



Synthesis and evaluation of a novel clean hydraulic fracturing fluid based on star-dendritic polymer



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ABSTRACT

This paper presents a novel clean hydraulic fracturing fluid using a star-dendritic polymer as thickening agent. The star-dendritic polymer consists of two components, a core and the beams. The core was prepared from the thioxanthone (TX) and the polyamidoamine (PAMAM) by a divergent synthesis procedure using the reagent excess method starting from ethylenediamine (EDA). Then the photo-polymerization process was carried out to make the PAMAM-8-TX and monomers reacts. After the synthesis, the dendrimer star polyacrylamide (DSPAM) was characterized by several tests to classify the monomers involved in the reaction and the architecture of the polymer. The results show that the DSPAM is in star-shaped.

The hydraulic fracturing fluid formulation was designed using the DSPAM as thickening agent. For the purpose of evaluating the performance of the new fracturing fluid, shear resistance, thermal stability, rheology property, viscoelasticity, proppant transportation and breaking ability were tested by several experiments. The results show that the fracturing fluid has an excellent shear resistance under high temperature. The apparent viscosity remains 140 mPa s after 2hr shearing when the testing temperatures are 90 °C and 140 °C. So the fracturing fluid has an acceptable thermal stability. The static proppant sedimentation velocity is from 0.038 cm/min–0.095 cm/min when the testing temperatures are 60 °C and 90 °C. The sedimentation velocity increases with the rising temperature when the sand proportion remains constant. In addition, the increasing of sand proportion could cut short the time of proppant settlement. The residual contents after breaking are hardly measured in various testing temperatures. A star-dendritic polymer was synthesized as a novel fracturing fluid thickening agent. The properties are acceptable to meet the requirement as the thickening agent due to the thermal resistance, shear resistance and proppant carrying ability of the fracturing fluid are quite effective in hydraulic fracturing treatment.

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1. Introduction

Hydraulic fracturing is the most effective way to recover the gas and oil from ultra-low permeability reservoirs and is a widely applied stimulation technique (Guo et al., 2015). In hydraulic

fracturing treatments, the fracturing fluid plays a key role as the agent to transfer the pressure and energy from surface to subsurface for the purpose to initiate a crack in the formation. With the development of hydraulic fracturing technique, the guar solutions has become the most common fracturing fluid. However, the drawbacks of them have been perceived such as the limited temperature range and the residuals after breaking (De Kruijff et al., 1993).

The modified guar solutions have been presented to overcome

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the disadvantages. The low molecular weight fracturing fluid based on modified guar without internal breakers has the stable and robust rheology property (Weaver et al., 2002). A novel hydrophobic modified guar has been synthesized. The grafted derivative is evaluated for hydraulic fracturing fluid by compared the viscosity with the carboxymethyl and carboxymethylhydroxypropyl guar gum (Bahamdan, 2005). A new thermal resistance fracturing fluid system has been adopted the carboxymethylhydroxypropyl guar gum as thickening agent and zirconium as crosslinker. This fracturing fluid could work under the temperature from 148 °C to 176 °C (Kalgaonkar et al., 2012).

Although the modified guar gum has a better performance, the increased cost will be another issue. The researchers focus on synthesizing the polymer using polyacrylamide (PAM) or polyvinyl alcohol (PVA) since the polymer based fracturing fluid has the better performance compared with guar gum base fluid. A polymer fracturing fluid has been polymerized by acrylic acid (AA), acrylamide (AM) and 2-acrylamide-2-methylpropanesulfonic acid (AMPS) (Funkhouser et al., 2003, 2010; Jeremy and Gary, 2009). It could be applied in 232 °C circumstance. A new thickening agent synthesized from AM, AMPS and certain amount of vinyl phosphate has been added which could be used in 176 °C formation (Carman and Gupta, 2011). A novel clean fracturing fluid using viscoelastic surfactant (VES) as thickening agent has been presented by Schlumberger (Samuel et al., 2000). There are many advantages of VES fracturing fluid such as no residuals, no insoluble substances and high capability of proppant transportation, however, the poor thermal resistance is still an issue when applying it in the field (Yang et al., 2013; Khair et al., 2011a,b; Sullivan et al., 2006). In recent years, many researchers agree that the hydrophobic associated polymer becomes more and more capable as the thickening agent in fracturing fluid formulation (Carman and Gupta, 2011; Gupta et al., 2012; Gupta et al., 2011a,b; Gupta, 2011). The hybrid fracturing fluid composed with VES and hydrophobic associated polymer has been studied to modify the thermal resistance of VES fracturing fluid (Eoff and Others, 2011; Shaefer et al., 2011; Gupta et al. b; Philippova and Khokhlov, 2010).

