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Synthesis and Evaluation of a Fluorine Containing Gas-Wetting Alteration Agent

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ABSTRACT

In this paper, fluorinated acrylate polymer FP415 was synthesized by emulsion polymerization and SiO_2 nanoparticles using improved Stober method. Using fluoropolymer to modify surface of SiO_2 nanoparticles, nanoparticles with gas wetting alteration ability was synthesized. The effect of air humidity on the wettability of core was quantitatively evaluated by the contact angle method. The study showed that the modified polymer FP505 had strong wetting alteration ability, and the wettability on the surface of core can be altered from liquid wettability to strong gas wettability .When the mass fraction of FP415 solution is 1%, the contact angle of the water phase and the oil phase can be increased from 27 ° ~ 0 ° to 143 °~ 39 ° on the untreated surface. After modification by nanomaterial, the contact angles of the oil phase became 139 °, the water phase became 130 °.

KEYWORDS: Fluoropolymer; nanomaterial; wettability alteration; gas wettability evaluation

INTRODUCTION

Water lock damage is one of the most serious damage types for condensate gas reservoirs. Laboratory studies have found that the wettability of the core can be changed from liquid wettability to strong gas wettability after the core is treated with fluoropolymers. After treatment, the wettability of reservoir rocks is changed into gas wettability, resulting in that the liquid phase contact angle

becomes larger, the viscous resistance is reduced, water recovery mobility, the water lock effect can be relieved, and the productivity can be recovered.

Fluoropolymers can give full play to their hydrophobic and oleophobic properties due to the presence of fluorocarbon bonds, it can alter the wettability of the surface of the core, and fluoropolymers modified by nanomaterials can enhance the wettability alteration ability. FC911 is a fluorine containing surfactant, which can establish gas wettability on the surface of quartz sand with the mixed liquid containing fluoropolymers. In this paper, the fluorinated acrylate polymer FP415, which can achieve wetting alteration, was prepared by selecting fluorine-containing monomers and acrylic acid. The wettability of FP415 was evaluated and nano-SiO_2 of 150nm was prepared. The gas wettability of the modified FP505 and the oil recovery were studied. Then, the FP505 and FC911 were compounded, and the gas wettability was evaluated again.

EXPERIMENT

Experimental drugs and instruments

Twelve fluorine-containing methacrylic acid （G04）, acrylic acid（AA）azodiisobutyronitrile (AIBN),N,N dimethylformamide（DMF）, trimethylamine, tetraethoxysilane (TEO), ammonia liquor, cetyl trimethylammonium bromide（CTAB）, Perfluorooctane sulfonate quaternary ammonium iodide(FC911, cationics), hexadecane from China Pharmaceutical Group Chemical Reagent Co., Ltd. absolute ethyl alcohol from Xilong Chemical Co., Ltd; core and sandstones from Shengli Oilfield; experimental water is distilled water.

DK-SII type electric thermostatic water bath(Shanghai senxin Experimental Equipment Co. Ltd), RCTbasic constant temperature heating magnetic agitator(Germany IKA company), SL200B type contact angle measuring instrument(Kenuo Industrial Co., Ltd.) AL204 electronic balance(Mettler Toledo (instrument) Shanghai Co. Ltd.) DHG-9053A electric heating constant temperature air blast drying box（Beijing science and Technology Co., Ltd. Li Kangda St.）BS355 core cutting machine （Deyang drilling material Co., Ltd.）JJ-1 force electric blender（Jintan Jiangsu medium and large instrument factory）.

Experimental method

Synthesis of fluoropolymer FP415

(1)Add 50mL DMF to the 250mL three-necked flask

(2) One half of a mixture of 0.25 g AIBN ,10 mL G04 and 2.5 mL acrylic acid (AA) were added to a three-necked flask

(3) The reaction temperature was controlled at 80 ℃ for 2h

(4)Then the remaining mixture was added to the reaction solution, react for 2h

(5)0.05 g azobisisobutyronitrile was added and the temperature of the reaction system was lowered to 0 ° C after keeping the temperature for 2 hours.

