Study on synthesis and properties of nano-organic boron cross-linked agent

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Abstract. In this paper, the surface modification of nanoparticles was done, and the organic boron crosslinking agent KB-2 was modified on the surface, and a kind of nano-organic boron crosslinking agent was prepared, and the performance evaluation was carried out. The experimental results show that the viscosity of the nano-material and guar gum is more than 70mPAs at 150 ℃ because of its tight net structure. Because nanoparticles can effectively increase the elastic modulus of the system and increase the carrying capacity, the damage rate of nano-organic boron cross-linking agent is 15.12%, lower than that of organic boron cross-linking agent 20%.

1. Introduction

Water based fracturing fluid is a dispersed medium with water, adding various treatment agents, especially water soluble polymers, to form a working fluid with strong comprehensive properties required for fracturing processes. The aqueous solution of a general water-soluble polymer and additive is called linear glue or viscous water fracturing fluid. When the linear adhesive is added to the crosslinking agent, it will form a viscoelastic crosslinked jelly, and the crosslinked jelly has some solid properties, but it can flow under certain displacement and pressure. The water-based fracturing fluid is widely used for its safety, cleanliness and easy to control its properties by additive. In addition to a very small number of particularly sensitive formations, water-based fracturing fluids can be applied almost to all oil and gas reservoirs and are the fastest developing and comprehensive system for fracturing fluid technology. Compared with the linear gel fracturing fluid, the cross-linked gel fracturing fluid it shows stronger viscoelasticity and plasticity, so it is better than linear gel fracturing fluid in hydraulic fracturing and sand carrying capacity, but it is more difficult to reduce viscosity, and the damage will be worse than linear gum [1].

The rheological properties of crosslinked gel fracturing fluids are influenced by many factors, such as crosslinking degree, temperature, shear rate and fluid formulation, so it is important to develop intelligent, efficient and low-cost cross-linking agents[2]. Inorganic boron cross-linking agent temperature is generally under 95 ℃, there are non-toxic, easy crosslinking, cheap, easy to break the rubber, residue and so on, but there is a fast crosslinking speed, pipe flow friction high, temperature resistance of the shortcomings, so its application in High-temperature deep well is limited. The organic boron crosslinking agent has high temperature resistance, good shearing resistance, delayed crosslinking (up to 3min), strong sand-carrying property, complete breaking gum, high return rate and low damage
to reservoir permeability. With the wide application of nanotechnology in oil and gas exploration and development, nano-materials can significantly reduce the dosage of thickener in water based fracturing fluids[3-5]. Nano-gel usually refers to a physical or chemically cross-linked polymer network composed of hydrogel particles, it is a nanometer scale water dispersion.

According to the formation of the chemical bond, gel is divided into two kinds: a chemical gel (polymer gel), the gel is cross-linked by the covalent bond formed by the three-dimensional network structure, the other is a physical gel, is a non-covalent bond formed by three-dimensional network structure.

In this paper, the surface modification of nanoparticles was done, and the organic boron crosslinking agent KB-2 was modified on the surface, and a kind of nano-organic boron crosslinking agent was prepared, and the performance evaluation was carried out.

2 experimental Ones

2.1 Reagents and instruments
Electronic balance: Sense quantity 0.001g; Stirrer: Wu Yin mixer; constant temperature water bath pot: precision ±1℃; Viscometer: six-speed rotating viscometer, RS6000 rheometer, pulse permeability tester.

Hydroxypropyl guar Gum (Kunshan), nano-silica (tin-line new material), KB-2 (China Petroleum Exploration Institute fracturing Center).

2.2 Experimental principle and preparation method

![Fig.1 Synthesis of nano-organic boron crosslinking agent](image)

By using the amine-containing silane coupling agent KH550 as the carrier, the water dispersed nano-crosslinking agent of surface modified boron was prepared by KB-2 as modifier, which can be dispersed rapidly under normal temperature and pressure.
Fig. 2 is a schematic diagram of the action of nanometer crosslinking agent and guanidine gum, which shows that the action of nanometer crosslinking agent and guanidine gum can form large and compact reticular structure. This is mainly because a large amount of boric acid on the surface of nanometer silica can be bonded with the adjacent cis-hydroxy hydroxyl group on the gum polymer chain, and the nanometer crosslinking agent has a larger spatial size. It is more easy to form intermolecular cross-linking with guanidine gum. In addition, the carrier nano-silica to the guanidine gum solution has a slight thickening effect, this means that nano-silica can be to a certain extent with guanidine gum polymer formation of hydrogen bonds, due to spatial steric resistance, only a small part of nano-silica surface hydroxyl and guanidine effect. It can be concluded that the gel formed by crosslinking of Nano-crosslinking agent has higher strength due to (1) The nanometer crosslinking agent has larger space size, the surface loads a lot of boron group, which is advantageous to the formation of intermolecular cross-linking. (2) The hydroxyl group on the surface of nanometer silica can be bonded with guanidine gum. (3) Nanometer silica can be used as the skeleton of the network structure of the crosslinking system of Nano-crosslinking agent.

2.3 Analysis of anti-temperature and shearing performance
The temperature and shear resistance of nano-organic boron crosslinking agent at 170s-1 Shear rate was determined by high-RS6000 rheometer, the mass concentration of Hydroxypropyl guar gum was 0.2% and the mass concentration of nanometer crosslinking agent was 0.3%. With the increase of shear time, viscosity gradually decreased, in 150 ℃ continuous shear 60min, its viscosity stability in 70mPas above, performance is better than common organic boron cross-linking agent.

Mainly because the nano-materials and guar gum through the hydrogen bonding, with a relatively tight network structure.
2.4 Analysis of core permeability damage

The mass concentration of nano-organic boron cross-linking agent was 0.3% added to 0.2% hydroxypropyl guar gum solution, and 5% diesel oil was broken in 90 ℃ water bath pot for 1 hours to investigate its damage to core.

Table 1 Damage experiment of nano-organic boron fracturing fluid broken system

|         | length, cm | diameter, cm | porosity, % | pore volume, mL | permeability, mD | permeability before damage, mD | injury permeability, mD | damage rate, % |
|---------|------------|--------------|-------------|-----------------|-------------------|-------------------------------|-------------------------|----------------|
| Sands tone | 5.567      | 2.504        | 22.41536    | 6.145045        | 288.7007          | 14.1451                      | 12.0058                | 15.12          |

Fig.3 rheological properties of nano-organic boron fracturing fluids

Fig.4 Damage experiment of nano-organic boron fracturing fluid broken system
The results show that the damage rate of the core is 15.12%, which is lower than the organic boron cross-linking agent 20%, and is much lower than the damage rate under 30% in the general technical condition of fracturing fluid.

The main reason is that nanoparticles can effectively increase the elastic modulus of the system and increase the carrying capacity.

3. Conclusion

With the wide application of nanometer technology in oil and gas exploration and development, nanomaterials can significantly reduce the dosage of thickener in water based fracturing fluid, the surface modification of nanoparticles is done, and the organic boron cross-linking agent KB-2 modified on its surface, and a kind of nanometer organic boron cross-linking agent is prepared, which can significantly improve the temperature and shear resistance and reduce the core permeability damage performance.

Acknowledgments

Basic research on new material system of wellbore working fluid (2016a-3903); National major scientific and technological special (reservoir transformation key fluid research and development, serial number: 2017ZX05023003) funded.

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