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Guar gels modified with single-walled carbon nanotubes for hydraulic fracturing

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This work investigates the rheology of crosslinked fracturing gels modified with single-walled carbon nanotubes (SWCNTs). Guar was used as a gelling agent. The SWCNT mass concentration in the gels varied from 0.01 to 0.1 wt%. Dependences of rheological characteristics on the SWCNT concentration were obtained. It was found out that nanotube additives can significantly change the effective viscosity of modified gels. It was shown for the first time that addition of a low concentration of single-walled nanotubes increases the microrheological elasticity index of crosslinked gels by two orders of magnitude and reduces their fluidity index by five times.

Keywords: hydraulic fracturing fluids, singlewalled carbon nanotubes, viscosity, rheology, microrheology.

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Hydraulic fracturing (HF) is the hardest operation in the oil and gas industry. To perform it successfully, the hydraulic fracturing fluid should have certain physical and chemical properties and satisfy numerous stringent operational requirements [1]. The use of cross-linked gels has largely determined the success in developing uptodate HF techniques. To cross-link the gels, boron, titanium or zirconium compounds are typically used, whose extraction from waste fluids is physically impossible. In this connection, research on developing new environmentally inert crosslinkers has recently become important. The results of recent studies [2–5] have shown that efficiency of the HF gels crosslinking may be increased by using nanoparticles. It was found out that, due to large specific surface area of nanoparticles, their concentration necessary to increase the effective gel viscosity is significantly lower than that of standard crosslinkers. In addition, nanoparticles are not susceptible to thermal degradation and are chemically inert. Despite the promising results, the mechanisms of crosslinking the gels with nanoparticles are not yet fully understood, and investigations in this field are being actively continued. The major part of studies is devoted to modifying HF fluids with spherical nanoparticles.

In this work, the effect of singlewalled carbon nanotubes (SWCNTs) on rheological properties of HF gels was studied for the first time. As an HF fluid gelling agent, crosslinked guar biopolymer was chosen. Modification was performed using singlewalled carbon nanotubes TUBALL™ („OCSiAl.ru"LLC, Novosibirsk, Russia). The nanotube mean diameter was 1.6 ± 0.4 nm, while the specific surface area was, as per BET data (Brunauer–Emmett–Teller method), 510 m^2/g. According to the atomic force microscopy data, the SWCNT length exceeded 4 μm, while their mean and bulk densities were 1.8 and 0.1 g/cm^3, respectively. The results of characterizing SWCNTs by electron microscopy of their suspensions with using electroacoustic spectrometry are presented in our recent paper [6].

The SWCNT concentration was varied from 0.01 to 0.1 wt%. Crosslinked gels with SWCNTs were prepared as follows. First, aqueous suspension of SWCNTs was prepared. The necessary amount of SWCNT powder and surfactant was put into a container with distilled water. As a surfactant, sodium lauryl sulfate was used. In all the cases, the surfactant concentration was the same as the respective SWCNT concentration. Next, the suspension was mechanically mixed at a high-speed disperser IKA of the stator-rotor type; this was followed by ultrasonic treatment with ultrasonic device „Volna" UZTA-0.4/22-OM (22 kHz, 400 W, 50%). The process of preparing the SWCNT suspension included several stages of mixing at high-speed (20 min) and ultrasonic (20 min) dispersers. Duration of ultrasonic treatment at the maximum power was 120 min. The minimal energy needed to be transferred to the suspension had to be at least $2000\,\mathrm{W \cdot h \cdot l^{-1}}$.

