jeffamine[®] Polyetheramines

Sample	Chemical formula	Molecular weight
D230	NH ₂ (CH(CH ₃)CH ₂ O) _{2.5} CH ₂ CH(CH ₃)NH ₂	230
D400	NH ₂ (CH(CH ₃)CH ₂ O) _{6.1} CH ₂ CH(CH ₃)NH ₂	430
T403	CH ₃ CH ₂ C(CH ₂ (OCH ₂ CH(CH ₃)) _x NH ₂) ₃ , ΣX = 5.3	440
EDR148	NH ₂ (CH ₂ CH ₂ O) ₂ CH ₂ CH ₂ NH ₂	148

been sought. The ammonium cation has a very similar hydrated volume as the potassium cation, and hence it is thought that these cations would function in an analogous way, that is by entering the clay sheets and replacing hydratable cations such as sodium. Patel et al.^{6,7} reviewed the development of ammonium (amine) derivatives as clay-swelling inhibitors in water-based drilling fluids and summarized their chemistry, functionality, and relative merits. Among the chemicals, polyetheramines possessing lower molecular weight and well water solubility are deemed to be most promising, owing to an outstanding combination of excellent inhibitive performance in the absence of salts, heat tolerance, environmentally benign character, and compatibility with drilling fluid formulations.^{4,6–11} Such amines are commercially available from Huntsman Chemicals, USA, as Jeffamine[®]. They contain primary amino groups attached to the end of polyether backbone-based either on ethylene oxide (EO), propylene oxide (PO), or mixed EO/PO segments.

Polyetheramines, mainly used as intercalating agent of nanocomposites, curing agent of epoxy resin, and chain extender of polyurethane, have not been applied for clay-swelling inhibitors until the early 2000s.^{6,7,11} To our knowledge, very few polyetheramines are used in the domain. To date, the question of how the molecular structure of polyetheramines influences their properties and mode of action with clays has not been well answered. In this article, the effects of structure parameters of polyetheramines (molecular weight, component of backbone, and number of amino endgroup) on inhibitive capabilities were investigated by two different test methods. A series of experiments including elemental analysis (EA), X-ray diffraction (XRD), and thermogravimetric analysis (TGA) were prepared to explore interactions of clays with polyetheramines of different structure parameters. The objectives are to establish correlations between the structure and the property of polyetheramine inhibitors, further understand the mechanism of action, and consequently offer a theoretical guidance for synthesis and application of the novel amines.

EXPERIMENTAL

Materials

Four polyetheramines were presented by Huntsman Chemical, USA. Their information of chemical formula and molecular weight, obtained from Huntsman, are summarized in Table I. Hexane diamine was of chemical grade and purchased from Tianjin Chemical Reagent, China. Experimental cuttings were obtained from the shale formation of Xinye HF-1 well depth of 700 m in Xinchang Gas Field (Sichuan, China). The clay

mineral used in this study was sodium bentonite supplied by Dagang Oilfield Group, China and determined to have a cation exchange capacity of 82 mmol/100 g. All materials were used as received without further purification.

Cuttings Rolling Test

In the absence and presence of polyetheramines, 50 g of shale cuttings (6–10 mesh) was rolled for 16 h at 40°C in 350 mL of deionized water in a stainless-steel aging jar. Then, the remaining cuttings were screened using a 40-mesh screen and washed with 10 wt % KCl solution, dried to a constant weight in an oven at 100°C, and then weighted to obtain the percentage recovered of the cuttings. Clearly, the more inhibitive the fluid, the higher the final recovery.

Bentonite Inhibition Test

In the absence and presence of 1 wt % polyetheramines, 400 mL deionized water with 5 wt % bentonite was stirred for 30 min. The samples were also rolled at 40°C for 16 h and then their Bingham-type rheological data were measured using a ZNN-D6 rotating viscometer (Tongchun, China). The equivalent amount of bentonite was added again into the samples and the procedure as previously described was carried out until the samples became too viscous to measure.

Fluid Loss Property Test

A bentonite stock dispersion was prepared by dispersing 14 g of bentonite into 350 mL of deionized water. The prepared bentonite dispersion was laid aside for 24 h before use. Various fluids were obtained with an addition of inhibitors into the bentonite dispersion. The filtrate volume of the fluids was measured using an SD-type medium-pressure filtration apparatus (Tongchun, China), according to the standard American Petroleum Institute (API) procedure, under the conditions of room temperature and differential pressure of 0.69 MPa.

