

Preparation of a nanosilica cross-linker and investigation of its effect on properties of guar gum fracturing fluid

Zifeng Zhang¹, Peisong Liu¹, Hao Pan¹, Mengyun Zhao², Xiaohong Li¹ ✉, Zhijun Zhang³

¹Engineering Research Center for Nanomaterials, Henan University, Kaifeng 475001, People's Republic of China

²Institute of Petroleum Exploration and Production, SINOPEC, Beijing 100083, People's Republic of China

³National & Local Joint Engineering Research Center for Applied Technology of Hybrid Nanomaterials, Henan University, Kaifeng 475001, People's Republic of China

✉ E-mail: xiaohonglihenu@126.com

Published in Micro & Nano Letters; Received on 10th October 2016; Revised on 5th February 2017; Accepted on 3rd March 2017

The development of hydraulic fracturing has created a huge demand for fracturing fluids with high performance and low formation damage in recent years. A nanosilica cross-linker precursor (NCP) was prepared by introducing boric acid to the surface of organic silica compound ($C_9H_{23}NO_3Si$, a silane coupling agent), the carrier. As-obtained NCP was transformed into nanoparticles (NPs) with a diameter of 10–35 nm by self-aggregation. The resultant NPs were used to crosslink low concentration of guar gum solution in order to improve the rheological and breaking properties of the fracturing fluid made of the NPs-cross-linked guar gum gels. Findings indicate that boric acid chemically reacts with the amino group of the silane coupling agent forming N–B bond via infrared analysis. The viscosity of NPs-cross-linked guar gum gels increases with the increase of particle size of NPs, which means that the particle size of NPs has a significant effect on the cross-linking efficacy, the guar gum gels cross-linked by a proper mass fractions of NPs exhibits good temperature resistance and shear resistance via rheometer. Moreover, the NPs-cross-linked guar gum gels possesses better breaking behaviour than the one cross-linked by borate.

1. Introduction: As a well-established stimulation technique for increasing oil production from a reservoir, hydraulic fracturing is often applied on conventional reservoirs with sandstone or carbonate rock [1]. Recently, it is also extended to unconventional reservoirs which are characterised by a very low permeability (10^{-5} to 10^{-9} Darcy), such as shale and coalbeds. Under such a low permeability, the ability of oil migrating to the wellbore is limited, which dissipates the production from such fields. To increase the production from the low-permeability reservoirs, it is necessary to increase their permeability through fracturing such as hydraulic fracturing. Usually, a fracturing fluid is injected under high pressure to hydraulically crack the reservoir rock in order to create fractures [2–5]. However, oil-based fracturing fluids used for hydraulic fracturing often bring about environment and safety concerns. This prompts the development of water-based fracturing fluids. Guar gum, a naturally occurring polysaccharide, a galactomannan harvested from *Cyamopsis tetragonolobus*, is a representative of water-based fracturing fluids currently used in hydraulic fracturing, and it consists of linear chains of (1→4)- β -D-mannopyranosyl units with α -D-galactopyranosyl units attached by (1→6) linkage [6]. Bishop *et al.* [7] reported that guar gum can be cross-linked with borates by way of its 3,4-cis-hydroxyl radical in the galactose side chains, leading to the formation of a three-dimensional network responsible for the gelation. Kramer *et al.* [8] found that the cross-linking of guar gum with borate is based on the hydrolysis of $B(OH)_4^-$ anion. Namely, B–OH can form hydrogen bonds with the cis-hydroxyl radical of the polysaccharide, thereby connecting two strains of guar gum, as illustrated in Fig. 1. As a gelling agent of water-based fracturing fluid, guar gum has good thickening ability, strong ability to control link-off etc., and it is widely used in domestic oil and gas fracturing. Nevertheless, the guar gum fracturing fluid cross-linked with B-containing inorganic compounds exhibits low crosslinking efficiency [9, 10], while the one cross-linked with organic borate has disadvantages attributed to a high cost, an increased liability to formation [11, 12]. To deal with this issue, some researchers tried to introduce nanomaterials to strengthen the performance of guar

gum fracturing fluid. For example, Hurnaus *et al.* [13] synthesised TiO_2 nanoparticles with different sizes by sol–gel method and investigated their rheological properties. They found that TiO_2 nanoparticles with a diameter of <10 nm exhibit good cross-linking ability and can effectively improve the viscoelastic properties of the gel. The mechanism of interaction between guar gum and hydroxyl groups on the surface of nanoparticles could be assigned to hydrogen bonding. However, in terms of the ability to improve the viscoelastic performance of guar gum fracturing fluid, nanomaterials still have shortcomings such as complex synthetic process, high cost etc.

