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Viscoelastic Properties of Oil-in-Water (o/w) Pickering Emulsion Stabilized by Surfactant–Polymer and Nanoparticle–Surfactant–Polymer Systems

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ABSTRACT: Oil in water (o/w) Pickering emulsion stabilized by a nanoparticle–surfactant–polymer system shows better thermal stability than the one stabilized by a surfactant–polymer system. The knowledge of the viscoelastic properties of these emulsion systems is important for their successful application for high pressure and high temperature conditions related to enhanced oil recovery (EOR). In this work, the viscoelastic behavior (G' and G'') of the Pickering emulsion stabilized by a nanoparticle–surfactant–polymer system has been investigated as a function of pressure (0.1–30 MPa) and temperature (298–371 K) and compared with conventional emulsion stabilized by a surfactant–polymer system. An oilfield polymer polyacrylamide (PAM) along with nanoparticles (SiO_2 and clay) and conventional surfactants are used for the formulation of Pickering o/w emulsion systems. Both the emulsion systems showed liquid-like behavior at 0.1 MPa with G'' dominance over the complete range of strain amplitude. It is observed that Pickering emulsions are found to be more stable at high pressure conditions as the pressure effect did not show any significant influence on the viscoelastic properties. Pickering emulsions behave like viscoelastic fluid at all pressure conditions as compared to the surfactant–polymer stabilized emulsion, wherein the storage modulus has shown rapid increase with increase in pressure from 0.1 to 30 MPa. In addition, Pickering emulsions showed better flowability by showing stable G'' values for varying conditions of temperature as compared to the surfactant–polymer stabilized emulsion. The stable viscoelastic response for Pickering emulsion is beneficial for their implementation at complex reservoir conditions.

1. INTRODUCTION

Viscoelastic fluids exhibit both the elastic and viscous characteristics when encountering deformation. The measurement of viscoelastic properties of fluids is an important aspect due to their vast practical applications, particularly in upstream oil and gas industry. The study on the viscoelastic measurements may provide several pieces of useful information, such as, evolution of dynamic viscoelastic properties, *viz.*, storage modulus (G') and loss modulus (G'').¹ The majority of the work based on viscoelastic behavior, both experimental and theoretical, are devoted to emulsion systems and complex fluids.^{2–5} Oil in water (o/w) Pickering emulsion is an important engineering product, covering many aspects of industrial applications, for example, in pharmaceuticals, food, agrochemicals, paints, cosmetics, and crude oil recovery. Knowledge of the rheological properties of emulsions is required to understand their long-term physical stability. This approach is useful in developing and expanding applications of Pickering emulsions, particularly for the oil and gas industry.

In an emulsion, one liquid is dispersed in another liquid in the form of droplets, and the emulsifiers, such as surfactant, polymer, and colloidal particles, are added to achieve the stabilization. Emulsifiers synergistically interact and adsorb at the oil–water interface to form a protective film to resist the droplet deformation. Droplet deformation caused by high pressure high temperature (HPHT) conditions are the important factors conceding the stability of o/w emulsions and subsequently affecting the rheological properties (G' and G''). Several literature studies are being carried out to

understand the effect of emulsifiers on the rheological properties of an emulsion system. The viscoelastic properties of the o/w emulsion stabilized by vegetable protein were investigated in the presence of polyoxyethylene glycol nonionic surfactant emulsifier.³ In another study, the nonionic non-ylphenol (Tergitol NP6) surfactant was observed to promote a significant increase in the viscosity and storage modulus of a hydrophobically modified alkali-swelling emulsion (HASE) polymer based solution.⁶ The addition of a filler (cellulose microfibrils) was sufficient to change the rheological behavior of a sodium acrylate hydrogel by disappearing the crossover point ($G' \gg G''$) and shear thinning behavior due to the formation of a physical network of fibrils in the system.⁷ It was previously shown that the o/w emulsion in the presence of a water-soluble polymer, such as xanthan gum, was stable against creaming and exhibited solid-like behavior due to the formation of a macroscopically stable structure of droplets.⁸

Polyacrylamide (PAM) has shown extensive interest as a stabilizer for numerous oilfield applications such as, viscosity enhancer, drilling fluid design and in EOR due to its favorable rheology, compatibility with other chemicals and cost-effectiveness.⁹ Recently, it is observed that PAM significantly helped in improving the thickening efficiency of aqueous phase making PAM an interesting polymer for EOR applications.¹⁰ It

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is well-known that partially hydrolyzed PAM (HPAM) is used more for enhanced oil recovery than simple PAM. However, the studies involving PAM and HPAM both are often reported in the literature for enhanced oil recovery studies.^{10–13} Indeed, many of the studies reported in the literature are related to the normal conditions of pressure and temperature. High temperature was typically observed to deform the stability and rheological behavior of o/w emulsion stabilized by conventional emulsifiers.^{14–16} High pressure condition was also found to result in the formation of large size bridging flocs by promoting interaction between emulsified droplets. As a result, this affects the viscoelastic properties (G' and G'') as compared with that of the unflocculated emulsion system.¹⁷ The information on rheological behavior of emulsion systems at HPHT conditions is necessary for their successful application related to upstream oil and gas industrial application, such as in enhanced oil recovery (EOR).

