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Supporting Information for
Properties of a novel imbibition polymer with ultra-high wetting
ability as fracturing fluid system

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Experimental Section

Materials

Acrylamide(AM), 2-acrylamido-2-methylpropanesulfonic acid (AMPS), ammonium persulfate (APS), ascorbic acid (VC), 2,2'-azo-bis(2-methylpropionamide) dihydrochloride (V-50), the above agents were analytically pure. Hydrophobic monomer (S-20) and NaCl solution (20000mg/L), and surfactant (CTAB) were made in laboratory. All chemicals were analytical reagent grade and were utilized without further purification.

Synthesis of polymer

The aqueous solution was prepared with the monomer total concentration of 25 wt% and surfactant CTAB content was 10% of the total monomer concentration. The mass ratio of reactive monomer was m (AM): m (AMPS): m (S-20) = 65: 25: 10. The solution was conducted deoxygenating for 60 min at 7~9°C. The initiator aqueous solution was prepared with a concentration of 0.04% (based on monomer total mass), the mass ratio of initiator was m (APS): m (VC): m (V-50) = 2: 1: 1. The reaction was conducted at 90 °C for 3.0h. Thus, colloidal products were obtained. White powder polymer NFW was obtained by smashing and drying at 90°C. Then, the polymer NFH was conducted with the same experiment method in which the

CTAB was removed. The synthesis process is showed in Scheme 1.

X-ray diffractometry (XRD)

The NFH and NFW were measured by X-ray diffraction measurements using an X-ray diffractometer with Cu, k_{α} radiation target at 40 mA and 40 kV and a scan rate of 1 ($^{\circ}$)/min, step size of 0.05 degree, with the scattering angle (2θ) ranging from 10° to 90° .

Thermogravimetric analysis (TGA)

TGA of NFH and NFW were measured by Thermo Gravimetric Analyzer (DSC 823 TGA/SDTA85/e). In this test, the protective gas and the purge gas were both 99.999% of nitrogen with 50 mL/min. The sample was heated from 30°C to 700°C with a heating rate of $10^{\circ}\text{C}/\text{min}$.

SEM of polymer

The morphology was investigated using an environmental scanning electron microscope (ESEM, Quanta 450, USA). The system of 0.3 wt% NFH and NFW which were treated in pure water for 90 min under 170 s^{-1} was prepared and dropped on glass slides to obtain samples for ESEM observation. All of samples were dried at 25°C and then frozen using liquid nitrogen. The frozen surfaces of the samples were observed with ESEM operating at an accelerating voltage of 20 KV. Then, the morphology of broken liquids was investigated using the same way. The broken liquids were prepared by 0.3 wt% NFH and NFW with 0.04% breaker APS at 60°C for 120 min.

TEM of broken liquid

The morphology was measured with a transmission electron microscope (H600A- II, FEI, USA). The sample angle was 0° . The samples were observed with TEM operating at an accelerating voltage of 20 KV. The gel breaking fluids were prepared by combining 0.3 wt% sample with 0.04% breaker APS at 90°C for 120 min. The gel breaking fluid was dispersed by ultrasonication.

Viscoelasticity

The viscoelasticity as a property of strain and frequency sweep for 0.3 wt% NFH and NFW solutions was measured using an Anton PPar rheometer with CP50-1-SN30644 plate fixture (diameter=0.099 mm). All samples were measured at 25°C to ensure the consistency of the experimental conditions.

Rheological behaviors

Rheological measurements were conducted on a HAAKE RS600 rheometer. These measurements were made with a cone. The rheology of NFH/NFW solutions with 0.3 wt% concentration was

measured at a temperature range of 30 °C~90 °C in pure water with a constant shear rate of 170 s⁻¹. Then, the rheology of NFH/NFW solutions was measured at a constant temperature of 90 °C in pure water under a shear rate of 170 s⁻¹.

Breaker

In order to analyze the property of gel breaking fluid, APS was added into the fracturing fluid to reduce the viscosity. Lower viscosity of fracturing fluid after breaking is easier to flow back. The gel breaking fluids were prepared by combining 0.3 wt% sample with 0.04 wt% APS at 60 °C.

Particle size of gel breaking fluid

Particle size was measured at a range of 0.6 nm~6 μm using laser particle analyzer (Zetasizer Nano-ZS, Malvern, UK). The concentration of gel breaking fluid is 0.3 wt% dissolved in water. Particle size characterization can reflect the existence of broken liquids in the solution to some extent.

Surface tension

The surface tension of surfactant and gel breaking fluid were measured using a surface tensiometer (Data Physics, Germany, DCAT21). The experimental procedure is as follows: firstly [11, 20-22], The platinum plate was burned after wash under alcohol flame to remove the adsorbed solution completely. Secondly, Measurements of the surface tension of pure water at room temperature were performed, which could calibrate the tensiometer. Last, the platinum plate was dipped in the solution to measure its surface tension. In all cases, more than three successive measurements were carried out, and the standard deviation did not exceed 0.2 mN/m.