In the present research, we introduce boric acid to the surface of organic silica compound (KH550, a silane coupling agent) so as to prepare a nanosilica cross-linker precursor (denoted as NCP). The as-prepared NCP would self-aggregate to form nanoparticles (denoted as NPs) with a diameter of 10–35 nm while its concentration is properly adjusted. In the meantime, we investigate the cross-linking reaction between the NPs and guar gum solution while the as-prepared NPs is combined with guar gum solution to afford gels. This Letter reports the preparation of the guar gum gels and the evaluation of its rheological and breaking properties.

2. Experimental

2.1. Materials: Boric acid (H_3BO_3 , analytical grade; Tiannjin Ruijinte Chemical Company Ltd; Tianjin, China), ammonium persulphate ($(NH_4)_2S_2O_8$, analytical grade; Tianjin Kemiou Chemical Reagent Company Ltd; Tianjin, China), ethanol (C_2H_5OH , analytical grade; Luoyang Chemical Reagent Factory; Luoyang, China), sodium hydroxide (NaOH, analytical grade; Tianjin Dalu Chemical Reagent Factory; Tianjin, China), and 3-aminopropyltriethoxysilane ($C_9H_{23}NO_3Si$, analytical grade; Sinopharm Chemical Reagent Company Ltd; Shanghai, China) were purchased from the manufacturers. Guar gum was supplied by Institute of Petroleum Exploration and Production of Sinopec.

2.2. Preparation of NCP and nanoparticles with different size: The NCP was prepared by the method established at our laboratory. Briefly, 12 g of boric acid was dissolved in ethanol (100 g) under

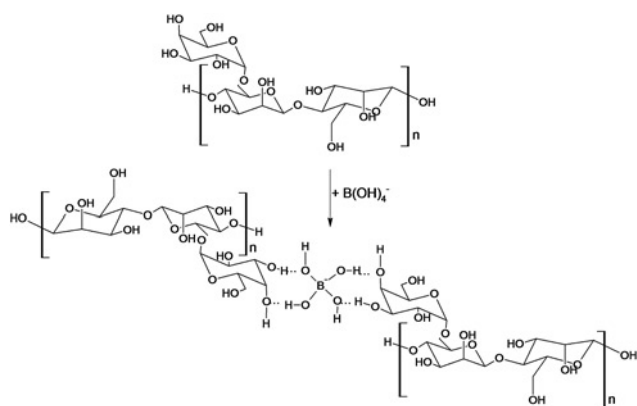


Fig. 1 Chemical structure of guar gum and proposed cross-linking mechanism between guar gum and B-containing compounds

30 min of magnetic stirring at 40°C. Into the mixed solution was slowly added 15 g of KH550 under stirring. The resultant pale yellow transparent liquid was stirred at 40°C for 15 min, followed by heating at 80°C for 150 min to afford a milky white liquid, the NCP. The as-obtained NCP (15% of solid content) was added into 30 ml of deionised water at different dosages (2.0, 4.0, 6.0 g and 8.0 g) under vigorous agitation to afford NPs (corresponding mass fraction of NPs is 1, 2, 3 and 4%) with different sizes through self-aggregate.