Oil in water (o/w) Pickering emulsion stabilized by nanoparticles is one of the suggested routes to provide the long-term stability with improved rheological behavior at HPHT conditions where the conventional emulsions are not stable.¹⁸ For Pickering emulsions, the presence of surfactant was observed to modify the wettability of nanoparticles to promote their adsorption at the oil–water interface making emulsion stable by reducing the coalescence.^{19,20} The Janus nanoparticles of two sides of different chemistry suggested promising solutions with advanced properties for the problems associated with the use of Pickering emulsions in material science and biomedicine.²¹ The significant increase in the elastic properties of olive oil–water emulsions stabilized by clay particles and surfactant is observed due to the formation of a mechanical barrier of particles around the droplets, preventing coalescence of emulsion droplets.²² The simultaneous use of clay and hydrophobin (protein) resulted in a long-term stable o/w Pickering emulsion with high G' , yield stress, and viscosity (1 Pa.s). The credit of higher stability and improved rheological properties was ascribed to the elasticity of a membrane emerging due to the synergistic interaction between clay and hydrophobin.²³ Another study of o/w Pickering emulsion stabilized by laponite particles also confirmed the formation of an elastic structure of oil droplets and particles, which helped in stabilizing the emulsions for long duration.²⁴ Recently, it has been observed that the inclusion of silica nanoparticles can suitably change the viscoelasticity of fluid systems such as polymer solution from a liquid-like (G'') to gel-like (G') behavior for EOR application at high temperature conditions.²⁵ In addition, the stability and rheological behavior of xanthan based fluids showed that the presence of high pressure helps to nullify the effect of increase in temperature thereby improving the rheological properties.²⁶ An excellent review on synthesis and rheological characterization of electrorheological and magnetorheological smart fluids was recently proposed.²⁷ It was reported that stabilizers, such as graphene oxide, clay, SiO_2 , Fe_2O_3 , and Fe_3O_4 , acted as surfactants and helped in developing Pickering based stable and smart composite materials using the Pickering emulsion polymerization method. These materials may show potential use in enhanced oil recovery or reservoir characterization using nanoparticles. The rheological characteristics of SiO_2 based Pickering o/w emulsion for subsurface EOR operations were investigated and presented with the significant advantages of emulsion use for EOR.¹⁸ In our previous work, we have shown that the nanoparticles (SiO_2 and clay) along with surfactant and oilfield

polymer, polyacrylamide (PAM), can be used to prepare thermally stable Pickering emulsion suitable for high temperature applications.²⁸ The information on the rheological characterization of these emulsion systems at HPHT conditions is necessary before they can be used efficiently.

In this study, we report the viscoelastic behavior (G' and G'') of Pickering emulsion stabilized by a nanoparticle–surfactant–polymer system and compared with those of o/w emulsion stabilized by a surfactant–polymer system (without nanoparticles) and for a pure aqueous solution of polyacrylamide at varying pressure (0.1 to 30 MPa) and temperature (298 to 371 K) conditions. Polyacrylamide, a commonly used water-soluble polymer for enhanced oil recovery, is being used along with nanoparticles (SiO_2 and clay) and surfactant for the formation of stable Pickering emulsion.

2. EXPERIMENTAL WORK

2.1. Materials. The details on the chemicals used in this study are listed in Table 1. The nanoparticles used are SiO_2 (15

Table 1. Details on the Chemicals and Nanoparticles Used in the Study

chemical/nanoparticles	purity, mass fraction	supplier
hydrophilic SiO_2 with APS: 15 nm	0.995	Sisco Research Laboratories
partially hydrophobic clay with APS: <80 nm	0.99	
polyacrylamide (PAM)	>0.90	SNF Floerger
sodium dodecyl sulfate (SDS)	0.90	Ranbaxy Fine Chemicals Limited

nm) and clay (<80 nm) provided by Sisco Research Laboratory, Mumbai, India (CAS No. 7631-86-9 for SiO_2 and 1332-58-7 for clay nanoparticles). All samples are prepared by using an accurate analytical weighing balance (Reptech RA-1012 with a repeatability of ± 0.0001 mg). The oil is purchased from a commercial retail outlet of Hindustan Petroleum Corporation Ltd., India. The supplied oil is lubricating oil with a flash point of around 488 K and density 0.97 gm/cc. The polymer polyacrylamide (PAM) of molecular weight 10^7 g/mol with purity >90.00% is used. Water used in all experiments is purified by deionization and filtration with a Millipore Elix-10 purification apparatus.