Then, the necessary amount of gelling agent was added to the suspension prepared in the above way and mixed again with an agitator for another 15 min. As a gelling agent, guar gum biopolymer (ALTRAFINE GUMS, India) 0.4 wt.% in concentration was used. After this, a linear gel got ready. To obtain the crosslinked gel, crosslinker was added and mixed until the Weissenberg effect was achieved. The mixing mode was not changed from the moment of putting the biopolymer into the container. As the crosslinker, sodium tetraborate in glycerin (0.1 wt.%) was typically used. Methodological studies have shown that this concentration of gelling agent and crosslinker is optimal for obtaining the necessary rheological properties of gels and also from the economical point of view. Visually, the carbon nanotubes distribution is uniform throughout the gel volume. The gels are colloidally stable and have well pronounced elastic

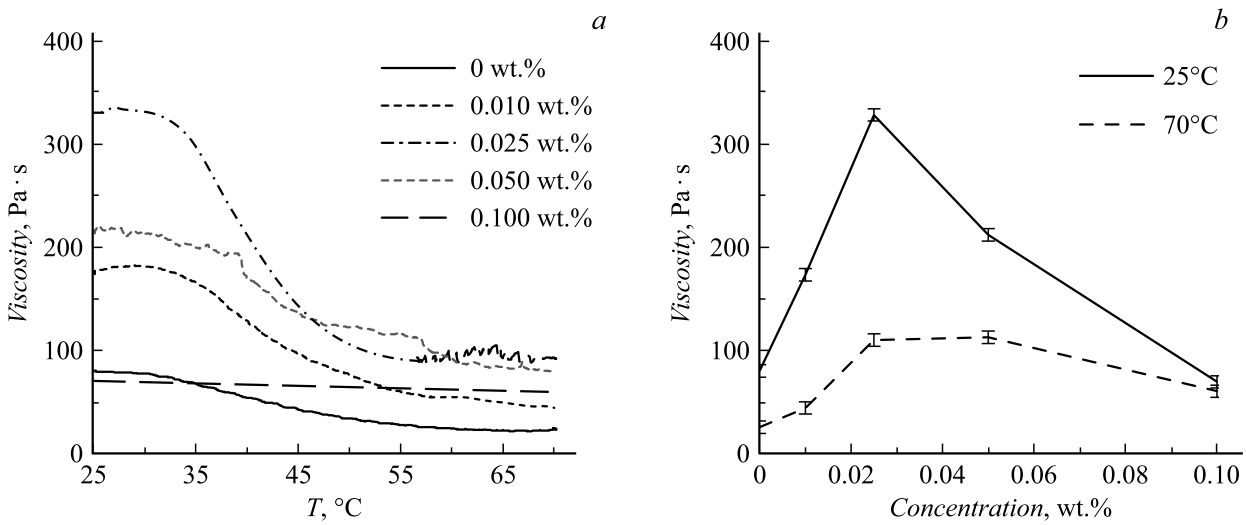

Figure 1. Effective viscosity of SWCNTmodified gels versus temperature (a) and concentration (b).

properties. Thus, numerous laboratory studies resulted in developing a recipe for obtaining stable SWCNTmodified gels.

We have also studied the temperature dependence of effective shear viscosity of the modified gel. HF gels have to possess high viscosity over a wide range of reservoir temperatures. In this study, the temperature was varied from 25 to 70°C. The gel viscosity was studied using rotational viscometer Brookfield DV2T (Ametek, USA) with cylindrical spindle LV-64. The viscometer allows measuring the viscosity coefficient in a wide shear rate range of 0.0212 to 42.4 s^{-1}. The measurement error confidence interval did not exceed 5%. Investigation of the crosslinked gel viscosity involved measuring the sample for 40 min at a fixed shear rate of 0.212 s^{-1}: the sample temperature was maintained equal to 25°C for the first 10 min, after which the sample was heated to 70°C at the rate of 2°C/min and then kept at this temperature. The viscosity values were measured every 2 s and then averaged. Thus, the temperature dependence of the effective gel viscosity was studied at different concentrations of carbon nanotubes (Fig. 1, a).