2.3. Characterisation of NCP: Transmission electron microscopy (TEM, JEOL JEM-2010) was used to observe the morphology and size of the prepared nanoparticles. A field environmental scanning electron microscope (ESEM; FEI Quanta-250, AFEI, USA) was used to observe microscopic features in the gel. A Zetasizer Nano ZS90 apparatus (Malvern Instrument; Maggie Company Ltd.; UK) was performed to determine the nanoparticle size of the aqueous dispersion of NCP by dynamic light scattering at 25°C. Three repeat measurements were conducted, and the average of the repeat measurements is reported in this Letter. The interaction between boric acid and KH550 silane coupling agent and NPs-cross-linked guar gum were investigated with an AVATAR-360 Fourier transform infrared spectrometer (FTIR; Nicolet Instrument Company, USA).

2.4. Preparation of NPs-cross-linked guar gum gels and evaluation of its rheological and breaking properties: 3.0 g of guar gum gelling agent was slowly added into 1.0 l of deionised water under vigorous stirring, and aqueous sodium hydroxide was added to adjust the pH

of the solution to be about 9. The resultant mixed solution was hydrated at 30°C for 2 h with an electric oven to afford the guar gum solution with a concentration of 3.0 g/l. The 100 ml of the resultant guar gum solution was separately added 4.0, 3.0, 2.0 and 1.0 ml (corresponding mass fraction of NPs is 1, 2, 3 and 4%) of the NPs cross-linker under stirring to obtain four cross-linked gel samples.

The rheological properties of the cross-linked gel samples was determined with a TA rheometer (model DHR-2; TA Instrument Company, USA). The elastic modulus and viscous modulus of the cross-linked gel samples versus frequency were recorded under a constant shear strain of 7% and a temperature of 25°C; and their viscometric response to temperature in the range of 30–75°C was recorded with a 25 mm parallel plate under a constant shear rate of 170 s^{-1} .

The gel breaking behaviour of the guar gum solution was evaluated with a FA2004 electronic balance (Shanghai Anting Electronic Instrument Factory; Shanghai, China). Briefly, 100 ml of the guar gum solution containing 0.04% NPs cross-linker and 0.05% breaker (relative to the guar gum solution) was heated at 80°C for 2 h with an electric oven to obtain the breaking liquid. The content of the residue was measured with the electronic balance. The viscosity of the breaking liquid was measured with a NDJ-1 rotational viscometer (Shanghai Jingketianmei Scientific Instrument Company; Shanghai, China).

3. Result and discussion

3.1. Characterisation of NCP and NPs: Fig. 2 presents the TEM images of NPs. The NPs were spherical and the particle size was about 10 nm. The surface-modified silane coupling agent was allowed to undergo hydrolysis-condensation process at room temperature to obtain NPs with different sizes [14, 15]. The nanoparticles with an average size of 10, 20, 30 and 35 nm (see Fig. 3) and good dispersibility in water were obtained by properly adjusting the mass fraction of NPs.

Fig. 4 shows the FTIR spectra of H_3BO_3 , KH550 and as-prepared NCP. The absorption bands at 3220 and 1634 cm^{-1} are assigned to the stretching vibration of O-H and bending vibration of H-O-H (Fig. 4a), which confirms the presence of crystal water and absorbed water in boric acid. The absorption peaks of B-O-B and B-O-H are located at 1430 and 1192 cm^{-1} . The absorption peaks of Si-O-C₂H₅ are located at 2974, 1457 and 1079 cm^{-1} , and the absorption bands at 3360 cm^{-1} was assigned to the stretching vibration of N-H (Fig. 4b). The absorption peak of N-B is located at 1344 cm^{-1} (Fig. 4c), which indicates that boric acid has been introduced on the surface of KH550 carrier via chemical interaction.