2.2. Preparation of Emulsions. The details on the preparation of o/w emulsion stabilized by nanoparticle–surfactant–polymer and surfactant–polymer system are given in our recent work.²⁸ Brief details are being provided here for reference. O/w emulsion systems are prepared using 1000 ppm PAM in aqueous phase. Oil volume fraction of 0.25 is used to prepare the emulsions. A surfactant, sodium dodecyl sulfate (SDS), is used along with a conventional detergent (with ingredients such as, 5–15% anionic surfactants; oxygen-based bleaching agents, viz., <5% nonionic surfactants, phosphonates, polycarboxylates; and zeolites) in the ratio of 43:57, respectively, in order to get surfactant mixture (henceforth referred as surfactant) with a hydrophilic–lipophilic balance (HLB) value of 9.98 close to that of oil (HLB = 10) used in this study. The critical micelle concentration (CMC) of 0.20 wt % for surfactant–polymer solution is determined by surface tension measurement using spinning drop video tensiometer (SVT 20N, Data Physics, Germany). The surfactant concentration slightly higher than CMC (CMC + 10% of CMC = 0.22

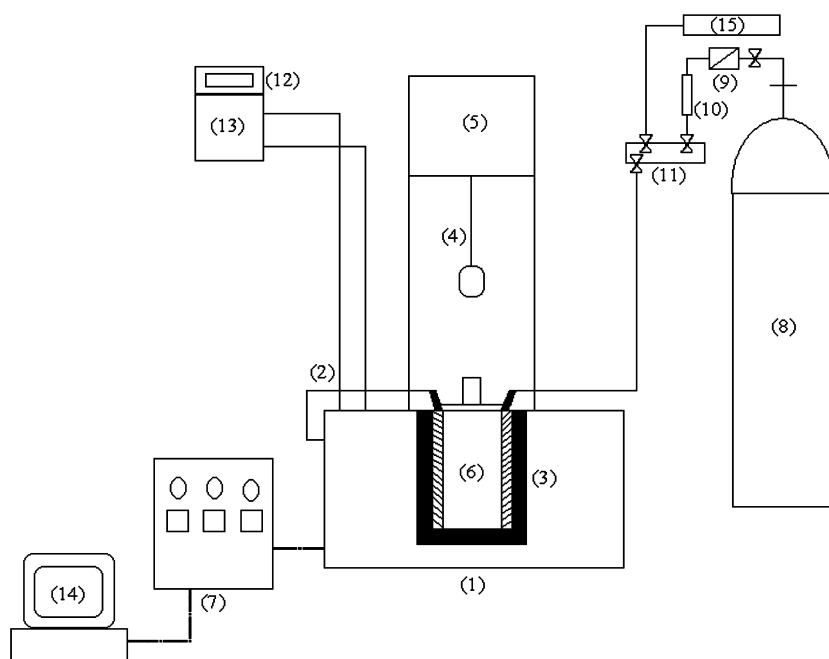


Figure 1. Schematic of the experimental setup used for the measurement of viscoelastic properties of emulsion. 1: High pressure high temperature compact rheometer; 2: Temperature and pressure sensor; 3: Thermal jacket; 4: Magnetic coupling; 5: Measuring head; 6: Pressure cup; 7: Data acquisition unit; 8: Gas cylinder; 9: Anti freezing gas heater; 10: Pressure regulator; 11: Pressure valves assembly; 12: Temperature control unit; 13: Escy circulator bath; 14: Computer; and 15: Hydraulic pump unit.

wt %) corresponding to 1000 ppm is used in the present study.²⁸ Oil is added simultaneously to the surfactant–polymer solution in batches, while stirring is done at a speed of 3000 rpm to obtain o/w emulsion stabilized by surfactant–polymer system. For the formulation of o/w Pickering emulsion, nanoparticles such as SiO₂ and clay of 1.0 wt % concentration are used by mixing a nanoparticle to a surfactant–polymer stabilized o/w emulsion stirring at 3000 rpm for 1 h at room temperature.²⁸

2.3. Experimental Set-up and Procedure. The dynamic rheological measurements are carried out at different pressure (0.1 to 30 MPa) and temperature (298 to 371 K) conditions in a compact controlled-strain rheometer MCR-52 (Anton Paar, Physica, Austria). The schematic diagram of the experimental setup with essential units to pressurize and heat the samples is shown in Figure 1. Emulsions are pressurized using a nitrogen gas filled in a pressure regulated cylinder. The outlet capacity of the pressure regulator is of maximum 15 MPa. To pressurize the emulsion samples at pressure levels of more than 15 MPa, an external hydraulic pump unit is used and attached to the pressure cup systematically using connectors. To increase the temperature of the emulsion samples, a silicon oil is circulated through the thermal jacket provided around the pressure cup. The temperature of the silicon oil is controlled using a temperature sensor (Pt-100) provided with a circulator bath (Escy Enterprises, India). The magnetic coupling is positioned over the head of the pressure-cup, and it is oscillated using a controlled torque to measure the deformation.

To ensure the linear viscoelastic (LVE) region for both o/w emulsion stabilized by surfactant–polymer and nanoparticle–surfactant–polymer systems, strain-sweep measurements were conducted to measure dynamic moduli in the range of 0.1 to 100% of the strain amplitude, while the frequency is kept constant at 10 rad s^{−1}.⁸ This approach is useful in determination of the LVE region (at which G' remains

constant with changing strain amplitude) and the critical strain (crossover point) above which G' decreases nonlinearly with further increase in the strain amplitude.^{8,29} Frequency-sweep measurements are expected to perform at an applied strain within the LVE region, in order to measure dynamic moduli at variable frequencies. Due to the insensitivity of the rheometer below 1.0% strain amplitude for the strain-sweep measurements, hence, these are reported above 1.0% of the strain amplitude. However, Pickering emulsion stabilized by a nanoparticle–surfactant–polymer system did not show the presence of LVE range satisfactorily for the entire range of the strain amplitude (1.0 to 100%) and pressure (0.1 to 30 MPa). The LVE range is expected to occur nearby strain amplitude of 1.0%, hence, we carried out the frequency-sweep measurements from 100 to 1.0 rad s^{−1} with low strain amplitude of 2.0% for Pickering o/w emulsion stabilized by nanoparticle–surfactant–polymer system.² This finding is consistent with the previous studies of a strain-sweep study for oil-in-water emulsions.² The storage modulus G' and loss modulus G'' are recorded as a function of the frequency and reported. Before the start of the measurements, each sample of the emulsion is mildly agitated for homogenization.