It was revealed that, first, the fluids under study were non-Newtonian (pseudoplastic) and their viscosity decreased with increasing shear rate. Second, the effective viscosity dependence on concentration was nonmonotonic. When SWCNT concentration is low (below 0.05 wt.%), the effective gel viscosity increases significantly. For instance, when the concentration is 0.025 wt.%, effective viscosity at 25°C increases 4.1 times with respect to that for the base gel; however, when the concentration continues increasing, it decreases (Fig. 1, b). The increase in viscosity is caused by interaction between the nanotubes and guar gum molecules with formation of a gridlike structure due to adsorption of micelles and enhancement of hydrogen bonds. However, at high concentrations of carbon nanotubes (above 0.05 wt.%), electrostatic repulsion between the micelles increases due to strong adsorption ability of the nanotube negative surface charge, which prevents crosslinking of guar molecules. When the considered SWCNT content in the gel is maximal, there is observed a viscosity decrease by 15% as compared to viscosity of the base crosslinked gel.

Analysis of the temperature dependence (Fig. 1, a) shows that effective viscosity of all the samples decreases significantly with increasing temperature. Viscosity of nanomodified gels was found to be less sensitive to temperature variations. For instance, viscosity of the nanoparticlefree base gel heated from 25 to 70°C decreased by 3.2 times, while that of gels with 0.025 wt.% of SWCNTs decreased by 2.9 times. When the SWCNT concentration continued increasing (up to 0.1 wt.%), the viscosity decrease with increasing temperature (from 25 to 70°C) was only 15%. The effect of a significant increase in viscosity at SWCNT concentrations below 0.05 wt.% was also preserved. This is very important for their practical application.

In fluids with high SWCNT content, a percolation network gets formed. Percolation begins at such critical SWCNT concentrations when the average distance between carbon nanotubes appears to be on the order of the range of van-der-Waals forces between them. The presence of the percolation network dictates the presence of viscoelastic properties in the fluids. Formation of the percolation network of carbon nanotubes is a threshold phenomenon promoting an increase in the modified gel viscosity with respect to that of the base gel. Viscoelastic characteristics of nanotubemodified HF gels were studied. For this purpose, microrheology analyzer Rheolaser MASTER (Formulaction, France) was used. The analyzerś operating principle is based on measuring dynamic scattering of laser radiation from particles (the method of diffusion wave spectroscopy). The device allows calculating the mean square displacement (MSD) of particles as a function of time during the gel

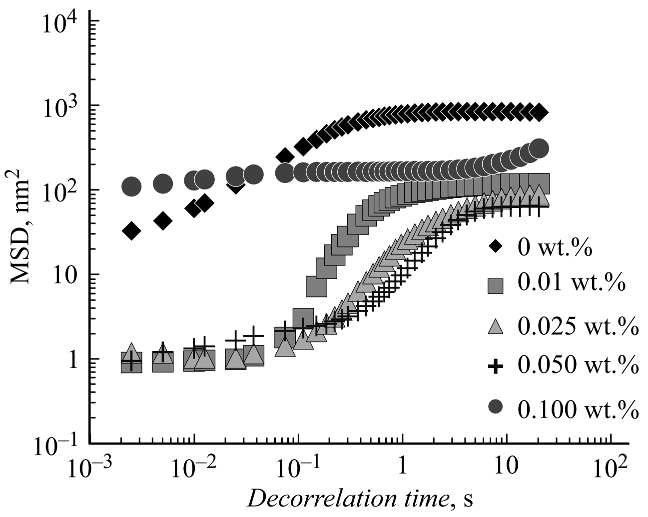

Figure 2. Plots of mean square displacement (MSD) of particles in gels with different SWCNT concentrations.

structure recovery to the state of viscoelastic equilibrium. A typical time dependence of MSD for gels with different singlewalled nanotube concentrations is presented in Fig. 2. Horizontal plateaus on the MSD plots (characteristic time of 10^{-1} to 10 s) represent the manifestation of the samplé s elastic properties. The MSD curve slope at the elasticity plateau characterizes the ratio between the elastic and fluidic behavior of the sample. Analysis of MSD shows that addition of nanotubes makes faster formation of elastic properties in the crosslinked gels. Based on the MSD curves behavior, it is possible to calculate the fluidity index characterizing the fluidś viscoelastic properties (Fig. 3, *a*). This parameter is reciprocal of the characteristic decorrelation time. If it is lower than 1 Hz, this means that the sample behaves like a viscoelastic fluid. Fluidity index of the base nanoparticle-free crosslinked gel free being in equilibrium was shown to be 0.17 Hz. Adding of nanoparticles reduces the fluidity index. This shows that formation of elastic properties is stronger in the case of the modified gels. Notice that adding of SWCNTs enhances manifestation of those properties. The minimal fluidity of gels is observed at the particle concentration of 0.05 wt.%.