A fluorinated acrylate polymer FP415 was obtained. The schematic diagram of the structure is shown in Figure 1

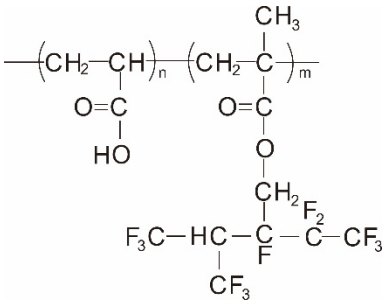

Figure 1: Schematic diagram of the structure of fluoropolymer

Synthesis of SiO_2 nanoparticles

Add 100mL ethanol, 5mLTEOS, 10mL of distilled water in the three-necked flask, stir well; 1.5 mL of aqueous ammonia (0.05 mol / L) was added and the pH of the solution was adjusted to 8 and the temperature was controlled to 40 ° C in the magnetic stirring for 6 hours; SiO_2 (100-150nm) was prepared after 2 h reaction under the heating temperature of 60 ℃.

The hydrolysis reaction of TEOS can be simply written:

$$\mathrm{Si(OC}H_2CH_3)_4 + 2H_2O \rightarrow Si(OH)_4 + 4CH_2CH_3OH$$

$$n\,Si(OH)_4 \rightarrow n\,\mathrm{SiO}_2 + 2n\,H_2O$$

Synthesis of modified fluoropolymer FP505

The synthesized nano-SiO_2 was mixed with the fluorine-containing monomer G04 in a mass ratio of 1: 1; 50 mL of DMF was added to a 250 mL three-necked flask, and 10 mL mixture of G04 and nano-SiO_2 and 2.5 mL of acrylic acid and 0.25 g of azobisisobutyronitrile was added to a three-necked flask by a dropping funnel, stirring for 2 h, the temperature was raised to 80 ℃ for 2h. Add the remaining mixture, and then kept for 2h, then supplemented 0.05g azobisisobutyronitrile, insulation for 2h.

The temperature of the reaction system was lowered to 0 ° C to obtain a modified fluoropolymer FP505.

Determination of contact angle

The contact angle method can simply and intuitively determine the gas wettability on solid surface, and according to the liquid phase contact angle, get quantitative understanding of gas wettability, so this paper uses the contact angle method to measure contact angle of rock system using JC2000D contact angle measuring instrument. In the experiment, the core was washed and dried with ethanol, then the surface of the core was smoothed. After aging for 24 hours in the fluoropolymer solution, contact angle of the core was measured, the core is water wetting when the contact angle is less than 75 °, and the rock is hydrophilic, the surface is hydrophobic and oleophobic while the contact angle between 75 ° and 105 °. The core is gas wetting when the contact angle of aqueous phase and oil phase are greater than 105 °.

RESULTS AND DISCUSSION

Evaluation of gas wettability of FP415

Table 1 shows the measured contact angle data after treating rock samples with different concentrations of FP415 solution. The experimental data shows that the contact angles of oil phase of the untreated core is 27 °, the aqueous phase is 0 °, respectively, which belong to strong liquid wetting.

When the core was treated with 0.1% polymer, the wettability changed significantly, and the contact angle of oil phase and water phase increased to 126 ° and 28 °. With the fluorinated polymer concentration continuing to rise, water contact angle remained at about 130 °.With the fluorinated polymer concentration continuing to rise, water contact angle remained at about 130 degrees. The contact angle of water phase reached 143 °, which is an obvious peak value when the concentration of fluoropolymer was 1%; when the concentration of fluoropolymer was higher than 1%, the change tends to be gentle.

It can be seen that the fluoropolymer FP415 has obvious wettability alteration effect on the core surface, and the optimum concentration is 1%.