3. RESULTS AND DISCUSSION

Dynamic oscillatory measurements are used to enumerate the elasticity and the maximum strain that the substance can tolerate before shear thinning. The characterization of the o/w emulsion system and the viscoelastic properties of the pure PAM aqueous solution is presented first followed by the details on the viscoelastic properties of o/w emulsion stabilized by surfactant–polymer and nanoparticle–surfactant–polymer systems.

3.1. Characterization of o/w Emulsions. The details on the preparation of o/w Pickering emulsion are provided in our recent work.²⁸ Brief details verifying the formulation of

Pickering emulsion are being provided here for the reference. To confirm the formation of Pickering emulsion, the interfacial emulsion structure and deposition of nanoparticles are examined by scanning electron microscopy (SEM) using a scanning electron microscope (ZEISSUltra-55, Germany). Interfacial tension (IFT) measurements are also conducted using spinning drop video tensiometer (SVT 20N, Dataphysics, Germany) to evidence the existence of nanoparticle barrier at the oil droplet surface. It is observed that the addition of nanoparticle to the surfactant–polymer emulsion reduces IFT significantly due to the enhanced adsorption of nanoparticles, facilitating the formulation of nanoparticle stabilized Pickering emulsion.²⁸ As compared to surfactant–polymer o/w emulsion, the Pickering emulsions were found to be more stable against creaming as shown in Figure 2. The rate of creaming for the

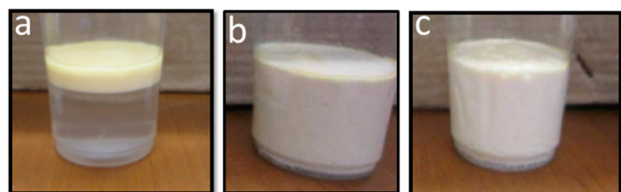


Figure 2. Photographic images of o/w emulsions stabilized by surfactant–polymer and nanoparticle–surfactant–polymer systems at 298 K. (a) surfactant–polymer emulsion just after 3 h of emulsification; (b-c) SiO₂ and clay o/w emulsions, respectively, after 23 days of emulsification.

surfactant–polymer emulsion is higher as compared to the nanoparticle–surfactant–polymer stabilized emulsion due to the relatively faster upward movement of the interface with time, which corresponds to the higher rate of creaming. The droplet size of the emulsions is determined using a particle size analyzer (Zetasizer Nano-S90, Malvern Instruments, UK) based on a light scattering technique. The initial droplet size of the surfactant–polymer stabilized o/w emulsion is observed to be around 6.77 μm as shown in Figure 3. The droplet diameter increases to 9.27 μm after 2 h of emulsification due to droplet coalescence. The droplet size for a nanoparticle–surfactant–polymer stabilized o/w emulsion is observed to be about 2.17 μm (SiO₂) and 3.65 μm (clay) after 23 days of emulsification followed by 5.95 μm (SiO₂) after 2 months.²⁸ The droplet size

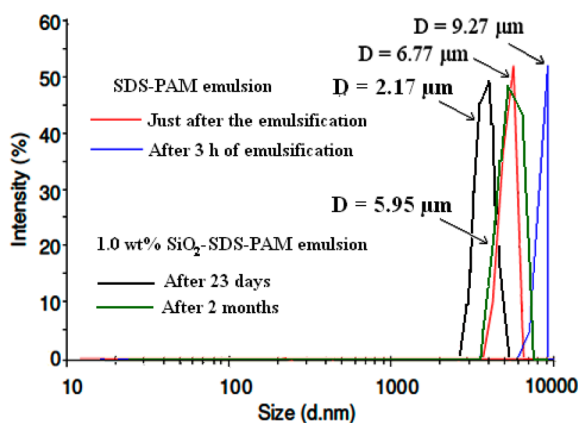


Figure 3. Droplet size determination for o/w emulsions stabilized by surfactant–polymer and nanoparticle–surfactant–polymer systems (SiO₂ stabilized) using the DLS technique at 298 K.²⁸

decreases in the presence of a nanoparticle, and the droplet size does not change significantly for nanoparticle–surfactant–polymer stabilized o/w Pickering emulsions for a period of more than a month, indicating that these emulsions do not coarsen by coalescence over a period of time.