Capillary test

The preparation of oil-wet capillary: the standard capillary with diameter 0.35mm. The steps were as follows [23-25]: (1) The carbon tetrachloride, benzene, acetone, ethanol (with the volume ratio of 7: 1.5: 1.5) were used to remove surface organic matter under. (2) The diluted hydrochloric acid solution (1: 10) and hydrofluoric acid solution (10 wt%) were successively used to roughen the capillary surface under ultrasound treatment for 30 minutes. (3) Using ultrasound with pure water to remove residual acid until pH was above 6.5 and the temperature is 105 °C. (4) The capillaries that were treated were completely submerged in the aging oil (mass ratio of crude oil, aviation kerosene, 90 asphalt was 25: 3) with a temperature of 60 °C for two or four weeks. (5) The deposited asphalt of capillary was cleaned by the kerosene for two minutes. Then, the capillary

was dried at 60 °C and oil-wet capillary was prepared. Fig.2 showed the schematic diagram of the capillary determination.

Contact angle

The preparation of sandstone slice: the complete sandstones were cut into standard columnar cores and the parameters of sandstone such as permeability and porosity were tested in this experiment. The thickness of sandstone slice was strictly controlled at 0.3 cm to ensure the simulated oil (with mass rate of crude oil: 90# asphalt: aviation kerosene was 2: 3: 5) imbibition into the core during the aging process. The slices were heated using toluene as solvent to dissolve the oil at 80 °C. Then, the toluene in the slice was dissolved by the methanol at 60 °C. The sandstone slices were dried at 100 °C to remove the residual methanol. Finally, the prepared slices were aged with simulated oil for one month at 60 °C [25-29].

The measurements of contact angles of all samples on sandstone slice were carried out by the sessile drop method using the SCA20 (Dataphysics Instruments GmbH, Stuttgart, Germany) shown in Fig.3. The contact angle (θ) is between solid-liquid and air-liquid. The oil droplets of the contact angle measurement were 1ml. The contact angle tests were carried out immediately after the oil droplets attached to the sandstone slice within about 1–2 min. The experiments were carried out at room temperature.

Atomic force microscope (AFM)

Atomic force microscope (model SPI3800N/SPA400, Japan) was used to test the surface morphology of the sample. The sample slice was placed in a special test holder which was adjusted to make the sample stable. The sandstone slice was soaked in the gel breaking fluid with a concentration of 0.3 wt% at 60 °C. The slice was the same with the contact angle test.

Computed tomography (CT)

The preparation of saturated core columns: the standard core column was cut into with a diameter of 9 mm and length of 2 cm to meet the requirements. The oil in the core was cleaned with a benzene and ethanol (volumetric ratio 3:1) mixture at oil-washing apparatus for 7 days. Then, the core was aged with the simulated oil at a pressure of 20 MPa for 2 weeks at 60 °C and the standard core column was obtained. The solution was prepared with a concentration of 0.3 wt%. The potassium iodide was used as a dopant with concentration of 4 wt%. The saturated core columns were measured via Zeiss Xradia 520Versa with a voltage of 60 KV, power of 5 w, resolution ratio

of 5.5 μm at 60 $^{\circ}\text{C}$.

Imbibition efficiency

The CTAB and gel breaking fluids were prepared respectively with a concentration of 0.3 wt% at 60 $^{\circ}\text{C}$. The saturated core column was prepared in the same method as the CT experiment. The sandstone was suspended by a string under an analytical balance to record the core weight constantly. The parameters such as the rate of imbibition and the recovery rate of imbibition were introduced as evaluation parameters based on the weighing method to compare the effects of infiltration under different conditions. The imbibition efficiency was calculated according to the formula (1) as below [27-30]:

$$R = \frac{\Delta m \times \rho_0}{(\rho_w - \rho_0)m_0} \times 100\% \quad (1)$$

where the R was the infiltration efficiency at t time, %; Δm was the sample quality increase, g; ρ_w was the density of solution, $\text{g}\cdot\text{cm}^{-3}$; ρ_0 was the density of simulated oil, $\text{g}\cdot\text{cm}^{-3}$; m_0 was the added weight of oil after the sandstone was saturated, g.

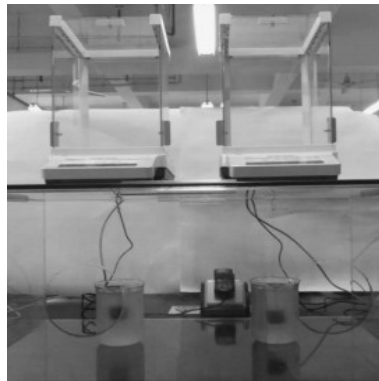


Fig.1. The experimental apparatus of imbibition.

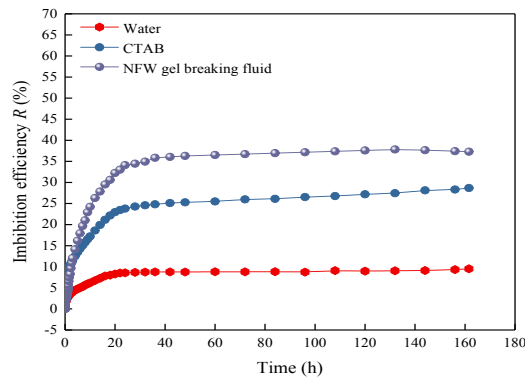


Fig.2. The imbibition efficiency of the gel breaking fluid with sandstone.