

Preparation and Properties of a Dispersing Fluid Loss Additive based on Humic Acid Graft Copolymer Suitable for Cementing High Temperature (200°C) Oil Wells

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ABSTRACT: A humic acid graft copolymer possessing both water-retention and dispersing properties in cement slurry was synthesized by grafting lateral chains of 2-acrylamido-2-methylpropane sulfonic acid (AMPS[®]), *N,N*-dimethylacrylamide (NNDMA), and acrylic acid (AA) onto a backbone of humic acid using aqueous free radical polymerization. The graft copolymer is composed of 20 wt % humic acid backbone and 80 wt % graft chain (molar ratio AMPS/NNDMA/AA = 1 : 0.31 : 0.03), it exhibits a M_w of 323 kDa and is highly anionic in cement pore solution. The influence of this specific molecular design on cement flow properties is unraveled. When tested at 200°C, the graft copolymer achieved very low cement fluid loss values (~50 mL) at low rheology. This behavior differentiates it from most common synthetic high temperature fluid loss additives which excessively viscosify cement slurries. The working mechanism of the graft copolymer was found to rely on adsorption onto the surface of hydrating cement. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

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INTRODUCTION

Crude oil (petroleum) and natural gas are among the most abundant fossil resources found in geological formations beneath the earth's surface in depths of up to 9000 m. For their recovery, oil and gas wells have to be constructed by drilling through multiple geological formations using water or oil-based drilling fluids. Water-based drilling muds use functional water-soluble polymers for water retention, e.g. for polymers based on *N*-vinylpyrrolidone.¹ In mature oilfields, aqueous solutions of viscosifying polymers are used for tertiary oil recovery (so-called chemical flooding).²

Since recent, an increasing number of oil and gas wells is characterized by excessively high temperatures (up to 260°C), high pressures (up to 1700 bar), and saline reservoir fluids that may contain numerous electrolytes such as NaCl, CaCl₂, MgCl₂, and MgSO₄ at total concentrations of up to 40 wt %. These wells need to be sealed by cementing a metal pipe (so-called casing) into the borehole.^{3,4} The primary objective of cementing such casing is to achieve complete zonal isolation. It prevents migration of fluids and gases between formations and of influxes into the borehole. Consequently, the cement sheath needs to withstand the various stresses occurring during the life of an oil well.^{5,6}

Cement dispersed in water presents a classical colloidal system whereby the cement particles attain an overall negative surface charge, as is evidenced by zeta potential measurement.^{7,8} The silicate phases C₃S and C₂S present in cement clinker produce a negative charge while the aluminates (C₃A and C₄AF) exhibit a positive charge. Thus, the charge distribution on the surface of cement is heterogeneous and provides anchoring sites for both cationic and anionic polyelectrolytes. Since silicates and thus negatively charged surfaces are prevalent in cement, anionic cement additives are most commonly used because they require less dosage to cover the fewer positively charged sites of the aluminate hydrates by adsorption.⁹

The addition of fluid loss additives (FLAs) to oil well cement slurries is of paramount importance to prevent loss of water (dehydration) of the cement slurry while it is being pumped down hole and placed between the porous formation and the casing. Currently, synthetic sulfonated copolymers present common high temperature (HT) fluid loss additives. Among them are for polymers based on 2-acrylamido methane propane sulfonic acid (AMPS[®]), *N*-vinylacetamide and acrylamide, or AMPS and *N,N*-dimethyl acrylamide.^{10,11–14} Their effectiveness is known to rely on adsorption on the surface of cement.¹⁵ A major drawback for these high molecular weight copolymers

($M_w > 1.5$ mio g/mol) is their excessive viscosifying effect. This is highly undesirable, because deep wells which exhibit ultra-high temperatures require increased slurry densities (>1.9 kg/L) to provide sufficient hydrostatic overburden pressure against the reservoir. Such cement slurries are characterized by low water and high cement content (water-to-cement ratio < 0.40). FLAs such as the aforementioned impart even more viscosity to those already highly viscous cement slurries which renders it extremely difficult to pump them over distances of e.g. 16 km. Consequently, substantial additions of dispersants are required to counteract this thickening effect. Such combinations are highly uneconomical and present a complex admixture system which is difficult to handle in the field.

Owed to the recent trend for constructing ultra-deep HT/HP wells, admixture technology suitable for those conditions is required. Relative to fluid loss additives, copolymers which exhibit stable performance at high temperature and possibly a dispersing effect are most desirable.

It is known that copolymerization provides an excellent way for the tailoring of macromolecules with specific chemical structures and for the control of properties such as hydrophilic/hydrophobic balances, rigidity, solubility, polarity, etc. These properties are regulated by the nature and distribution of the monomeric units along the copolymer chains and depend on the physico-chemical properties of the co-monomers used.^{16,17} Here, highly anionic AMPS-NNDMA-AA terpolymer blocks were grafted onto a humic acid backbone with tailor-made co-monomer composition that involves a significant amount of pronounced hydrophilic AMPS and acrylic acid monomers which produce flexible units and ionize completely in aqueous solution, in contrast to the less polar NNDMA monomer which renders the polymer chain more rigid and less hydrophilic as a result of the steric effect induced by the CH_3 groups linked to the amide. On the basis of this concept, a dispersing fluid loss additive was designed, synthesized and characterized. Its performance in oil well cement slurries was compared to that of a viscosifying graft copolymer presented in an earlier article.¹⁸

Exceptional temperature stability was probed by performance testing at 200°C , and the influence of the specific graft chains on the flow behavior of cement was established. In addition, its working mechanism was verified from filter cake permeability, adsorption, and zeta potential measurements.