Adsorption Measurement

Aqueous dispersions of bentonite with the polyetheramines in the concentration range of 0–1.5 wt % were prepared by adding 14 g of bentonite into 350 mL polyetheramine solution directly. Dispersions were shaken for 16 h at 40°C to reach the adsorption equilibrium. Afterward, the sediment was collected by centrifugation at 13,000 rpm for 20 min. The obtained sample was redispersed in water to remove unadsorbed polyetheramine remaining in solution. This procedure was repeated five times until the supernatant water from centrifugation was found to be free of polyetheramine. This was monitored by measuring the pH of the washing water, which should be similar to that of the dispersed bentonite without polyetheramine, that is, pH = 8.0. One part of the sediments was dried in a vacuum oven at 90°C and grounded to powders for the measurements of EA, XRD, and TGA. The other part of the sediments was used for XRD measurements directly.

The Vario EL CUBE elemental analyzer (Elementar, Germany) was used to measure the nitrogen weight percent of samples. The adsorbed amount, expressed as milligram polyetheramine in per gram of bentonite, could be calculated using the following equation:

$$\text{Adsorbed amount} = \left(\frac{NW}{1 - \frac{NW}{14n}} \right) \times 10^3$$

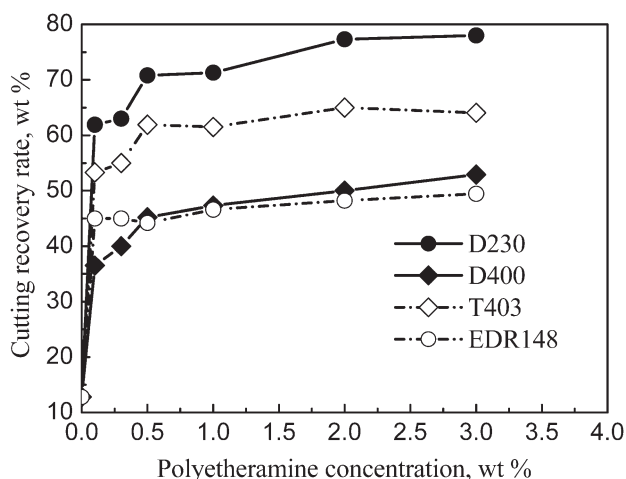


Figure 1. Variation of cutting recovery rate with polyetheramine concentration.

where N is the determined nitrogen weight percent of samples, and W and n are the molecular weight and number of amino endgroup of polyetheramine, respectively.

X-ray Diffraction

XRD analysis was performed by using an X'pert PRO MPD diffractometer (PANalytical, Holland) with $\text{CuK}\alpha$ radiation at a generator voltage of 45 kV and current of 40 mA. Samples were measured at scanning angle of 2θ from 3 to 12° .

Thermogravimetric Analysis

TGA was conducted with SDT Q600 (TA, USA) at a heating rate of $20^\circ\text{C}/\text{min}$ from room temperature to 800°C in a high-purity flowing nitrogen atmosphere.

RESULTS AND DISCUSSION

Inhibitive Properties

The method commonly used in industry to determine swelling in reactive clays and shales is the cutting rolling test.³ The recovery results of cuttings treated with polyetheramines in the concentration range of 0–3 wt % are shown in Figure 1. It can be seen that with the addition of polyetheramines into water, the cutting recovery rates are increased and change very slowly as polyetheramine concentrations are further increased, meaning that four polyetheramines are very efficient clay-swelling inhibitors, that is, that a small dosage of polyetheramines can attain optimal swelling inhibition. However, differences in the cutting recovery rate still occur between the polyetheramines. Both diamines of D230 and D400 have a uniform constitutional repeating unit of PO, but a differential molecular weight. Evidently, the former possesses lower molecular weight and conclusively much better inhibitive properties. The reason is discussed in detail below. As compared with D230 diamine, EDR148 diamine inversely shows a much worse inhibitive property although molecular weight of polyetheramines further reduces from 230 to 148. It should be attributed to the substitution of hydrophilic EO for hydrophobic PO on the backbone which is not beneficial to expel interlayer water molecules of clays.^{7,11} Besides, the methyl group α to the amino group plays

other significant role. When the inhibitor possesses a PO backbone, the protonated amino cation is found closer to the clay surface than for EO backbone⁴ and thereby strengthening the inhibition effect.