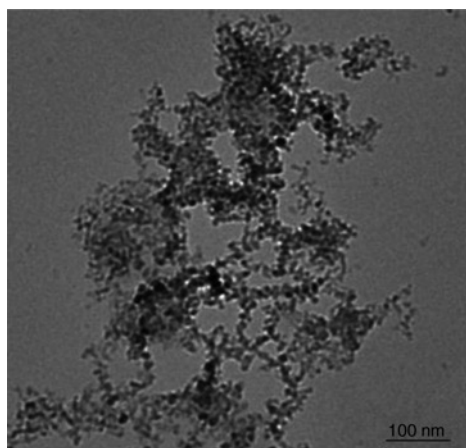


Fig. 2 TEM image of NPs

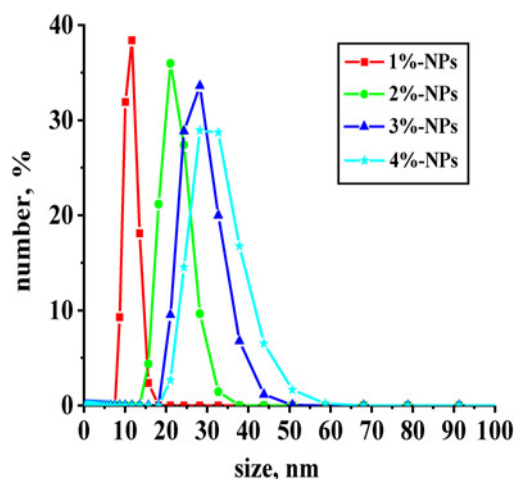


Fig. 3 Number-weighted particle size distribution determined by light dynamic light scattering

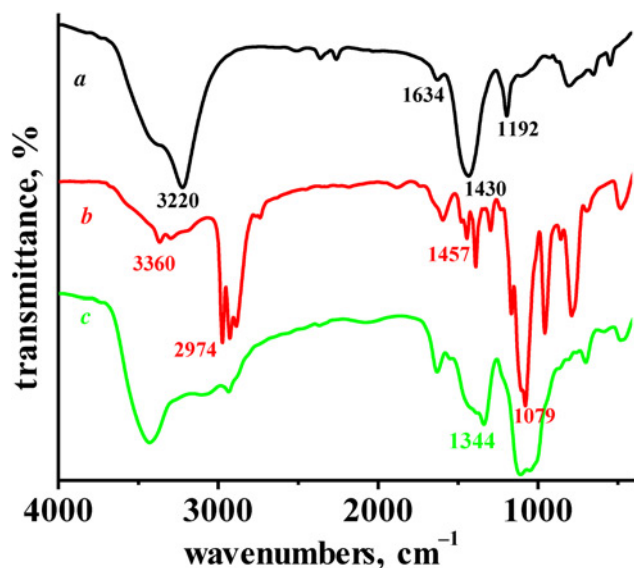


Fig. 4 FTIR spectra of
a H_3BO_3
b KH550, and
c NCP

Fig. 5 schematically illustrates the formation mechanism of NPs, where three steps of chemical reaction are involved. Namely, when H_3BO_3 is added into KH550, the -OH group of H_3BO_3 reacts with the $-\text{NH}_2$ group of KH550 to achieve chemical bonding between H_3BO_3 and KH550 yielding NCP (Fig. 5a). The NCP undergoes partial hydrolysis to allow its $\text{Si}-\text{O}-\text{C}_2\text{H}_5$ group to be transformed into $\text{Si}-\text{OH}$ group (Fig. 5b), thereby yielding NPs via self-condensation (Fig. 5c). The substitution of the active -OH group of NCP by the organic chains leads to steric hindrance, thereby preventing NCP from further agglomerating [24]. Fig. 6 shows the FTIR spectra of NPs, guar gum and NPs-cross-linked guar gum. In the spectra of the NPs-cross-linked guar gum system, no additional peak could be observed, indicating that formation of covalent bonds between the guar gum and the NPs can be excluded. However, a clear shift of the bands for guar gum occurring in the 1079 cm^{-1} . To be specific, the bands observed for guar gum at 1079 cm^{-1} shifted to 1092 cm^{-1} when guar gum was mixed with NPs. It is important to note that NPs does not show any significant