EXPERIMENTAL SECTION

Materials

Oil Well Cement. An API Class G oil well cement ("black label" from Dyckerhoff AG, Wiesbaden, Germany) corresponding to American Petroleum Institute (API) Specification 10A was used.¹⁹ Its clinker composition was determined through powder Q-XRD technique using *Rietveld* refinement (Table I). The amounts of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and hemi-hydrate ($\text{CaSO}_4 \cdot 0.5 \cdot \text{H}_2\text{O}$) were measured by thermogravimetry. Free lime (CaO) was quantified following the extraction method established by *Franke*.²⁰ The specific surface area was determined using a Blaine instrument (Toni Technik, Berlin, Germany), and the specific density was measured by helium

Table I. Phase Composition (XRD, *Rietveld*), Specific Density, Specific Surface Area (*Blaine*), and d_{50} Value of API Class G Oil Well Cement Sample

C_3S (wt %)	59.6
C_2S (wt %)	22.8
C_3A_c (wt %)	1.2
C_4AF (wt %)	13.0
Free CaO (wt %)	< 0.3
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (wt %)	2.7 ^a
$\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$ (wt %)	0.0 ^a
CaSO_4 (wt %)	0.7
specific density (kg/L)	3.18
Specific surface area (cm^2/g)	3058
d_{50} value (μm)	11

C_3S : tricalcium silicate ($\text{Ca}_3(\text{SiO}_4)\text{O}$); C_2S : dicalcium silicate (Ca_2SiO_4); C_3A_c : cubic modification of tricalcium aluminate ($\text{Ca}_9\text{Al}_6\text{O}_{18}$); C_4AF : tetra calcium aluminate ferrite ($\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$).

^aMeasured by thermogravimetry.

pycnometry (Quantachrome Instruments, Boynton Beach, FL). The average particle size (d_{50} value) was obtained using a laser granulometer (1064 instrument from Cilas, Marseille, France).

Silica Flour. A commercial sample of silica flour (SSA-1 from Halliburton GmbH, Celle, Germany) containing (wt %) quartz 97.60, CaO 0.57, MgO 0.18, Al_2O_3 0.17, TiO_2 0.06 (determined by X-ray fluorescence) and LOI 1.40 was used. Its specific surface area (*Blaine method*) was $1857 \text{ cm}^2/\text{g}$, while the average particle size (d_{50} value) was $32.7 \mu\text{m}$. Specific density of the silica flour was found to be 2.65 kg/L .

Synthesis of the Dispersing Graft Copolymer. The humic acid graft copolymer was prepared by grafting AMPS, NNDMA, and AA onto a humic acid backbone via aqueous free radical copolymerization using sodium persulfate as initiator. In a typical experiment, 117 mL of a 14.5 wt % aqueous solution of commercial potassium humate (HA 2 from Borregaard Lignotech, Sarpsborg, Norway) and 160 mL of DI water were placed in a 1-L four-necked flask equipped with stirrer, thermometer, and N_2 inlet. The pH of the solution which initially was 9.2 was adjusted to 12 by feeding of 13.5 g of sodium hydroxide pellets into the flask. Next, in this order: 50 g of AMPS (2404 monomer from Lubrizol, Rouen, France), 15 g of NNDMA (Sigma-Aldrich, Munich, Germany), 1.2 g of acrylic acid (Merck KGaA, Darmstadt, Germany), 0.30 g of EDTA (Sigma-Aldrich, Munich, Germany), and 1 g of defoamer (TEGO ANTIFOAM MR 2123, an organo-modified polysiloxane from Evonik Goldschmidt GmbH, Essen, Germany) were added to the solution of potassium humate. The feed molar ratios of AMPS, NNDMA, and AA were $1 : 0.63 : 0.07$, and the weight ratio between backbone and graft chain was $20 : 80$. While stirring, nitrogen gas was bubbled through the solution for 1 h. Then, the temperature was increased to 50°C and the first amount of $\text{Na}_2\text{S}_2\text{O}_8$ initiator (4.0 g) was added. After 50 min of reaction time, the second portion of the initiator (4.0 g) was added. Grafting was continued for another 70 min, while the temperature was increased to 60°C . There, the mixture was left to react for an additional

hour before the temperature was again increased to 80°C for another hour to complete the reaction. Finally, the liquid was cooled to room temperature and the reaction was quenched by addition of 4.8 g sodium pyrosulfite ($\text{Na}_2\text{S}_2\text{O}_5$). The product yields a dark, viscous, odorless liquid which was diluted with 300 mL of DI water. Thus, a dark brown, 14 wt % aqueous solution possessing low viscosity and a pH value of 7.0 was obtained. The characteristic properties of the graft copolymer are summarized in Table III.