3.2. Viscoelastic Properties of PAM Aqueous Solution.

The strain-sweep measurements for pure PAM aqueous solution (1000 ppm) were carried out to understand the effect of pressure and temperature on the viscoelastic behavior. Figure 4 shows the dynamic rheological data (G' and G'') for PAM aqueous solution. At 0.1 MPa pressure, the viscoelastic moduli of the polymer solution are found to be $G' \approx 3.11$ and $G'' \approx 1.11$ Pa at about 1.5% of the strain indicating that the PAM solution is solid-like. The strain dependence of G' of polymer solution at 0.1 MPa indicates a region of linear viscoelasticity with a plateau in G' over a limited region of small strain (1.5 to 3.0%), above which G' displays a decreasing trend, possibly due to the relaxation and disentanglement of polymer molecules. Loss modulus (G'') first exhibits a plateau in G'' up to 30% of the strain and then decreases slightly thereafter (see Figure 4a). This indicates that polymer solution at 0.1 MPa exhibits viscoelastic behavior with elasticity for a small range of strain and liquid-like nature for the entire range of the strain amplitude. The crossover point (gel-point, where $G' \approx G''$) is observed to be at about 8.49% of the strain amplitude (see Figure 4a).

A noteworthy feature in the viscoelastic property of the PAM aqueous solution is observed at high pressure conditions (>0.1 MPa). The increase in pressure is accompanied by the pronounced enhancement in the magnitude of G' indicating solid-like behavior (see Figure 4a). It is observed that the storage modulus of the polymer solution increases by about 2 orders of magnitude for G' and reaches to about 110 Pa at 10 and 30 MPa (at 1.5% strain), which is much higher than the value of G' at 0.1 MPa (Table 2). In addition, the values of the storage modulus remain unchanged and overlap for high pressure conditions of 5, 10, 20, and 30 MPa (Figure 4a shows the data only for 0.1, 10, and 30 MPa for the sake of brevity). It is observed here that G' is always higher in value with plateau behavior as compared with G'' at high pressure conditions (Figure 4a), which is a characteristic behavior of gel.³⁰ As compared to 0.1 MPa, G'' at 30 MPa decreases with an increase in strain amplitude showing a minimum value at around 10–11% of the strain and then increases thereafter. Figure 4b shows sample results on the frequency-sweep measurements carried out at an applied strain (10%) in the LVE region for high pressure (30 MPa) condition at 298 K. It is to be noted here that the high pressure conditions of 5, 10, and 20 MPa and high temperatures of 298, 313, 333, 353, and 371 K showed similar values on viscoelastic moduli. It is expected here that the presence of high pressure nullifies the effect of temperature on the rheological behavior of PAM solution (also observed in our earlier studies²⁶). As observed from Figure 4b, the storage modulus G' of the polymer solution at 30 MPa is essentially independent of the frequency with higher values than loss modulus values, which confirms the characteristic behavior of gel as realized from strain-sweep experiments. The viscoelastic moduli of the polymer solution (shown in Figure 4b) indicate that the crossover point in moduli does not appear over the complete range of exercised frequency at 30 MPa as compared to 0.1 MPa. In other words, the aqueous PAM polymer solution shows viscoelastic nature at normal pressure (0.1 MPa)

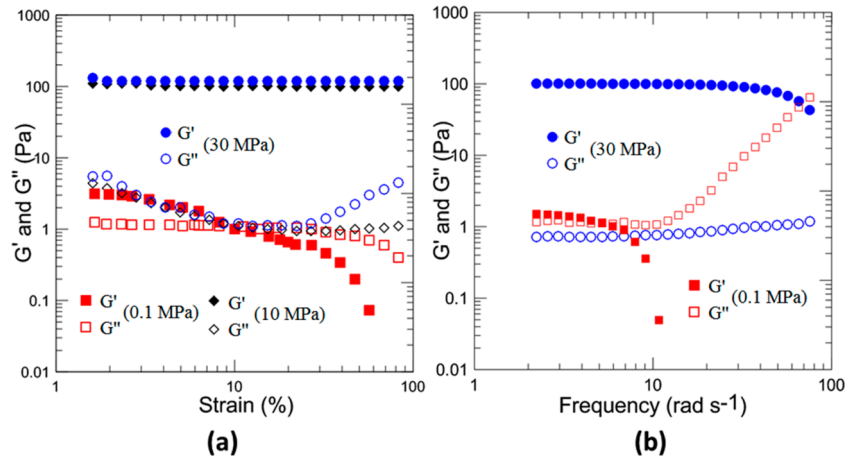


Figure 4. (a) Strain-sweep measurements for 1000 ppm PAM aqueous solution at 298 K and 0.1, 10, and 30 MPa at a constant frequency of 10 rad s⁻¹; (b) frequency-sweep measurement for pure PAM aqueous solution at 0.1 and 30 MPa at strain amplitude of 10% (LVE range). G' (solid symbols) and G'' (open symbols).