It is known that the hydration of sodium cations is one of the major driving forces for the swelling of clays. The polyetheramines act mainly via the cation exchange mechanism.^{6,7} Some reports^{4,7} have indicated that the inhibitor molecules should be polycationic, because this can result in a “pinning effect” where various parts of the molecule bind to either clay surface. It means that the molecule is less likely to be exchanged by other cations as it requires simultaneous release from multiplex adsorption points. In our studies, as compared with D400 diamine, T403 has similar molecular weight and PO structure, but has three amine groups in each molecule, thereby determining that T403 necessarily possesses a higher cutting recovery rate (Figure 1).

The bentonite inhibition test is used routinely as a screening method to determine the ability of a product to prevent bentonite from swelling and maintain a low rheological profile. This method is designed to simulate the incorporation of highly active drilled solids into a drilling fluid similar to what occurs while drilling water-sensitive shales in the real-time field application.⁶ The dependences of yield point (YP) and apparent viscosity (AV) of the samples on bentonite concentration are shown in Figure 2. When there is no polyetheramine, the values of YP and AV rapidly increase with increasing bentonite concentration. With the introduction of 1 wt % polyetheramines, the curves of YP and AV versus bentonite concentration move to the right region in the graphs. The more evident the right shift of the curve, the more excellent the inhibitive performances of the corresponding polyetheramine. All the results of rheological data agree well with those of the cutting recovery rate, indicating that the structure of lower molecular weight, polyether backbone based on PO, and abundant amino group appears to decide improved inhibitive properties of polyetheramine.

Fluid Loss Property

In general, the negative surface charge of bentonite is easy to be neutralized and screened by the positive charge and hydrophobic backbone of organic cations, respectively.^{12,13} As a result, the ζ -potential and hydrated shell thickness of bentonite particle are obviously reduced. At a macroscopic level, it is reflected into an elevated filtrate volume of the fluid. Figure 3 shows the effects of the concentration of polyetheramine and hexane diamine on the API filtrate volume. As expected, the API filtrate volume steeply increases with increasing concentration of hexane diamine. When hexane diamine concentration exceeds 1 wt %, evident flocculation occurs in the bentonite dispersion. However, it is surprisingly found that with the addition of polyetheramines, all the filtrate volumes almost keep constant irrespective of the type and concentration of polyetheramines. According to the view of Qiu and coworkers,¹¹ it should be ascribed to weak protonation and alkalescence of polyetheramines, producing only a mild neutralization to negative charge of bentonite particle. Besides, we think that oxygen atoms of the polyetheramine backbone play a more predominant role in

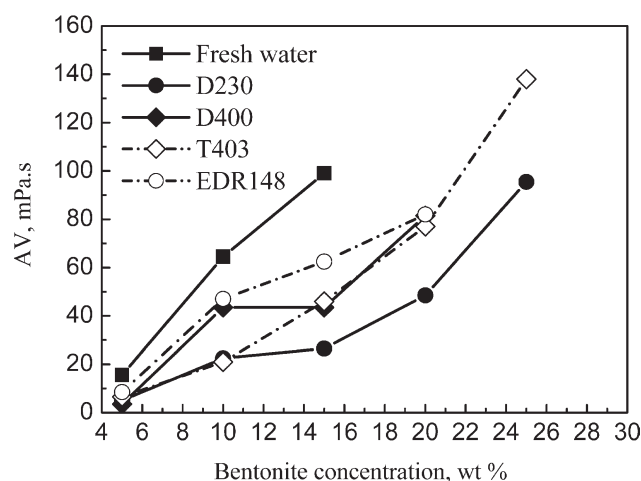
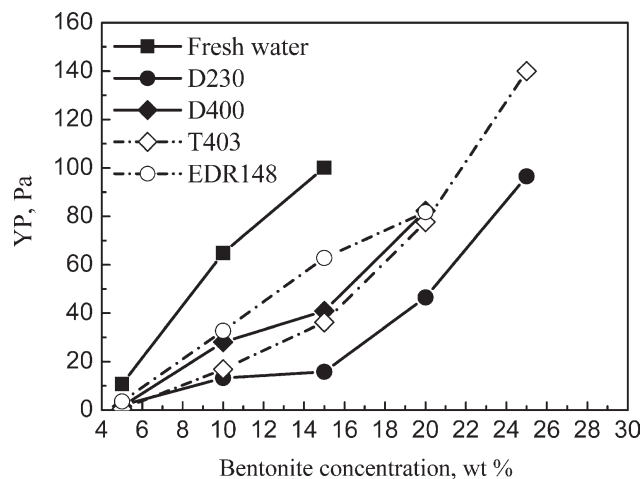