Table 1: The contact angle of rocks soaked by different concentrations of FP415

concentration of FP415 /%	0	0.1	0.3	0.5	0.7	1	3	5	7
contact angle（water interface）/°	27	126	123	131	132	143	115	105	104
contact angle（oil interface）/°	0	28	23	20	40	39	44	63	59

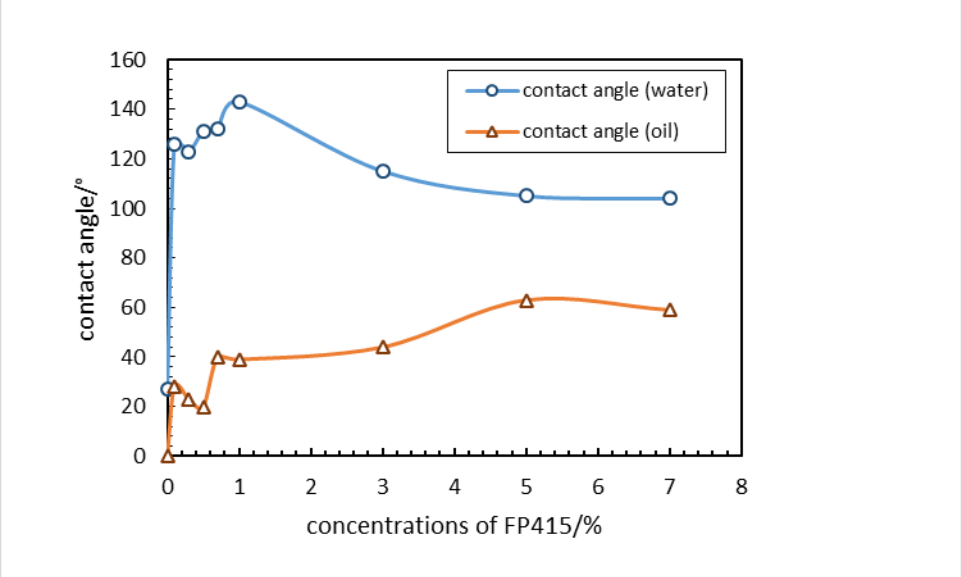

Figure 2: The gas phase contact angle of rocks soaked by FP415 with different concentration

Chemical Modification of Nano - SiO_2 by FP415 and Its Evaluation of Performance

Evaluation of the gas wettability of FP modified nano-SiO_2

Table 2 shows the measured contact angle data after treating rock samples with different concentrations of nano-SiO_2 and FP415 solution. The experimental data show that the wettability of

the oil phase is obviously changed after the treatment of nano-SiO_2. After adding 0.1% nano-SiO_2, the contact angle of oil phase changes from 40 ° to 93 °, from oil wetting to neutral gas wetting. The mechanism is mainly the microscopic effect of nanomaterials and the synergistic effect of oleophobicity of the polymers, which makes the hydrophobicity of the nanomaterials more obvious, while the hydrophobicity of the nanocomposites is restrained. The contact angle is about 105 °.

Table 2: The contact angle of rocks soaked by different concentrations of nanometer SiO2 and FP415 of 1% concentration.

concentrations of nano-SiO2/%	0	0.1	0.3	0.5	0.7	1
contact angle（water interface）/°	143	129	128	90	108	110
contact angle（oil interface）/°	40	93	99	89	85	90