Table 2. Viscoelastic Properties of Surfactant–Polymer and Nanoparticle–Surfactant–Polymer o/w Emulsions as a Function of Pressure at 298 K

sample	strain-sweep test	strain amplitude (%)	T (K)	dynamic moduli (Pa)					
				0.1 MPa		10 MPa		30 MPa	
				G'	G''	G'	G''	G'	G''
polymer aqueous solution	10 rad s ⁻¹	1.5	298	3.11	1.11	110	4.30	110	5.60
surfactant–polymer emulsion	10 rad s ⁻¹	1.5	298		1.82	5.30	6.98	103	20.10
SiO ₂ emulsion	10 rad s ⁻¹	1.5	298		0.74	16.2	9	41	16
clay emulsion	10 rad s ⁻¹	1.5	298		0.92	1.27	4.15	4.61	6.70

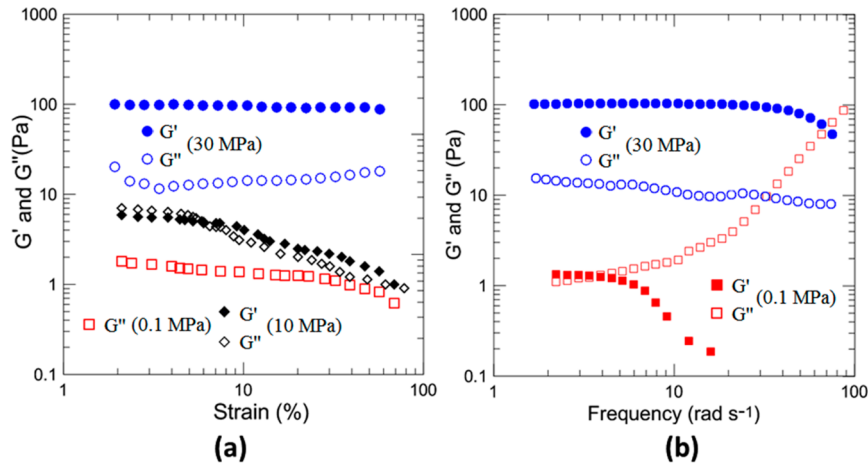


Figure 5. Effect of pressure on G' (solid symbols) and G'' (open symbols) for a surfactant–polymer stabilized o/w emulsion system at 298 K: (a) strain-sweep tests (frequency 10 rad s⁻¹) at 0.1, 10, and 30 MPa; (b) frequency-sweep test at 0.1 and 30 MPa at strain amplitude of 10% (LVE range).

conditions and gel-like at high pressure (10 and 30 MPa) conditions.

3.3. Viscoelastic Properties of Surfactant–Polymer o/w Emulsion. Figure 5 shows the effect of pressure on the viscoelastic behavior of the o/w emulsion stabilized by a surfactant–polymer system at 0.1, 10, and 30 MPa at 298 K. Table 2 shows the data for this emulsion system as a function of pressure at 298 K. It is observed that the storage modulus G' of the emulsion stabilized by the surfactant–polymer system is much lower than 0.1 Pa at 0.1 MPa and, hence, cannot be detected and, therefore, is not visible in Figure 5a. At 0.1 MPa,

the rheological behavior is completely dominated by the loss modulus G'' .³¹ As the pressure increases to 10 MPa and subsequently to 30 MPa, G' become visible and increased with an increase in pressure. At 10 MPa, values of both the moduli are close for the entire range of strain; however, the crossover point is visible around 5% of the strain amplitude. At 30 MPa, $G' > G''$, indicating a solid-like behavior of the emulsion. In addition, with increase in pressure from 10 to 30 MPa, G' increases from 5.3 Pa (10 MPa) to 103 Pa (30 MPa, see Table 2) indicating that the liquid-like nature of surfactant–polymer o/w emulsion is transforming into gel-like with increase in

pressure (Figure 5a). The reason may be attributed to the high pressure which induces an increase in the extent of droplet flocculation and reflected as the increase in the solid-like behavior.³²

Figure 5b shows the results for the frequency-sweep measurements at 0.1 and 30 MPa and 298 K conducted with strain amplitude of 10% ensuring the measurements are within LVE range. The frequency dependence of a surfactant–polymer emulsion system at 30 MPa is observed to be similar to that of a highly flocculated emulsion system showing a clear plateau region in G' and $G' > G''$ for all frequencies. It is to be noted here that the frequency-sweep measurements on G' and G'' cease to be the same with an increase in temperature above 298 K at 30 MPa. As compared to 0.1 MPa, the crossover point is not achieved at 30 MPa over the entire range of frequency probably due to the narrow LVE range (see Figure 5b).³ The results showed that the intensity of pressure indicates a profound effect on the viscoelastic behavior of surfactant–polymer o/w emulsion systems and that the emulsion changes its behavior from liquid-like to solid-like as the pressure increases from 0.1 to 30 MPa.

Figure 6 shows the effect of temperature (298 to 371 K) on the viscoelastic properties of the emulsion stabilized by a

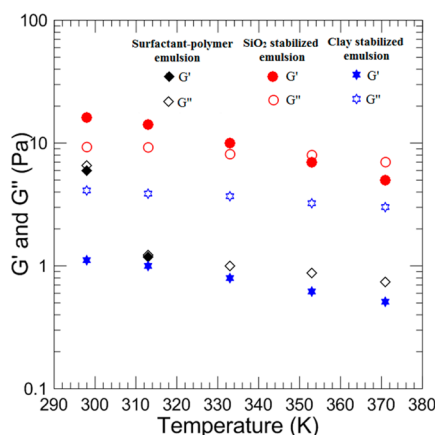


Figure 6. Effect of temperature (298 to 371 K) on G' (solid symbols) and G'' (open symbols) for o/w emulsions stabilized by surfactant–polymer and nanoparticle–surfactant–polymer systems at 10 MPa.