Figure 2. Plot of YP and AV versus bentonite concentration.

the process. Among the four polyetheramines, EDR148 may be regarded as a chemical that increases two oxygen atoms at the base of hexane diamine. The modification by incorporating of

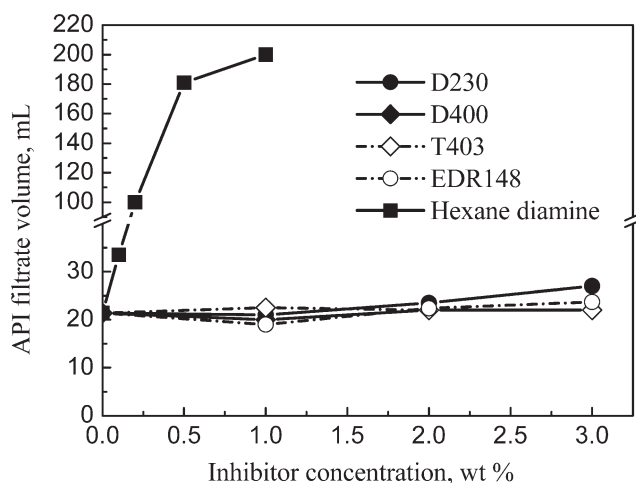


Figure 3. Dependence of API filtrate volume on concentration of polyetheramine and hexane diamine.

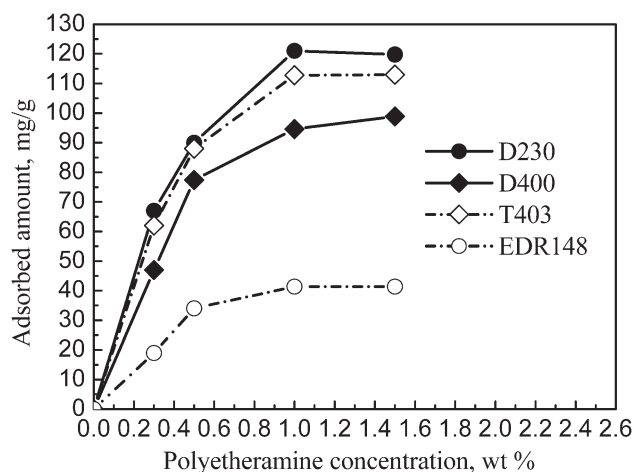


Figure 4. Adsorption isotherms of polyetheramines.

oxygen atoms in alkyl chains converts the hydrophobic character of hexane diamine to more hydrophilic,¹⁴ and thereby reducing hydrophobic screening bentonite particles and adverse effect on fluid loss properties.

Adsorption Isotherms

Adsorption isotherms are shown in Figure 4. All the polyetheramines display a certain affinity for bentonite surface, with an increase initially and a leveling off at higher polyetheramine concentration. It accords with the characteristics of Langmuir-type adsorption. Previous studies^{10,14-16} have revealed that the adsorption of polyetheramine involves more than just an ion-exchange mechanism alone. The possibilities include (1) hydrogen bonding of ether oxygen and unprotonated amino group of polyetheramine with silanols and structure hydroxyl group of bentonite, (2) hydrophobic interaction between alkyl chain of polyetheramine and siloxane surface of bentonite. In our studies, D230 is provided with not only low molecular weight, resulting in convenient intercalation of polyetheramine molecule into interlayer spaces of bentonite¹⁶⁻¹⁸ but also hydrophobic repeating unit of PO, consequently, adsorbed largely on bentonite. The adsorbed amount of polyetheramine appears to depend much more on its chemical (hydrophilic or hydrophobic) character instead of molecule weight.¹⁴ It can be used to explain the reason why EDR148 possesses the poorest adsorbability in the four polyetheramines. However, it is worth noting that there is a practical limit to increasing the hydrophobicity. If the backbone is too hydrophobic, the inhibitor molecule will not be water soluble.

As compared with D230, the adsorbed amount of T403 and D400 decreases, but to various extents. Obviously, the decreases should be ascribed to the steric hindrance as mentioned before, derived from increasing molecular weight. Theoretically, each T403 can adsorb to three reactive sites of bentonite, whereas D400 at best adsorb on two reactive sites via an ion-exchange mechanism. From here, we see that multipoint absorption is beneficial in the increase of adsorbed amount. It is consistent with our experimental results (T403 > D400).