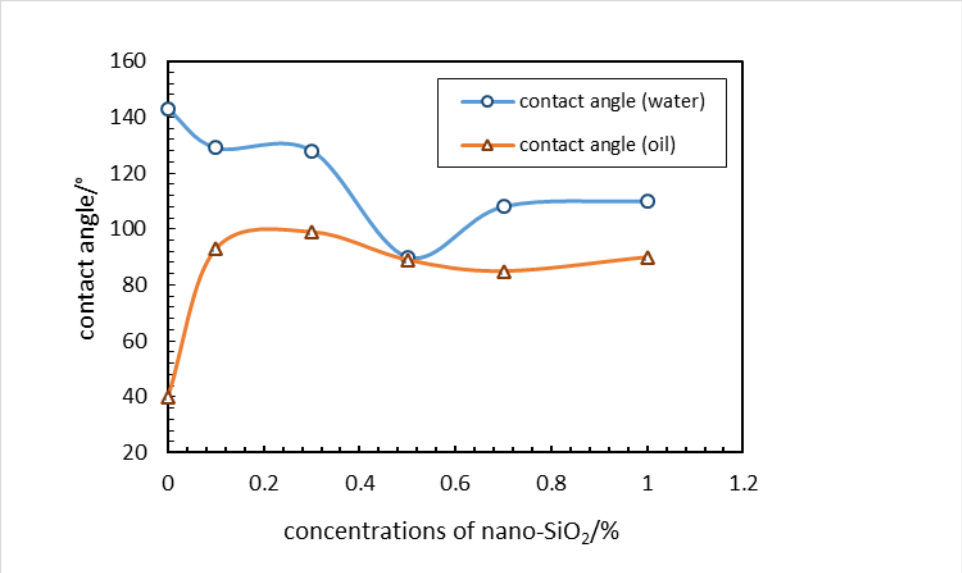

Figure 3: The water-oil phase contact angle of rocks soaked by nanometer SiO_2 with different concentrations and FP415 of 1% concentration.

Gas-Wettability Evaluation for Nanoscale Compound of SiO_2+ FP415 and FC911

Table 2 shows the measured contact angle data for treating samples with different concentrations of nano-FC911, 1% FP415 and 0.3% nano-SiO_2 solution. According to the experimental data, the oleophobicity was improved obviously after being treated with FC911. When the concentration of FC911 was 0.5%, the contact angle of the oil phase reached 122 °, and the wetting alteration occurred obviously. But the effect on the contact angle of the aqueous phase is not very good.

Table 3: The contact angle of rocks soaked by different concentrations of FC911 and FP415 of 1% concentration and nano-SiO_2 of 0.3% concentration.

concentrations of FC911/%	0.1	0.3	0.5	0.7	1
contact angle（water interface）/°	104	86	55	78	64
contact angle（oil interface） /°	108	107	122	118	107

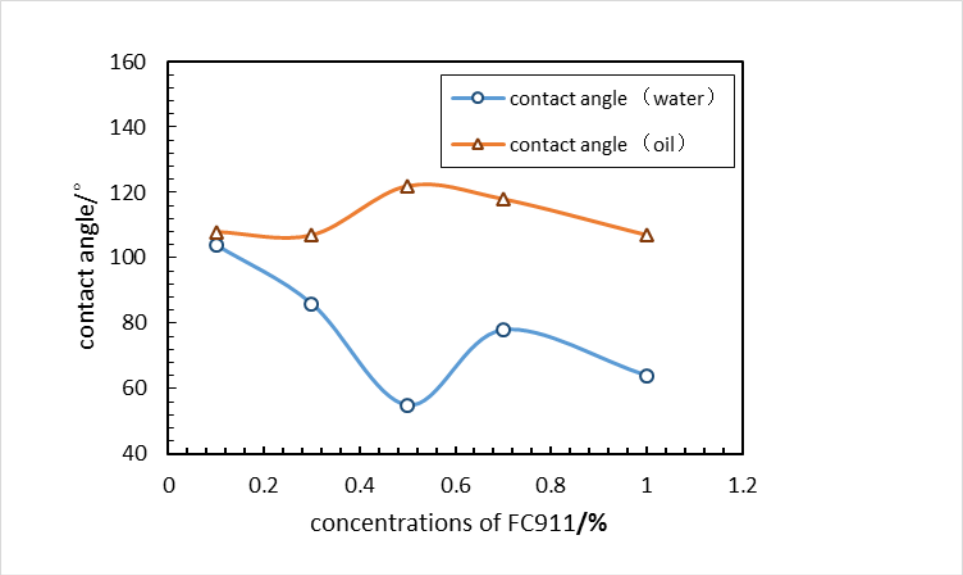

Figure 4: The contact angle of rocks soaked by different concentrations of FC911 and FP415 of 1% concentration and nanometer SiO_2 of 0.3% concentration.