surfactant–polymer (and nanoparticle–surfactant–polymer system which will be discussed later) at 10 MPa. It is observed that, at low temperature of 298 K, G'' is slightly higher than G' , showing viscous behavior. As the temperature increases above 298 K, both moduli decrease in magnitude and come closer (~ 1.2 Pa) at 313 K indicating gel-point. A further increase in temperature above 313 K, the G' values reach below the detection limit and viscous behavior dominates with decreasing trends, probably due to the temperature induced destabilization of the emulsion. The similar type of effect of temperature was observed for the viscoelastic properties of a copolymer consisting of ethylene oxide (EO) and propylene oxide (PO).³³ The conclusions are consistent with our observation on the emulsion stabilized by a surfactant–polymer system, that they are thermally unstable and thus limits their use for high temperature applications.²⁸

3.4. Viscoelastic Properties of Nanoparticle–Surfactant–Polymer o/w Emulsion. Figure 7 represents the strain-sweep measurements for Pickering o/w emulsions stabilized by a nanoparticle–surfactant–polymer system containing 1.0 wt % nanoparticle (SiO_2 and clay) at 0.1, 10, 30 MPa and 298 K. At 0.1 MPa, it is observed that both the emulsion systems (SiO_2 and clay) show liquid-like behavior due to dominance of G'' over the complete range of strain amplitude. As the pressure increases from 0.1 to 30 MPa, both G' and G'' increase. However, in the case of SiO_2 stabilized emulsion (Figure 7a), the presence of a crossover point is visible at all pressure conditions of 0.1, 10, and 30 MPa as against clay stabilized emulsion (Figure 7b), which did not show the same for the entire range of strain amplitude of 1 to 100%; however, it is expected to occur at less than 1% strain amplitude for clay stabilized emulsions (Figure 7b). Pickering emulsions stabilized by particles such as SiO_2 and clay have been investigated by various researchers.^{34,35} The viscoelastic behavior of emulsions can differ strongly depending upon the type of nanoparticle used. In this study, viscoelastic measurements showed that the G' for SiO_2 emulsions is considerably higher as compared to clay emulsions (see Figure 7), which indicates that the interfacial film formed at the oil–water interfaces with SiO_2 is more elastic than the one formed with clay. No viscoelastic region was observed for clay emulsions as shown in Figure 7b, which also concurs with literature observation for the same nanoparticles.³⁶ We also believe that the remarkable differences

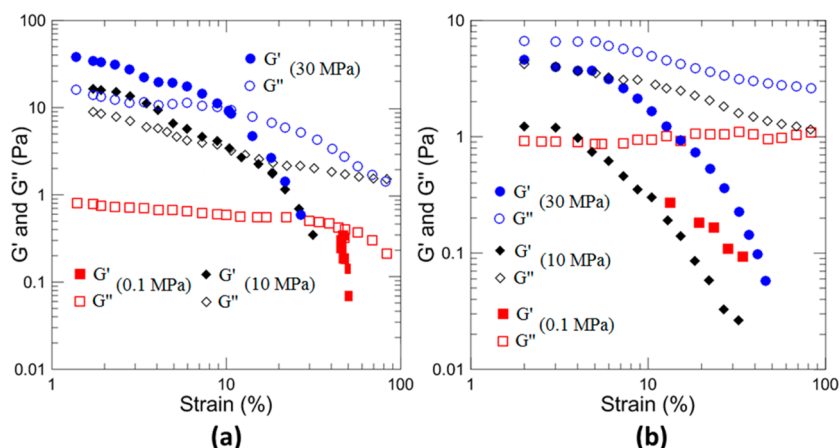


Figure 7. Strain-sweep measurements (frequency 10 rad s^{-1}) at 298 K and 0.1, 10, and 30 MPa. (a) 1.0 wt % SiO_2 stabilized; (b) 1.0 wt % clay stabilized o/w emulsions. G' (solid symbols) and G'' (open symbols).

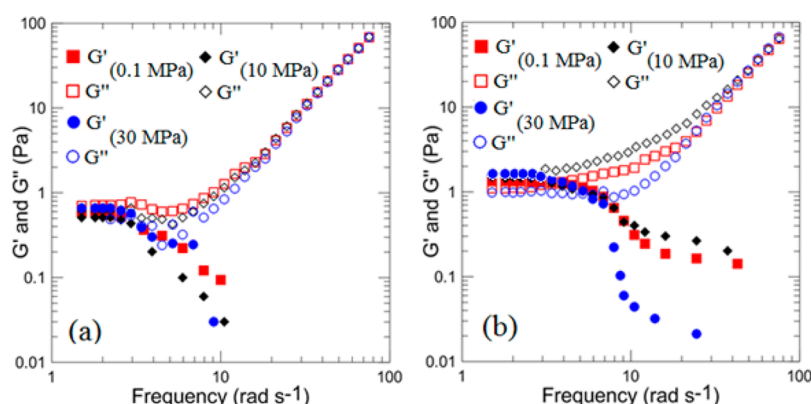


Figure 8. Frequency-sweep measurements carried out at strain amplitude of 2% at 298 K and 0.1, 10, and 30 MPa. (a) 1.0 wt % SiO₂; (b) 1.0 wt % clay stabilized Pickering emulsions. G' (solid symbols) and G'' (open symbols).