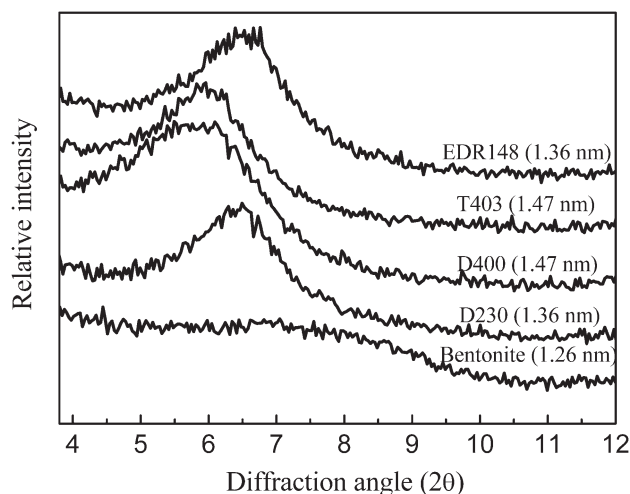


Figure 5. XRD patterns of dry bentonite untreated and treated with 1 wt % polyetheramines.

X-ray Diffraction

The XRD patterns of dry bentonite untreated and treated with 1 wt % polyetheramines are shown in Figure 5 in which the basal spacing calculated according to Bragg's equation is also shown. The untreated bentonite displays a broad and diffuse basal reflection with the peak maximum at around 7° (1.26 nm). Once the bentonite is modified by the polyetheramines, the basal reflection moves toward lower diffraction angle and shows a narrower and higher intensity. It verifies the relatively regular intercalation of the polyetheramines into interlayer spaces of bentonite. In addition, it can be seen that the basal spacing of polyetheramine–bentonite composites seems to be associated only with the molecular weight of polyetheramines. Previous studies^{19,20} show a basal spacing of pure montmorillonite ranging from 1.0 to 1.3 nm, which is owing to different origins of clay and different drying methods. The thickness of montmorillonite without interlayer water is 0.96 nm, and the van der Waals diameter of a methyl group is about 0.4 nm.¹⁶ The spacing at D230 and EDR148 loading is about 1.36 nm, indicating that both the polyetheramine molecules lie flat on the clay layer-forming monolayer arrangement. The same results have also been gained by other researchers.^{10,11,21} For T403-bentonite and D400-bentonite composites, their basal spacing (ca. 1.47 nm) is higher than that expected for the fully extended conformation (1.36 nm). It is possibly owing to higher molecular weight and gauche conformations of the two polyether-

Table II. Loading Density of Polyetheramines in the Clay Interlayer at 1 wt % Polyetheramine Concentration

Sample	Γ (mg/g)	T_1 (nm)	Loading density (g/cm ³)
D230	121.0	1.36	0.91
D400	94.6	1.47	0.54
T403	112.8	1.47	0.65
EDR148	41.4	1.36	0.31

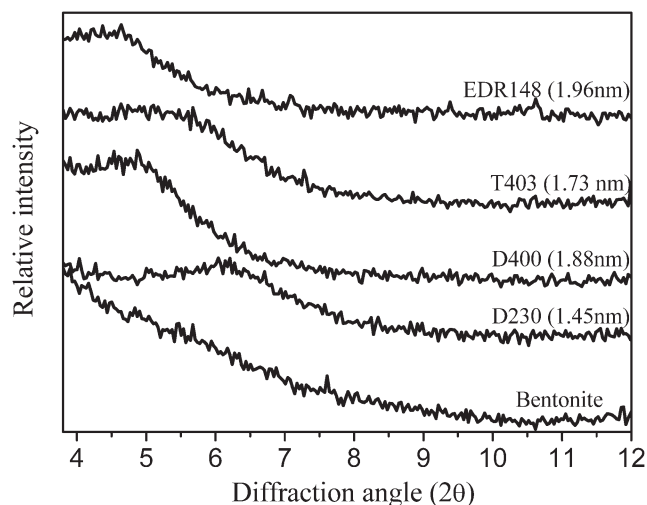


Figure 6. XRD patterns of wet bentonite untreated and treated with 1 wt % polyetheramines.