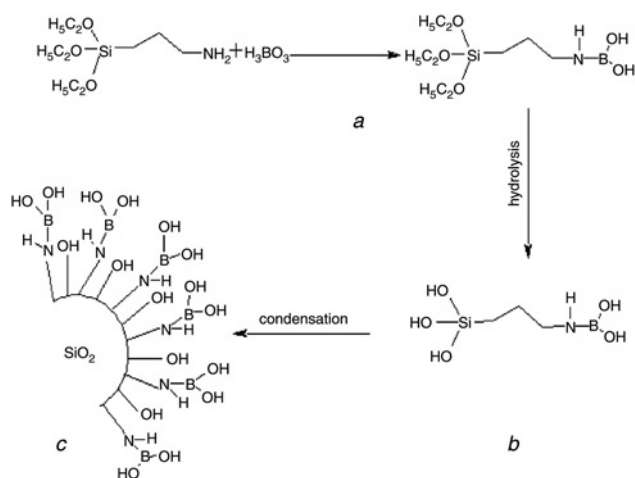


Fig. 5 Schematic illustration of the formation of NPs
a NCP
b The hydrolysate of NCP
c NPs

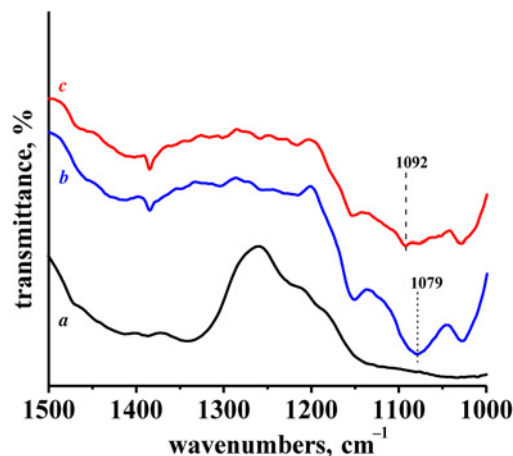


Fig. 6 FTIR spectra of
a NPs
b Guar gum, and
c NPs-cross-linked guar gum

absorption at this wavenumber. The occurrence of a similar shift for NPs-cross-linked guar gum system suggests that the NPs cross-link guar gum through hydrogen bonds. This type of interaction was also reported for guar gum which had absorbed onto several oxide minerals [16].

3.2. Rheological properties of NPs-cross-linked guar gum: Fig. 7 shows the elastic and viscous moduli of various NPs-cross-linked guar gum gels. It can be seen that the elastic modulus rises with frequency, this increase in the elastic modulus could be attributed to an increase in the crosslink density of the guar gel. At higher frequency, the polymer chains could be intertwined more closely in order to maintain sufficient interchain contacts, therefore, the higher crosslink density could be achieved. The elastic and viscous moduli of the guar gum gels tend to increase with the increase of the cross-linker mass fraction. Particularly, the guar gum gel cross-linked by 4% of NPs exhibits the highest elastic modulus as the frequency rises from 0 to 100 rad/s. Besides, the viscous modulus tends to rise with increasing cross-linker concentration at low frequencies, whereas the elastic modulus

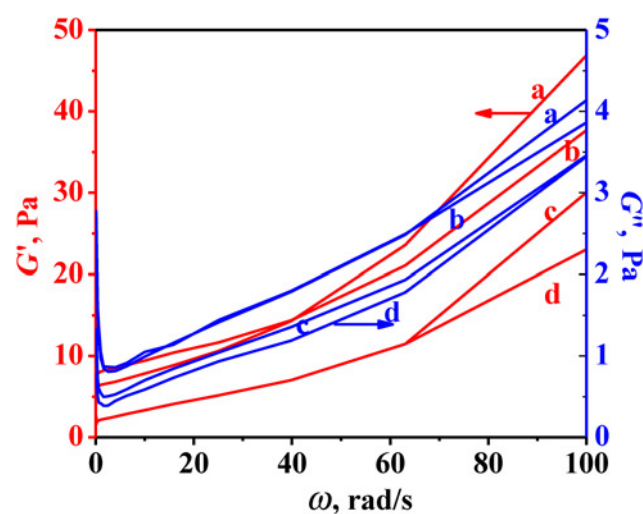


Fig. 7 Elastic and viscous moduli of NPs-cross-linked guar gum gels (concentration: 3.0 g/l; pH = 9) with different mass fraction of NPs cross-linker
a 4%
b 3%
c 2% and
d 1% at 25°C and a shear strain of 7%