in viscoelastic behavior of these emulsions may be attributed to the stronger interaction of SiO₂ nanoparticle with surfactant than clay, which changed the wettability of SiO₂ nanoparticle to enhance the interfacial adsorption.^{34,35} The crossover point for the SiO₂ stabilized emulsion is observed to be around 50%, 10%, and 8% of the strain amplitude at 0.1, 10, and 30 MPa, respectively. As seen from Figure 7, the LVE range is expected below 2% of the strain amplitude.²

Therefore, we performed frequency-sweep tests for both the Pickering emulsions at 2% strain amplitude. The frequency-sweep data for these emulsions at 2% strain amplitude at 0.1, 10, and 30 MPa and 298 K is presented in Figure 8 (a–b). The results indicate that the emulsions behave like a viscoelastic fluid at all pressure conditions of 0.1, 10, and 30 MPa. The values on G' are initially marginally greater than G'' up to the small range of frequency for these emulsions, where the crossover point is located and then G'' increases rapidly with a decrease in G' indicating the dominance of liquid-like behavior. The crossover frequency for the SiO₂ stabilized emulsions at 0.1, 10, and 30 MPa is observed to be around ~ 2.2 rad s⁻¹ (Figure 8a), while for clay stabilized emulsions they are found to be around 4 (0.1 MPa), 2.5 (10 MPa), and 6.5 rad s⁻¹ (30 MPa) as shown in Figure 8b.

In contrast to surfactant–polymer o/w emulsion, the strain dependence of the viscoelastic behavior of 1.0 wt % SiO₂ stabilized emulsion indicates the presence of a crossover point (above which G' exhibits rapid decrease) at all pressure conditions (0.1 to 30 MPa); therefore, the overall behavior of the SiO₂ stabilized emulsion can be considered as a viscoelastic fluid (Figure 5a). As shown in Table 2, the effect of pressure did not show any significant influence on the viscoelastic moduli of the SiO₂ and clay stabilized emulsion systems as against the surfactant–polymer stabilized emulsion, wherein the storage modulus has shown a rapid increase with an increase in pressure from 0.1 to 30 MPa. This means that the nanoparticle stabilized emulsion shows better flowability suitable for reservoir EOR application. The addition of nanoparticles in the surfactant–polymer emulsion system significantly improves the viscoelasticity by providing a steric resistance against pressure induced droplet flocculation that forms by the adsorption of nanoparticle at the oil–water interface in the presence of polymer PAM and surfactant.²⁸ The studies on the shear viscosity vs shear rate of these emulsions prepared in this study are recently published in our recent work.³⁷ The Pickering emulsions showed stable rheological behavior with marginal influence of HPHT conditions on shear

viscosity. The information on dynamic moduli will certainly help to understand the viscous or elastic behavior of these emulsion systems during flow-through annuli or porous media, thus affecting the performance of EOR operations in addition to the information on shear viscosity of these emulsion systems.^{37,38}

The effect of temperature (298 to 371 K) on the viscoelastic behavior (G' and G'') of Pickering emulsions (SiO₂ and clay) at 10 MPa for strain amplitude of 1.5% is shown in Figure 6. It is observed that the values of G' for both the emulsions decrease with an increase in temperature. The reason may be attributed to the temperature induced marginal decrease in the viscosity of emulsion. In addition, the increase in temperature also transforms the solid-like nature into liquid-like at about 334 K (Figure 6), where $G' \approx G''$ for the SiO₂ stabilized emulsion. On the other hand, the clay stabilized emulsion showed a dominating liquid-like (G'') behavior over the complete range of temperature at 10 MPa. In contrast to surfactant–polymer emulsion, Pickering emulsion stabilized by a nanoparticle in the presence of surfactant and polymer showed a temperature independent stable liquid-like behavior. The credit may be attributed to the deposition of a nanoparticle on a droplet surface that makes droplet destabilization much more difficult which was not possible for the emulsion stabilized by a surfactant–polymer system.²⁸

4. CONCLUSION

Pickering emulsion is a very promising tool that could be used at high pressure high temperature applications, particularly for the upstream oil and gas industry because of their improved rheological stability. This study presents the effect of HPHT conditions on the viscoelastic behavior (G' and G'') of oil-in-water (o/w) emulsions stabilized by nanoparticle–surfactant–polymer (SiO₂ and clay-PAM-SDS). The results are compared with the conventional o/w emulsion stabilized by a surfactant–polymer system. We conclude that both the pressure and temperature influences the storage modulus (G') and loss modulus (G'') of surfactant–polymer stabilized emulsion, which is not favorable for an efficient EOR process. Pressure induces the major effect on viscoelastic properties of these conventional systems by increasing the G' by about 2 order of magnitude. It is observed that the nanoparticle stabilized Pickering emulsion showed relatively stable viscoelastic behavior for varying conditions of pressure and temperature. The study indicates that the addition of nanoparticles in the surfactant–polymer o/w emulsion system provides noteworthy

stable viscoelastic behavior at HPHT conditions, indicating their suitable use for oilfield applications as compared to conventional emulsion.

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Notes

The authors declare no competing financial interest.

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