In addition, the microrheology analyzer allows determining the elasticity index calculable through the MSD plateau level (Fig. 3, *b*). It was found out that adding of nanotubes with the concentration of 0.05 wt.% increases the gel elasticity index by two orders of magnitude. In this case, the nanotubeconcentration dependence of the elasticity index of crosslinked gels is nonmonotonic. The SWCNT concentration at which the gel elasticity increases to the maximum is 0.05 and 0.025 wt.% at the temperatures of 25 and 70°C, respectively.

Thus, results of the sudy have shown for the first time that adding of a low SWCNT concentration (below 0.05 wt.%) increases the effective viscosity of crosslinked gels by 4 times and makes it less sensitive to temperature variations, reduces the fluidity index by 5 times, and, in contrast, increases the gel elasticity index. Thus, using SWCNT additives to control the properties of HF fluids seems promising.

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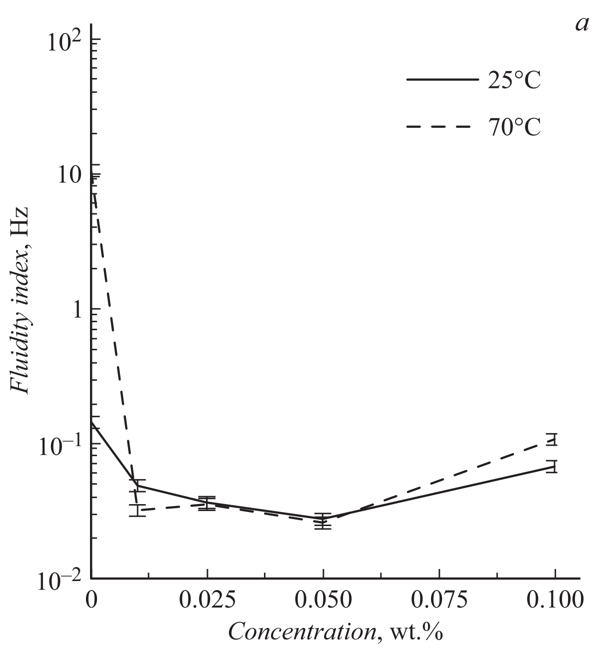

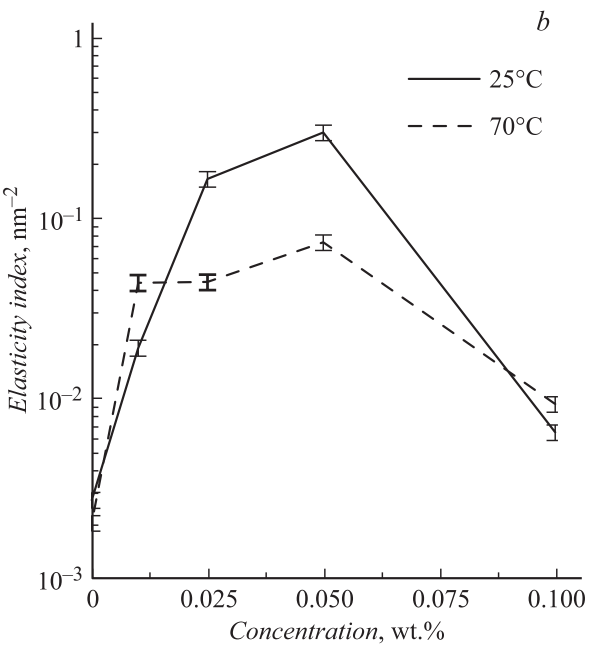

Figure 3. Results of microrheological investigation: fluidity index (*a*) and elasticity index (*b*) of the SWCNTmodified gels.

Conflict of interests

The authors declare that they have no conflict of interests.

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