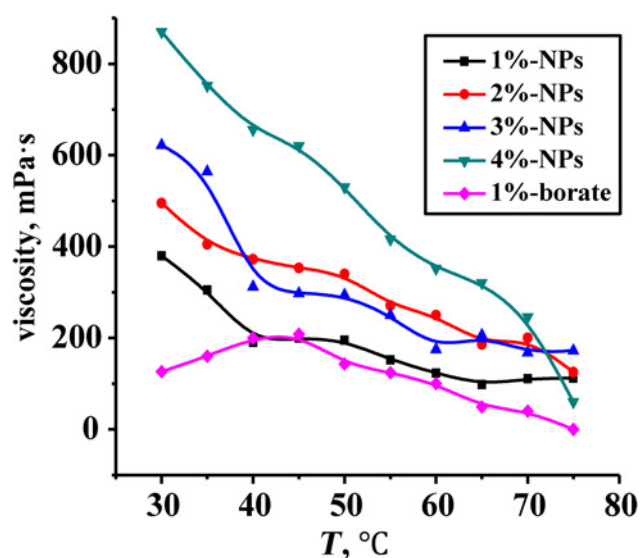


Fig. 8 Viscosity-time curves of NPs-cross-linked guar gum gels with different mass fractions (1, 2, 3 and 4%) of NPs cross-linker and 1% of borate (3.0 g/l guar gum, pH = 9) measured at a shear rate of 170 s^{-1}

tends to rise therewith in almost the entire frequency range. This could be related to the skeleton based on nanoparticles [17, 18]. Namely, the NPs with a larger particle size can be better attached to the cis-hydroxyl group of the guar gum polymer, thereby providing more cross-linked bonds between the polymer chains and increasing the elastic and viscous moduli of the guar gum gel. In other words, the particle size of NPs has a significant effect on the cross-linking efficacy of the guar gum [19]. Moreover, the NPs-cross-linked guar gum gels have higher G' values (elastic modulus) rather than G'' values (viscous modulus) in the entire frequency range, which means that polymer chain network is formed in the NPs-cross-linked guar gum gels [20, 21].

During hydraulic fracturing, the fracturing fluid was first prepared on the ground, and then it was injected into the wall. The temperature of the guar gum fracturing fluid increases with increasing depth of well. The stability of the guar gum fracturing fluid would be deteriorated at a high temperature, which is harmful to the fracturing performance. Fig. 8 shows the viscosity-time curves of NPs-cross-linked guar gum gels (concentration: 3.0 g/l; pH = 9) with different mass fractions (1, 2, 3 and 4%) of NPs cross-linker and 1% of borate measured at a shear rate of 170 s^{-1} . As the temperature increases from 30°C to 75°C , the viscosity of the guar gum gels, whether cross-linked by NPs or by borate, decreases, which indicates that both the NPs-cross-linked guar gum and borate-cross-linked guar gum are unstable at a high temperature. Particularly, the guar gum fracturing fluid cross-linked with 4% of NPs exhibits the highest viscosity, which is attributed to the formation of large and sophisticated guar gum polymer chain network in the presence of NPs with an increased particle size. Moreover, although the NPs-cross-linked guar gum gel is unstable at a high temperature, it possesses a better temperature resistance than the borate-cross-linked guar gum gel. Fig. 9 presents ESEM micrographs of (Fig. 9a) NPs and (Fig. 9b) borate-cross-linked guar gum gels. It shows that NPs-cross-linked guar gum gels form larger and sophisticated network structure than borate-cross-linked ones, which we attributed to the bigger the particle size of cross-linker that could further attach to the cis-hydroxyl groups on guar polymer to maintain sufficient interchain contacts to provide enough crosslinks to achieve larger and sophisticated network structure.