Synthesis of a Comparative Graft Copolymer. For comparison, a viscifying graft copolymer possessing a similar molecular weight as the dispersing graft copolymer, but a different monomer composition was synthesized following the same procedure as described in a previous article for a viscifying graft copolymer.¹⁸ In the present preparation, the same feed molar ratios of AMPS, NNDMA, and AA of 1 : 1.46 : 0.07 as used for the previous viscifying graft copolymer were used (50 g of AMPS, 35 g of NNDMA, and 1.2 g of AA). Also, the weight ratio between the humic acid backbone and the graft chain was kept constant at a weight ratio of 20 : 80. In the preparation, nitrogen gas was bubbled through the stirred solution for 1 h after the flask has been charged with the monomers, sodium hydroxide, EDTA, and defoamer, as presented in Ref. 18. Next, temperature was increased to 60°C and the first amount of $\text{Na}_2\text{S}_2\text{O}_8$ initiator (20.8 g) was added. After 50 min of reaction time, the second portion of the initiator (20.8 g) was added accordingly. Grafting was continued for another 70 min while the temperature was increased to 70°C. There, the mixture was left to react for an additional hour before the temperature was again increased to 80°C for another hour to complete the reaction. Finally, the liquid was cooled to room temperature and the reaction was quenched by addition of 6.25 g of sodium pyrosulfite ($\text{Na}_2\text{S}_2\text{O}_5$). The product yields a dark, highly viscous, odorless liquid which was diluted with 300 mL of DI water to obtain a dark brown, 7.3 wt % aqueous solution with a pH value of 4.0. The characteristic properties of this graft copolymer are summarized in Table III.

Cement Retarder. A commercial sample, HR[®]-25 from Halliburton GmbH, Celle, Germany containing tartaric acid was used.

Instruments and Procedures

Q-XRD was performed on a Bruker axis D8 Advance instrument (Bruker, Karlsruhe, Germany) with Bragg-Bretano geometry using Cu K_α ($\lambda = 1.5406 \text{ \AA}$) radiation and using Topas 3.0 software. X-ray fluorescence was performed on a spectrometer from PANalytical, Almelo, NL.

For size-exclusion chromatographic (SEC) analysis, a Waters Alliance 2695 (Waters, Eschborn, Germany) separation module equipped with RI detector 2414 (Waters) and an 18 angle dynamic light scattering detector (Dawn EOS, Wyatt Technologies, Clinton, IA) was used. The polymer was separated on a precolumn and two Aquagel-OH 60 columns (Polymer Laboratories, distributed by Varian, Darmstadt, Germany). Aqueous 0.2M NaNO_3 solution (pH 9 w/50 wt % aqueous NaOH) was used as eluant (flow rate 1.0 mL/min). A d_n/d_c value of 0.156 mL/g (value for polyacrylamide²¹) was used for calculation of M_w and M_n . The specific anionic charge amounts of the

polymers were determined in DI water, 0.1M NaOH (pH 13) and cement pore solution (CPS), using a PCD 03 pH apparatus (BTG Müttek GmbH, Herrsching, Germany). Cement pore solution was freshly prepared by vacuum filtration of neat API Class G cement slurry (w/c ratio 0.44). Charge titration was carried out according to a literature description.²²

Cement slurries were prepared in accordance with the procedures set forth in *Recommended Practice for Testing Well Cements*, API Recommended Practice 10B, issued by the American Petroleum Institute, using API Class G oil well cement and deionized water. At first, cement was dry blended with SSA-1 silica flour at a weight ratio of 65 : 35. This blend was mixed with DI water at a water-to-cement (w/c) ratio of 0.48 and a water-to-solids (w/s) ratio of 0.31 (solids = cement + silica) using a blade-type laboratory blender manufactured by Waring Products (Torrington, CT). In general, the graft copolymer solution was added to the mixing water while powdery HR-25 retarder was dry blended with cement.

Rheology of the slurries was determined on a FANN 35SA (Fann Instruments Company, Houston, TX) rotational viscometer, equipped with RI rotor sleeve, B1 bob and F1 torsion spring. HTHP thickening times of cement slurries were measured at 200°C under 400 bar pressure using a consistometer model 8240 (Ametek Chandler Engineering, Broken Arrow, OK). After mixing, the slurries were poured into the HTHP consistometer cell and the time to reach 70 Bc (Bearden unit of consistency) was designated as cement slurry thickening time. Stirred cement fluid loss was measured at 200 C using an HTHP stirred fluid loss cell (model 7120 from Chandler Engineering, Tulsa, OK) following a norm issued by the American Petroleum Institute (API).²³

Adsorbed amounts of admixtures were determined from the cement filtrate collected in the respective fluid loss test applying the depletion method, i.e. it was assumed that the decrease in the polymer concentration before and after contact with cement solely resulted from interaction with cement. This assumption was confirmed through a solubility test of the admixtures in cement pore solution over 3 days. No precipitation was observed. A High TOC II apparatus (Elementar, Hanau, Germany) equipped with a CO_2 detector was used for quantification of the carbon content present in the filtrated solutions. Quantification of adsorbed amounts of the individual polymers was done by using the nitrogen content as a marker for the graft copolymer and the difference between the nitrogen content and the TOC value for quantification of the retarder.

Zeta potential measurement was performed at room temperature on an electro acoustic spectrometer (DT-1200 from Dispersion Technology, Bedford Hills, NY) using the cement slurry (w/c ratio of 0.48) mixed according to API RP 10B procedure, except that no homogenization was carried out in the atmospheric consistometer.

RESULTS AND DISCUSSION

Polymer Characterization

The free radical copolymerization process used here produces a relatively homogeneous graft copolymer which exhibits a polydispersity index of ~ 2.4 (see SEC diagram in Figure 1). From

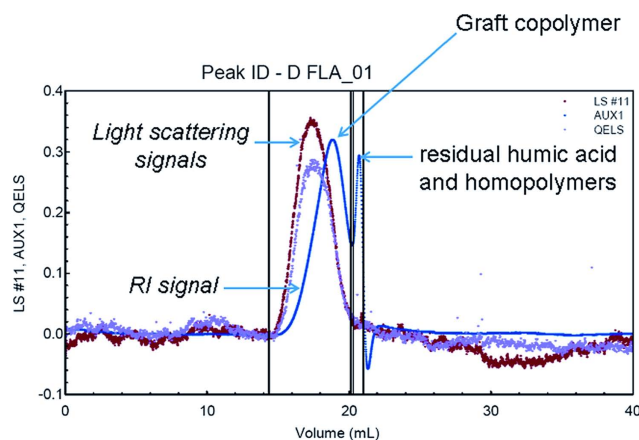


Figure 1. Size-exclusion chromatogram of the graft copolymer as obtained from synthesis. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

SEC data, a turnover rate for the monomers of 83% was calculated, indicating an incomplete reaction.