amines.^{4,14,22} Hence, we think that T403 and D400 still adopt the mode of monolayer arrangement on the clay layer, but the arrangement is relatively incompact. For the bentonite treated with 1 wt % polyetheramines, the loading density of polyetheramines in the interlayer can be estimated using the following equation:

$$\text{Loading density} = \frac{\Gamma D T_2}{T_1 - T_2} \times 10^{-3}$$

where Γ is adsorbed amount (Figure 4), T_1 is the basal spacing of the composites (Figure 5), and D and T_2 are the density (2.7 g/cm³) and thickness (1 nm) of montmorillonite platelets,¹⁶ respectively. The correlative data are summarized in Table II. The higher loading density indicates a denser polyetheramine layer. Suter et al.⁴ think that for realizing optimization of inhibitive properties, cationic inhibitor should possess a properly long hydrophobic backbone and form a dense monolayer in the

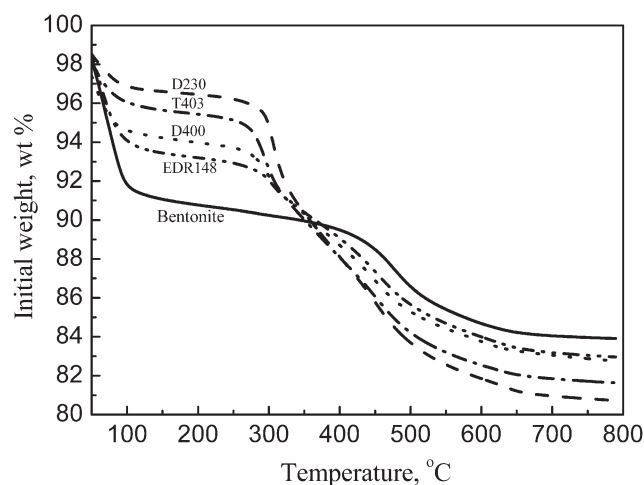


Figure 7. TGA curves of bentonite untreated and treated with 1 wt % polyetheramines.

interlayer of clay. In our experiment, it appears that only D230 meets the demands.

In addition, Figure 6 shows the XRD results of wet bentonite untreated and treated with 1 wt % polyetheramines. It is observed that the basal spacing of the samples is higher than that of corresponding dry samples, because of water molecules ingress. In the wet state, the higher basal spacing also means that the sample is easy to be hydrated. Especially for the untreated bentonite, the amount of interlayer water is so large that no basal reflection is detected in our measurement range.

Thermogravimetric Analysis

TGA patterns of bentonite and bentonite modified with 1 wt % polyetheramines in the temperature range of room temperature -800°C are shown in Figure 7. It is universally accepted that below 200°C , the decomposition of organic polymer-modified clay should be associated to the removal of bound water from the interlayer of clay.¹⁷ Then, polymer degradation happens. Clays begin losing structural hydroxyl groups only above 600°C and maintain their layered structure up to 800°C .²³ It can be found that all studied polyetheramines are able to decrease the mass of bound water adsorbed on bentonite. The better the inhibition and adsorption abilities of polyetheramines are, the lower the mass loss is. It indicates that excellent adsorptive capacity is a precondition of improving inhibitive properties, whereas lower mass of bound water is a foregone conclusion of the process. In addition, TGA curves show an intersection point at about 360°C , thereafter the order of thermal stability fully reverses. It may be attributed to the thermal degradation of polyetheramines.

CONCLUSIONS

In this article, a systematic study is performed via a series of test methods of cutting rolling, bentonite inhibition, API filtration, EA, XRD, and TGA, to investigate structure/property relationships of polyetheramines as clay-swelling inhibitors in water-based drilling fluids. The results show that polyetheramines of lower molecular weight are easy to insert the interlayer space of clays. The backbone of hydrophobic PO instead of hydrophilic EO is helpful to the adsorption of inhibitor on clays and expelling interlayer-bound water molecules. If multi-amino groups occur in a polyetheramine molecule, the cation exchange would get strengthened. Theoretically, polyetheramines fully provided with above constitutional features can form a dense monolayer in the interlayer of clays and thereby have superior inhibitive properties. In addition, the polyetheramines do not deteriorate filtration properties of the drilling fluids as a result of relatively hydrophilic oxygen atoms embedded in alkyl chains. It indicates their excellent compatibility with drilling fluid formulations. The biological toxicity and thermal stability of polyetheramines will be reported in a following article.

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