3.3. Breaking behaviour of guar gum gels cross-linked by borate and NPs: Traditional fracturing fluids use viscosifying agents (such as Guar gum and its derivatives) to support and carry the proppant. However, guar gum forms insoluble residue which

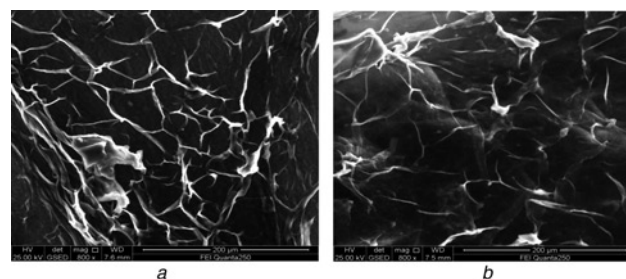


Fig. 9 ESEM micrographs of
a NPs and
b Borate-cross-linked guar gum gels

Table 1 Breaking behaviour of guar gum gels cross-linked by borate and NPs

Cross-linker	Breaker	Residue content (g/l)	Viscosity (mPa·s)
borate	$(\text{NH}_4)_2\text{S}_8$	228	1.90
NPs	$(\text{NH}_4)_2\text{S}_8$	173	1.65

plugs pore throats and causes impaired leak-off, thereby causing fatal damage to tight and shale gas reservoirs [22, 23]. Table 1 shows the breaking performance of the guar gum gels cross-linked by borate and NPs. The residue content of the guar gum gels cross-linked by borate and NPs are as much as 228 and 173 g/l. This indicates that the guar gum gel cross-linked by NPs causes less damage than traditional guar gum gel cross-linked by borate. Meanwhile, the breaking liquid viscosity of the guar gum gel cross-linked by NPs is lower than that of the counterpart cross-linked by borate, which means that NPs as the cross-linker facilitates the thorough breaking of the guar gum gels. However, gel breaking mechanism is not clear and needs further study.

4. Conclusion: A NCP was prepared by introducing boric acid to the surface of silane coupling agent as the carrier, where the boric acid was combined with the silane coupling agent through N-B bond. Resultant NCP was allowed to undergo hydrolysis under different concentrations yielding NPs with different sizes. The as-obtained NPs were adopted as the cross-linkers to prepare guar gum fracturing fluids. The measurements of the elastic and viscous moduli of the cross-linked guar gum gels demonstrate that the NPs-cross-linked guar gum gel exhibits better temperature resistance and shear resistance than the one cross-linked by borate. In the meantime, the guar gum gel cross-linked by NPs exhibits better breaking behaviour than the one cross-linked by borate. The good rheological properties and breaking behaviour indicate the as-obtained guar gum fracturing fluid could find promising application in the extraction oil of low-permeability reservoirs.

5. Acknowledgments: This research was financially supported by the National Natural Science Foundation of China (grant no. 21371047) and Plan for Scientific Innovation Talent of Henan Province (grant no. 164200510005).

6 References

- [1] Sovacool B.K.: 'Palm oil-based biofuels and sustainability in south-east Asia: A review of Indonesia, Malaysia, and Thailand renewable. sustainable', *Energy. Rev.*, 2014, **37**, pp. 249–264
- [2] Barati R., Hutchins R.D., Friedel T., *ET AL.*: 'Fracture impact of yield stress and fracture-face damage on production with a three-phase 2D model', *SPE. Prod. Oper.*, 2009, **24**, pp. 336–345