Next, chemical composition of the graft copolymer (prepared from AMPS: NNDMA: AA at a molar ratio of 1 : 0.63 : 0.07) was determined. Elemental analysis of the purified copolymer confirmed successful incorporation of S and N containing monomers into the graft copolymer (see Table II). According to this data, 92.94 wt % of AMPS, 45.83 wt % of NNDMA, and 39.53 wt % of AA were incorporated. This suggests a molar ratio of 1 : 0.31 : 0.03 for the graft chain which differs from the feed molar ratio of 1 : 0.63 : 0.07. The difference is explained by the fact that AMPS and NNDMA exhibit alternating polar factors (AMPS: $Q_e = 0.39$, 0.22; NNDMA: $Q_e = 0.41$, -0.26) and thus tend to polymerize at a 2 : 1 molar ratio. Whereas acrylic acid, due to its similar Q and e values (0.82, 0.81) tends to preferentially undergo homopolymerization.²⁴ On the basis of this analysis, a chemical structure is proposed for the graft copolymer (Figure 2).

Molecular properties of the synthesized dispersing graft copolymer were determined by SEC (Table III). A comparison of its properties with those of a viscosifying graft copolymer composed of AMPS:NNDMA:AA at a molar ratio of 1 : 1.54 : 0.02 prepared according to a literature description¹⁸ revealed that the dispersing graft copolymer which is characterized by a significantly lower NNDMA content exhibits much lower molecular weights (e.g. M_w : 323,200 vs. 577,400 Da). Consequently, the *Brookfield* viscosity of its aqueous solution is significantly lower than that of the viscosifying graft copolymer.

In cement pore solution, the specific anionic charge amount of the graft copolymer was found to be 3545 $\mu\text{eq/g}$ which indicates a strongly anionic additive as a result of the large number of carboxylate, sulfonate, and phenolate functionalities. For comparison, the viscosifying graft copolymer prepared according to¹⁸ exhibits a slightly higher anionic charge of 3826 $\mu\text{eq/g}$.

Fluid Loss Control Performance

To determine the effectiveness of the graft copolymer for fluid loss control, dynamic filtration properties of cement/silica flour slurries (slurry density 1.94 kg/L) containing increased dosages

(0.4–1.8 % bwoc) of the graft copolymer at a fixed addition of 2.0% bwoc of HR[®]-25 retarder were measured at 200°C under stirring condition. The results are exhibited in Figure 3.

In general, API fluid loss values decrease exponentially with increasing graft copolymer dosage. The minimum concentration of FLA needed to achieve an API fluid loss value of below 100 mL/30 min lies at 1.0% bwoc. This value represents a relatively low dosage, considering the harsh temperature conditions. The data confirms high effectiveness of the dispersing graft copolymer in fluid loss control application under the very severe condition of 200°C.

Dispersing Property

Rheology of cement/silica slurries containing the dispersing and the viscosifying graft copolymer, and of a commercial lignite-based graft copolymer manufactured according to a patent description²⁵ (HALAD[®]-413 from Halliburton GmbH, Celle, Germany) were compared at 95°C. At this temperature, no addition of HR[®]-25 retarder was required, thus the values indicate the effect of individual polymers. The results are displayed in Table IV. The graft copolymer exhibits remarkable cement dispersion with increased dosages, while addition of the viscosifying graft copolymer results in excessively high viscosity values which are unacceptable for field use. Thus, the viscosifying polymer relies on combination with a dispersant to facilitate its field application. In addition, a comparison with the lignite-based commercial graft copolymer shows that the latter also possesses a viscosifying effect. This data confirms the novelty of the graft copolymer describe here.

One might speculate whether the different behaviors of the new dispersing and the previous viscosifying graft copolymer are solely owed to their different molecular weights which are presented in Table III. For clarification, a modified viscosifying graft copolymer was synthesized as comparative polymer following exactly the description used for preparation of the previous viscosifying polymer,¹⁸ except that a higher initiator dosage and an increased temperature (60–70°C) were used to obtain a polymer with a M_w of ~ 331 kDa which was comparable to that of the dispersing graft copolymer (~ 323 kDa), but much lower

Table II. Elemental Analysis Data for Graft Copolymer, Humic Acid, and Graft Chain

Elements	Graft copolymer found (%)	Humic acid found (%)	Graft copolymer calculated ^a (%)	Graft chain calculated ^b (%)
C	38.0	38.7	39.9	40.5
H	6.3	3.7	5.4	5.8
O	36.0	41.5	28.7	25.3
N	6.0	1.0	6.2	7.4
S	7.9	0.8	8.5	10.5
Na	1.9	0.5	8.5	10.5
K	1.2	13.8	2.8	–

Note: O content calculated as difference to 100%.

^aCalculation based on number of moles of monomers added. ^bCalculation based on weight proportion of monomers and humic acid added (80:20 wt %).