There are many shortcomings of the guar gel fracturing fluid, the polymer fracturing fluid and VES fracturing fluid according to the previous literature review. For instance, the relatively poor shear resistance and high cost. Many scholars have introduced the star-dendritic polymer which has the better shear resistance property. This polymer has been applied in the enhanced oil recovery and lubricant (Xue et al., 2005; Covitch, 1998; Ver Strate et al., 1986; Kiovsky, 1979). However, it is found that few research works on the star-dendritic polymer as the thickening agent in fracturing fluid formulation were published. In this paper, the authors have synthesized a new star-shaped polymer and carried out a series tests to characterize the architecture of it. Then a fracturing fluid formulation based on the new polymer has been presented. At last, the shear resistance, rheology property, viscoelasticity, proppant transportation ability and breaking ability have been tested in this study to prove the capability of this star-dendritic polymer as the thickening agent of fracturing fluid.

2. Synthesis methodology

2.1. DSPAM synthesis

This new dendritic polymer consists of two major components, a core and the beams, as shown in Fig. 1.

The core of the star-shaped polyacrylamide is a water soluble initiator: thioxanthone modified polyamidoamine (TX-PAMAM) which prepared from the thioxanthone (TX) and the polyamidoamine (PAMAM).

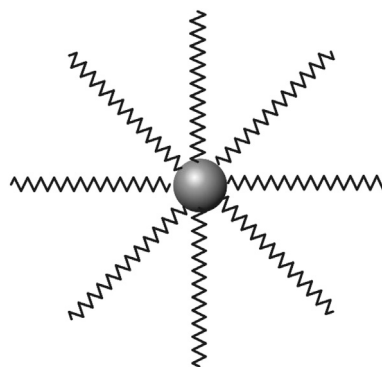


Fig. 1. The demonstration of the structure of this new star-shaped polyacrylamide.

The PAMAM was selected as the initiator due to its molecular structure and synthesis mechanism were relatively simple in contrast with others. Besides the PAMAM has a higher aqueous solubility than the other initiators, such as the polypropyleneimine (Jiang and Yin, 2004a,b). It was prepared by a divergent synthesis procedure using the reagent excess method starting from ethylenediamine (EDA). The reiteration of this procedure relates to the generation of the dendrimer, which means the G1 polymer has eight terminal amino groups (Peterson et al., 2001). In our study, the 2-epoxy-thioxanthone (2-EP-TX) was used as the photoinitiator radical to modify the PAMAM. If eight 2-P-TXs reacted with one G1 PAMAM, the PAMAM-8-TX would be generated. In this paper, the reaction mechanism of the synthesis of PAMAM-8-TX is as the same as the synthesis of DAB-4-TXOC since the reaction radicals are the same (Jiang et al., 2005a).

Then the photopolymerization process was carried out. The PAMAM-8-TX and monomers, includes acrylamide (AM), 2-acrylamide-2-methyl propyl sulfonic acid (AMPS) and 2-methacryloyloxyethyl-dimethyle-n-dodecylammoniumbromide (DMDA), were dissolved in the distilled water in certain concentrations (Ye and Huang, 1998). The solution was exposed in the condition of ultraviolet light for at least 0.5hr so the TX groups were activated into triplet state and the free radicals would cause the copolymerize or homopolymerize with the monomer units to generate the dendrimer-star polyacrylamide (DSPAM). After the reaction, the product was dried in the oven and cut into fine powders for the next step. The principle of chemical reaction and the total work flow are as shown in Fig. 2 (a) (Corrales et al., 2006) and Fig. 2 (b) (Jiang et al., 2005a; Jiang and Yin, 2004b), respectively.

2.2. Polymer characterization

The characterization process needs to be performed to classify the monomers involved in the reaction and the architecture of the DSPAM.

The image of infra-red spectrum of DSPAM is as shown in Fig. 3. It was recorded by Beijing Ruili WQF-520 Fourier Transform Infrared Spectroscopy (FTIR) spectrometer. The samples were prepared as KBr disc. According to the IR result, the inflection points of the curve represent that diverse characteristic groups includes $-\text{SO}_3\text{H}$ (1172 cm^{-1}), $-\text{CH}_3$ (1454 cm^{-1}), and the quaternary ammonium salt (945 cm^{-1}) and so on exist on the structure of DSPAM. This means the AM, AMPS and DMDA have taken participate in the formulating of DSPAM.

Fig. 4 shows the image of ultraviolet (UV) spectrum. It was recorded in CHCl_3 and H_2O solution (the concentration is $5.0 \times 10^{-5}\text{ mol/L}$ in terms of DSPAM) by Shimadzu UV-1800

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