Chemical Modification of Nano-SiO_2 by FP415 and Evaluation of Its Performance

The polymer was synthesized by mixing the nano-SiO_2 and the fluorine-containing monomer in the mass ratio of 1: 1, and the FP505 was obtained after chemical modification of FP415.

Evaluation of gas wettability of FP505

Table 2 shows the measured contact angle data for treating rock samples with different concentrations of nano-FP505 solution. From the experimental data, after chemical modification, the fluoropolymer FP505 has good gas wettability, while the water phase in a low concentration with strong gas wettability, contact angle can reach 139 °, oil contact angle can reach 102 °.

Table 4: The contact angle of rocks soaked by different concentrations of FP505

concentrations of nano-FP505/%	0	0.1	0.5	1	5	7
contact angle（water interface）/°	27	139	130	135	129	122
contact angle（oil interface）/°	0	87	91	102	97	85

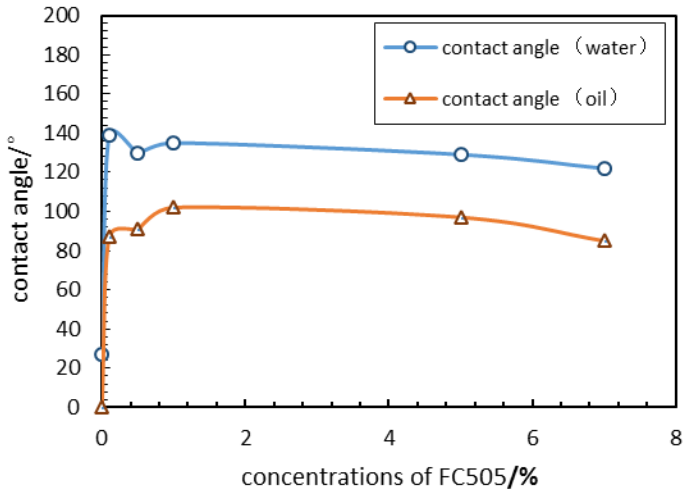

Figure 5: The contact angle of rocks soaked by different concentrations of FP505.

Evaluation of oil recovery Effectiveness

The crude oil evenly on the surface of the glass sheet, the clean slide cover slides in oil wipe, ensure that there is no bubble between two pieces of glass. Placed in 80 degrees Celsius oven drying for two hours, and then placed in the configured nano-fluid solution, aging 24 hours after the slide to observe the situation.

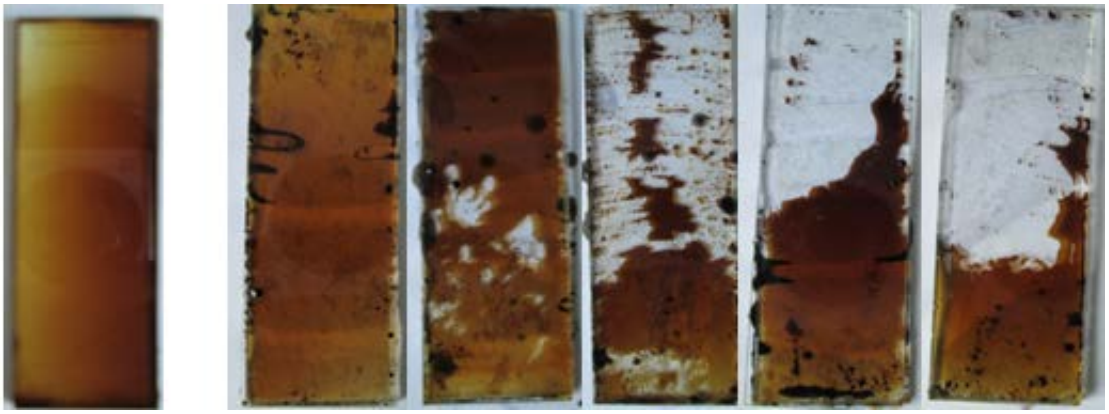

Figure 6: The slide dealt by different concentrations of FP505 24 hours.