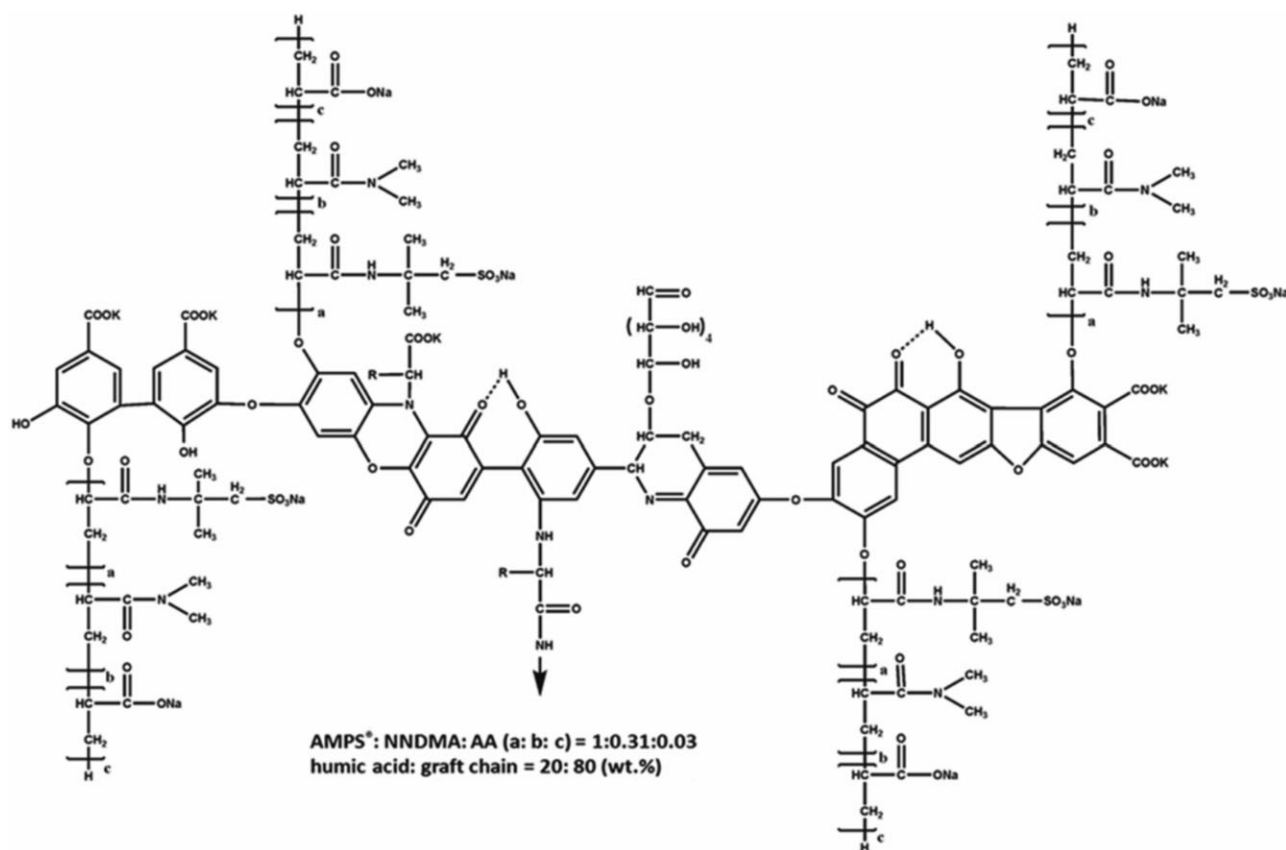


Figure 2. Proposed chemical structure of the synthesized graft copolymer.

than that of the previous viscosifying graft copolymer which exhibited an M_w of ~ 577 kDa (Table III).

Furthermore, rheological measurements of cement/silica slurries holding the modified viscosifying graft copolymer were performed, and the results were compared with those obtained from the dispersing and the high molecular weight viscosifying graft copolymer (Table IV). It was found that the modified graft copolymer, despite its molecular weight being comparable to that of the dispersing graft copolymer, still exhibited a very significant viscosifying effect. This result clearly signifies that the molar composition and the properties derived thereof present the key factor for the interaction of such graft copolymers with cement, and not the molecular weight.

We attribute the differences in the behaviors of the dispersing and the comparative graft copolymer to their distinctly different

molecular architectures and rigidity of the side chains. First, it is well established that in free radical copolymerization, higher initiator concentration and higher temperature result in shorter chain lengths. Hence, the comparative polymer can be expected to contain a higher number of shorter lateral chains, thus leading to a graft copolymer with significantly higher grafting density than the dispersing copolymer which possesses fewer, but longer side chains. A graphical sketch of the different architectures of the two graft copolymers is presented in Figure 4.

Another aspect which can impact the influence of both polymers on the rheology of cement slurries is the different conformational flexibility of their side chains. It is well established that a high AMPS content produces copolymer chains with a high degree of hydrophilicity and anionic character over a wide range of pH because of the strongly ionizable sulfonate group.

Table III. Characteristic Properties of Different Graft Copolymers and of Humic Acid, as Obtained from SEC

Polymers	M_w (g/mol)	M_n (g/mol)	PDI (M_w/M_n)	Brookfield ^a viscosity (mPa·s)
Dispersing graft copolymer	323,200	133,400	2.4	14
Viscosifying graft copolymer ^b	577,400	266,300	2.2	40
Comparative graft copolymer ^c	331,300	130,200	2.5	24
Humic acid	68,940	21,180	3.3	12

^aMeasured in 2.0 wt % aqueous solution @ 100 rpm using spindle no. H 1. ^bPrepared according to literature.¹⁸ ^cPrepared according to literature¹⁸ but at increased initiator dosage and temperature.