- [3] Lan O., Ghanbari E., Dehghanpour H., *ET AL.*: 'Water loss versus aking time: spontaneous imbibition in tight rocks', *Energy. Technol.*, 2014, **2**, pp. 1033–1039
- [4] Zou Y., Ma X., Zhang S., *ET AL.*: 'The origins of low-fracture conductivity in soft shale formations: an experimental study', *Energy. Technol.*, 2015, **3**, pp. 1233–1242
- [5] Zhang M., Guo W., Lei Z.: 'Patent analysis of shale gas technology in China and implications for its exploitation', *Energy. Technol.*, 2014, **2**, pp. 1040–1045
- [6] Goel N., Shah S.N., Yuan W.L., *ET AL.*: 'Suspension characteristics of borate-crosslinked gels: rheology and atomic force microscopy measurements', *J. Appl. Polym. Sci.*, 2001, **82**, pp. 2978–2990
- [7] Bishop M., Shahid N., Yang J., *ET AL.*: 'Determination of the mode and efficacy of the cross-linking of guar by borate using MAS 11B NMR of borate cross-linked guar in combination with solution 11B NMR of model systems', *Dalton. Trans.*, 2004, **17**, pp. 2621–2634
- [8] Kramer J., Proud'home R.K., Wiltzius P.A., *ET AL.*: 'Comparison of Galactomannan crosslinking with organotitanates and borates', *Colloid. Polym. Sci.*, 1988, **266**, pp. 145–155
- [9] Harris P.C.: 'Chemistry and rheology of borate-crosslinked fluids at temperatures to 300F', *J. Pet. Technol.*, 1993, **45**, pp. 264–269
- [10] Palisch T.T., Vincent M., Handren P.J.: 'Slickwater fracturing: food for thought', *SPE. Prod. Oper.*, 2010, **25**, pp. 327–344
- [11] Mardoch L.C., Germanovich L.N., Numer J.: 'Analysis of a deformable fracture in permeable material', *Anal. Method. Geomech.*, 2006, **30**, pp. 529–561
- [12] Mesmer R., Baes C.Jr.: 'Acidity measurements at elevated temperatures. V. Aluminum ion hydrolysis', *Inorg. Chem.*, 1971, **10**, pp. 2290–2296
- [13] Hurnaus T., Plank J.: 'behavior of titania nanoparticles in cross-linking hydroxypropyl guar used in hydraulic fracturing fluids for oil recovery', *Energy. Fuels.*, 2015, **29**, pp. 3601–3608
- [14] Bernards T.N.M., Van Bommel M.J., Boonstra A.H.: 'Hydrolysis-condensation processes of the tetra-alkoxysilanes TPOS,TEOS and TMOS in some alcoholic solvents', *J. Non-cryst. Solids.*, 1991, **134**, pp. 1–13
- [15] De G., Karmakar B., Ganguli D.: 'Hydrolysis-condensation reactions of TEOS in the presence of acetic acid leading to the generation of glass-like silica microsphere in solution at room temperature', *J. Mater. Chem.*, 2000, **10**, pp. 2289–2293
- [16] Ma X., Pawlik M.: 'Role of background ions in guar gum adsorption on the oxide minerals and kaolinite', *J. Colloid Interface Sci.* 2007, **313**, pp. 440–448
- [17] Sinton S.W.: 'Complexation chemistry of sodium borate with poly (vinyl alcohol) and small diols: a boron-11 NMR study', *Chem. Phys. Macromol.*, 1987, **20**, pp. 2430–2441
- [18] Pezron E., Ricard A., Lafuma F., *ET AL.*: 'Reversible gel formation induced by ion complexation. 1. Borax-galactomannan interactions', *Chem. Phys. Macromol.*, 1988, **21**, pp. 1121–1125
- [19] Yount W.C., Loveless D.M., Craig S.L.: 'Strong means slow: dynamic contributions to the bulk mechanical properties of supramolecular networks', *Chem. Phys. Macromol.*, 2005, **44**, pp. 2746–2748
- [20] Tayal A., Pai V.B., Khan S.A.: 'Rheology and microstructural changes during enzymatic degradation of a guar-borax hydrogel', *Chem. Phys. Macromol.*, 1999, **32**, pp. 5567–5574
- [21] Maerker J.M., Sinton S.W.: 'Rheology resulting from shear-induced structure in associating polymer solutions', *J. Rheol.*, 1986, **30**, pp. 77–79
- [22] Maloney D.R., Gall B.L., Raible C.J.: 'NonDarcy gas flow through propped fractures: effects of partial saturation, gel damage, and stress', *SPE. Prod. Eng.*, 1989, **4**, pp. 417–422
- [23] Xu B., Hill A.D., Zhu D., *ET AL.*: 'Experimental evaluation of guar-fracture-fluid filter-cake behavior', *SPE. Prod. Oper.*, 2011, **26**, pp. 381–387
- [24] Jal P.K., Patel S., Mishra B.K.: 'Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metal ions', *Talanta*, 2004, **62**, pp. 1005–1028