The experiment found that the untreated samples did not change significantly, while aging treatment with the increase of concentration of the FP505 solution, oil recovery effectiveness is gradually obvious.

Gas-Wettability Evaluation for FP505 and FC911 Compound

Table 5 shows the measured contact angle data after treating rock samples with different concentrations of nano-FC911 and 1% concentration of FP415 solution. From the experimental data, after the mixture of FP505 and FC911, the modified effect is obvious, the contact angle of oil phase and water phase can reach 139 ° and 130 ° respectively, which shows that FC911 and FP505 have good compatibility . The optimum concentration of FC911 was 0.7%.

Table 5: The contact angle of rocks soaked by different concentrations of FC911 and FP505of 1% concentration.

concentrations of nano-FC911/%	0	0.1	0.3	0.5	0.7	1
contact angle（water interface）/°	135	130	130	136	139	125
contact angle（oil interface）/°	102	110	115	125	130	120

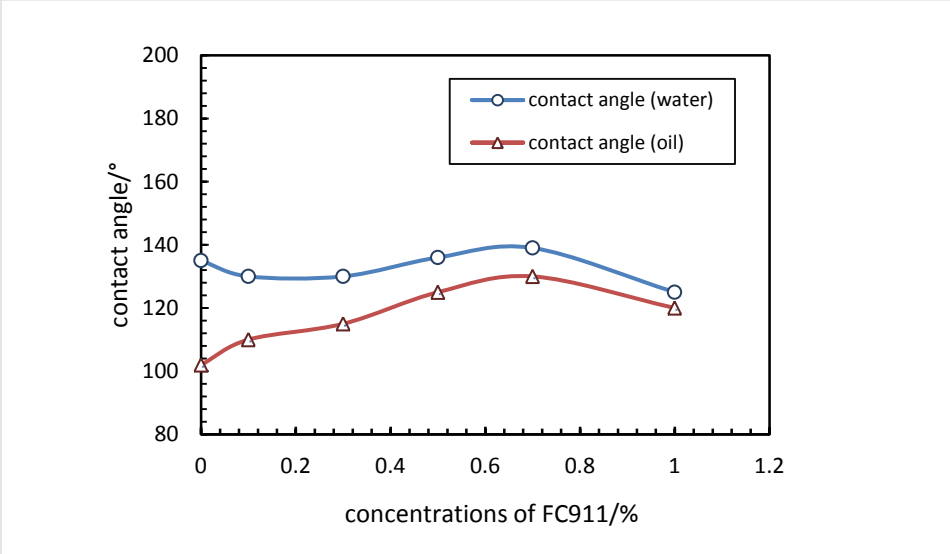

Figure 7: The contact angle of rocks soaked by different concentrations of FC911 and FP505 of 1% concentration.

CONCLUSIONS

(1) The FP415 has the best alteration effect on core surface with the concentration of 1%, between which the contact angle of water phase and oil phase was 143 ° and 39 °, respectively.

(2) FP415, physically modified by Nano-SiO_2 cannot realize the strong gas wetting. FP505 was obtained after chemical modification of FP415, The contact angle was up to 135 °, and the oil phase could reach neutral gas wetting, of which the contact angle was up to 102 °, with good cleaning efficiency.

(3)When the concentration of FP505 was 1% and the concentration of FC911 was 0.7%, the contact angle between water phase and oil phase reached 139 ° and 130 °, and the wetting effect of FP505 and FC911 was enhanced obviously after proper FP505- FC911 compound.

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