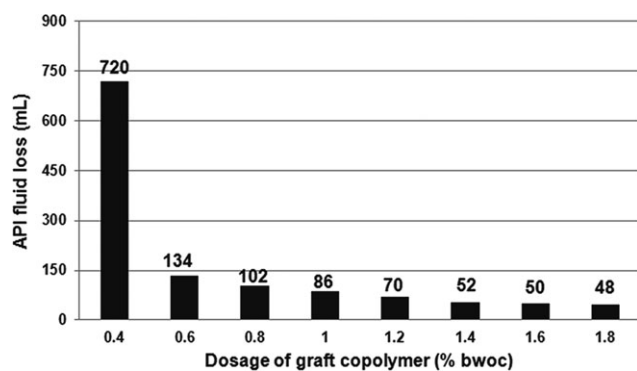


Figure 3. API fluid loss of Class G cement/silica (65 : 35% wt/wt) slurries containing increased dosages of graft copolymer and of 2.0% bwoc of HR-25 retarder, measured at 200°C and 70 bar differential pressure under stirred condition.

In addition, such lateral chains exhibit high conformational flexibility and coiling in aqueous solution. Whereas, high NNDMA contents produce relatively stiff polymer chains, as a result of dominant steric interaction between the amide CH_3 functionalities.²⁶ Hence, the comparative graft copolymer which possesses a very high amount of NNDMA in its side chains can be expected to present a rather rigid macromolecule, with stiff lateral chains attached to the main chain. Such conformation is favorable for generating a viscosifying effect in solution. In addition, it is known that polymer chains that are rich in NNDMA exhibit a strong water sorption and swelling behavior.²⁷ Contrary to this, the dispersing graft copolymer possesses highly flexible, dangling lateral chains because its main monomer component is AMPS and not NNDMA. As a result, this polymer cannot viscosify aqueous solutions and solid suspensions, as is also indicated by its significantly lower Brookfield viscosity (Table III). Instead, with its highly flexible lateral chains, it can easily anchor on multiple sites on the surface of hydrating cement and thus produce a dispersing effect.

All these observations allow to conclude that the specific molar composition of the lateral chains chosen here presents the very criteria for obtaining such dispersive graft copolymer.

Effect of Combined Retarder and Graft Copolymer on Rheology

In practical oil well cementing at bottom hole temperatures of 200°C, addition of sufficient amounts of HT-effective retarders is necessary to delay the set of cement sufficiently long to achieve a pumping time (cement thickening time as determined on the HT/HP consistometer) of at least 4 h. This was found to occur at a dosage of 2.0% bwoc of HR[®]-25 retarder.

In previous studies, it has been established that upon combination of one admixture with another, their functional properties can change drastically as a result of additive-additive interaction.^{28,29} To investigate such potential perturbation, the rheology of cement/silica slurries containing both the graft copolymer and HR[®]-25 retarder was examined. The results are presented in Table V. The data signifies that the presence of the retarder causes cement slurry viscosity to increase with increased graft

copolymer dosage. This trend is opposite to what was observed for the individual graft copolymer. It suggests that some interaction between both admixtures occurs, as was confirmed later. However, at dosages of 1.0–1.4% bwoc that present the dosage range of graft copolymer required to achieve a field practical cement fluid loss, rheology is still lower than for the viscosifying or the lignite-based copolymer. It is also sufficiently low to allow pumping of the slurry.

Working Mechanism of the Graft Copolymer

A series of experiments was devised to uncover the mechanism of this graft copolymer as fluid loss additive. First, the correlation between API fluid loss, filter cake permeability and dynamic filtrate viscosity as obtained at 200°C from slurries containing both the graft copolymer and HR[®]-25 retarder (2.0% bwoc) were established. The results are presented in Table VI. According to this data, the dynamic filtrate viscosity of the slurries is fairly independent of graft copolymer dosage. This means that filtrate viscosity has no significant impact on the fluid loss performance. Conversely, filter cake permeability decreases rapidly with dosage and a direct relationship with API fluid loss is apparent. For example, permeability decreases from 422 μD at 0.4 % graft copolymer dosage to $\sim 10 \mu\text{D}$ when $\geq 1.4\%$ of copolymer was added. At the same time, API fluid loss is reduced from 720 mL to ~ 50 mL/30 min (see Table VI). This signifies that the working mechanism of this graft copolymer relies on reduction of filter cake permeability.

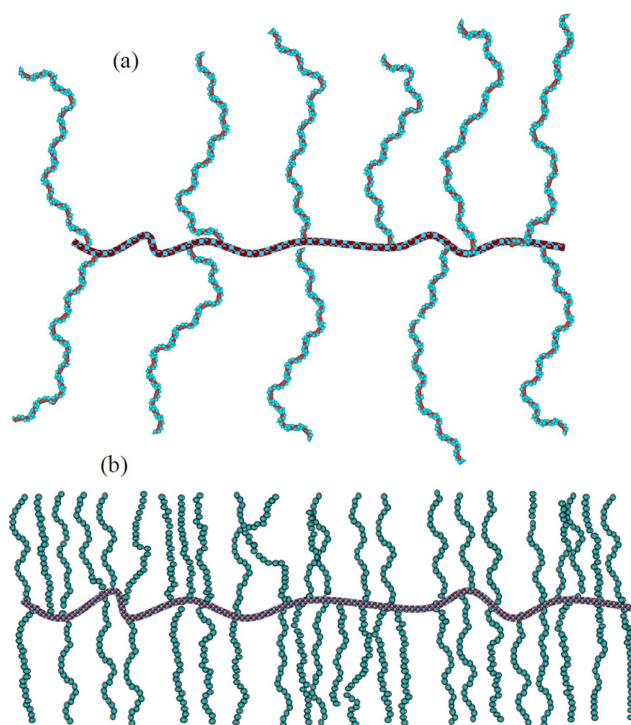


Figure 4. Illustration of molecular architectures of (a) dispersing graft copolymer possessing few and flexible side chains and (b) the comparative viscosifying copolymer possessing numerous and stiff lateral chains. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Rheology (Shear Stress) of API Class G Cement/Silica Slurries (w/c = 0.48) Containing Addition of Various Graft Copolymers, Measured at 95°C and at Different Shear Rates

Copolymer dosages (% bwoc)	Shear stress values (lbs/100 ft ²) @ 95°C at shear rate (rpm)					
	300	200	100	6	3	600
Dispersing graft copolymer ($M_w = 323,200$ Da)						
0.0	200	173	124	59	58	248
0.2	191	165	121	46	42	237
0.4	138	82	49	23	21	206
0.6	89	58	28	7	5	165
0.8	80	53	24	5	4	158
1.0	74	51	20	2	1	135
Viscosifying graft copolymer ($M_w = 577,400$ Da)						
0.2	172	132	98	30	28	265
0.4	160	124	84	38	33	272
0.6	>300	252	165	52	48	>300
0.8	>300	>300	200	64	57	>300
1.0	Too thick to test					
Lignite-based graft copolymer (HALAD [®] -413)						
0.2	224	181	161	43	32	>300
0.4	234	178	134	22	14	>300
0.6	>300	239	163	49	35	>300
0.8	>300	204	149	44	34	>300
1.0	280	201	125	37	25	>300
Comparative viscosifying graft copolymer ($M_w = 331,300$ Da)						
0.2	183	135	122	74	65	228
0.4	196	138	105	50	48	>300
0.6	>300	220	149	49	47	>300
0.8	>300	>300	>300	82	69	>300
1.0	Too thick to test					

Table V. Rheology (Shear Stress) of API Class G Cement/Silica Slurries (w/c = 0.48) Containing the Dispersing Graft Copolymer and 2.0% bwoc of HR[®]-25 Retarder, Measured at 95°C and at Different Shear Rates

Graft copolymer dosage (% bwoc)	Shear stress values (lbs/100 ft ²) @ 95°C at shear rate (rpm)					
	300	200	100	6	3	600
0.0	131	109	67	19	17	>300
0.4	150	83	41	4	3	>300
0.6	180	129	54	6	4	>300
0.8	259	144	68	8	6	>300
1.0	244	140	64	8	5	>300
1.2	>300	179	96	11	7	>300
1.4	>300	258	150	17	12	>300
1.6	>300	215	135	14	9	>300
1.8	>300	248	143	14	8	>300
Viscosifying graft copolymer according to ¹⁸						
0.2	Too thick to test					
0.4	Too thick to test					
Lignite-based graft copolymer according to Ref. 34						
1.0	>300	>300	250	29	16	>300

Table VI. API Fluid Loss, Dynamic Filtrate Viscosity, and Filtercake Permeability of API Class G Cement/Silica Slurries ($w/c = 0.48$) Containing Different Dosages of Dispersing Graft Copolymer and 2.0% bwoc of HR[®]-25 Retarder, Measured at 200°C

Graft copolymer dosage (% bwoc)	Dynamic filtrate viscosity (mPa s)	Filtercake permeability (μ D)	API fluidloss (mL)
0.4	0.30	422	720 ^a
0.6	0.31	52	134
0.8	0.31	33	102
1.0	0.32	24	86
1.2	0.32	16	70
1.4	0.33	9	50
1.6	0.36	9	52
1.8	0.37	8	48

^aDehydration of cement slurry in less than 30 min.

To investigate the reason behind the reduced filter cake permeability, adsorption of the graft copolymer and of the retarder on the cement/silica solids was investigated.

Adsorption Behavior

Since the graft copolymer is an anionic polyelectrolyte with dispersing property, it was speculated that this graft copolymer may function by adsorption on cement, as has been demonstrated before for AMPS-based copolymers.¹⁵ Thus, the adsorbed amounts of the graft copolymer and of the retarder in the combination were analyzed. The results are displayed in Figure 5. In general, the adsorbed amount of the graft copolymer increases almost linearly. No saturation plateau (complete surface coverage) is achieved at the dosages tested. This signifies strong electrostatic attraction of this highly anionic polymer on the positive surface of cement. Another observation from Figure 5 is that the adsorbed amount of the copolymer still increases even when API fluid loss remains stable at ~ 50 mL (see Figure 3). This effect can be explained as follows: API filtrates of < 50 mL/30 min are produced by dehydration of the first layers of the cement filter cake. Release of this “spurt loss” is always necessary to produce a tight filter cake. Thus, continued adsorption beyond the dosage of 1.4% does not contradict the working mechanism by adsorption.

Conversely, the working mechanism of the retarder was found to rely on precipitation from cement pore solution. Precipita-

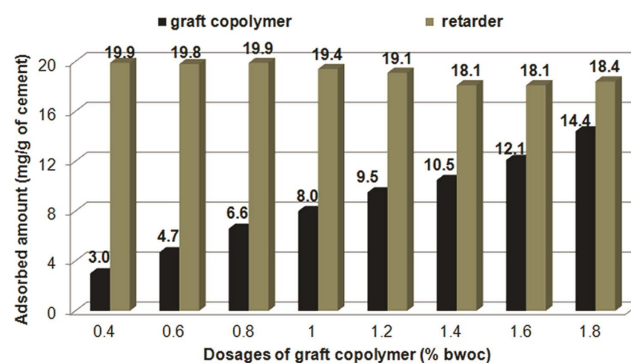


Figure 5. Adsorption of graft copolymer and of HR-25 retarder (dosage: 2.0% bwoc), measured from cement filtrates collected at 200°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tion (plausibly of calcium tartrate) occurred almost instantaneously when HR-25 retarder was added to cement pore solution. At retarder dosages up to 1.2% bwoc, the amount precipitated was quite constant (19–20 mg/g cement) and independent of graft copolymer dosage. Above this concentration, the retained amount of retarder decreased by ~ 1 mg/g of cement. This effect is owed to partial co-precipitation of the retarder and the graft copolymer, as was confirmed by a decreased total organic nitrogen (TON) content of unadsorbed graft copolymer in presence and absence of the retarder (see Table VII). There, it was found that at graft copolymer dosages above 1.0 % bwoc, significant co-precipitation of the unadsorbed graft copolymer with the retarder occurs.

At 200°C, an adsorptive working mechanism of the graft copolymer appears to be almost impossible because ettringite, a cement hydrate formed from tricalcium aluminate and calcium sulfate present in cement, presents the main mineral for adsorption of anionic admixtures [9]. However, ettringite is known to be stable only at temperatures up to $\sim 80^\circ\text{C}$ to 115°C .^{30–33} Thus, it is practically absent at 200°C as was evidenced by XRD patterns obtained from dry cement/silica specimens cured at 200°C (XRD diagrams not shown here). Apparently, the graft copolymer adsorbs onto other hydrate phases formed under the hydrothermal conditions existing at 200°C. The specifics of this mineralization process and its consequences for the anchoring possibilities of anionic polyelectrolytes will be the subject of another study.

Table VII. Co-precipitation of HR[®]-25 Retarder and of Graft Copolymer in Cement Pore Solution Derived From TON Measurement

Graft copolymer dosage (% bwoc)	TON ^a of graft copolymer only (mg/L)	TON of graft copolymer in presence of HR [®] -25 retarder (mg/L)	Reduction in TON ^a content (mg/L)	Reduction in graft copolymer concentration (%)
0.8	743	715	28	3.9
1.0	1054	960	94	9.8
1.2	1190	936	254	27.1

^aTON means total organic nitrogen concentration in supernatant.

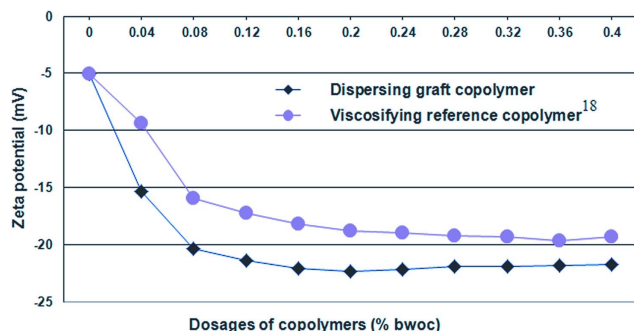


Figure 6. Zeta potentials of cement/silica slurries ($w/c = 0.48$) with added graft copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Electro Kinetic Properties

The zeta potentials of cement/silica slurries titrated with individual dispersing and viscosifying graft copolymer solutions are displayed in Figure 6. The neat cement slurry (no polymer present) exhibits a charge of -5 mV. Stepwise addition of the anionic graft copolymers further decreases the charge to more negative potentials until a point of saturation is achieved. The dispersing graft copolymer shows more pronounced negative zeta potentials than the viscosifying graft copolymer. Thus, it induces a higher electrostatic repulsion between the cement particles. This behavior explains its superior capability to dis-agglomerate cement particles. The curves confirm the adsorptive mechanism for the graft copolymer. Apparently, with increased polymer dosage, more and more of the FLA is loaded onto the surface of cement until a state of saturation (adsorption equilibrium) is reached. There, the zeta potential attains a constant value.

CONCLUSION

A humic acid-(AMPS-*co*-NNDMA-*co*-AA) graft copolymer that presents a dispersing cement fluid loss additive has been synthesized using aqueous free radical copolymerization. It reduces cement fluid loss effectively, even at temperatures as high as 200°C . A low NNDMA and high AA content provides dispersing properties to this polymer which are most advantageous when formulating cement slurries of high density as required on ultra-deep wells. Its working mechanism was found to rely on reduction of filtercake permeability which is achieved by adsorption of the graft copolymer on cement and possibly silica particles. Adsorption was confirmed by TOC and zeta potential measurements. Apparently, this adsorptive anchoring of the graft copolymer is hardly affected by temperature. Through this mechanism, the copolymer constricts the pores of the filtercake and thus reduces the loss of water from the cement slurry.

The study shows that cement additives such as the graft copolymer described here can be engineered to make them suitable for high density cement slurries required on ultra-high temperature high pressure wells possessing particularly low water to cement ratios. Here, the tailored composition of the lateral chains contained in the graft copolymer translates into a specific molecular

architecture and conformational behavior which provides the desired dispersing effect. As the oil industry in their quest to explore the crude oil resources for the next decades is venturing into ever deeper reservoirs, more of such additives will be required and the performance envelope needs to be pushed to withstand temperatures even as high as 260°C .

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