

Enhancing Rheological Properties of Hydrophobically Associative Polyacrylamide Aqueous Solutions by Hybridizing with Silica Nanoparticles

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ABSTRACT: Organic/inorganic hybrid aqueous solutions were prepared by mixing silica nanoparticle suspension and hydrophobically associating polyacrylamide (HAPAM) solution, and their rheological behaviors were examined in both pure water and brine in comparison with HAPAM. It was found that HAPAM/silica hybrid exhibits viscosity enhancement in aqueous solution and better heat- and salt- tolerances than HAPAM. Meanwhile, their long-term thermal stability is also improved. Cryo-TEM observation reveals that a reinforced three-dimensional network structure of HAPAM/silica hybrid is formed. These improved properties are attributed to the formed hydrogen bond between carbonyl groups in HAPAM skeleton and silanol functionalities in silica nanoparticles in the hybrid system, and the silica nanoparticles in the hybrid act as physical crosslinkers between macromolecules. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40876.

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INTRODUCTION

Hydrophobically associating polyacrylamide (HAPAM) is derived by incorporating a relatively small amount of hydrophobic group (generally <2 mol %) onto a polyacrylamide backbone.¹ Such polymers have been extensively studied during the last two decades in both academic and industrial laboratories due to their unique rheological behavior, which arises from their ability to produce weak intra- and intermolecular interactions between the hydrophobic groups allocated along the polymer chains. In the dilute concentration regime, intramolecular hydrophobic interactions lead to coil contraction,² while above critical association concentration (CAC), a transient network is formed via intermolecular hydrophobic associations, resulting in substantial viscosity enhancement.³ These associations can be further reinforced by the addition of electrolyte,⁴ and can be reversibly destroyed/reformed when correspondingly increasing or decreasing shear rate.⁵ Owing to these unique properties,

HAPAM polymers have been applied in various stages of oilfield industry,⁶ including tertiary oil recovery,^{7–11} drilling fluids,¹² oilwell stimulation,^{13,14} to name but a few.

However, the viscosity buildup ability of HAPAM aqueous solution is weakened sharply upon increasing temperature,⁵ which impedes its applications in high-temperature oil reservoirs. The decrease of the solution viscosity by elevated temperature could be attributed to the impairment of the hydrophobic effect due to the increased mobility of the polymer chains, which gives rise to loss of inter-chain liaisons and an increase in copolymer solubility as the temperature increases.^{15–19} Meanwhile, similar to the parent polyacrylamide (PAM), the amide pendant group in HAPAM molecule is readily hydrolyzed into carboxylic group in high temperature environment,²⁰ thus the final anionic polyelectrolyte is sensitive to the presence of inorganic salt particularly divalent cations such as Ca²⁺ and Mg²⁺ which commonly present in oilfield brines. From both theory and application

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points of view, how to reinforce the intermolecular hydrophobic associations and avoid the hydrolysis of amide group of HAPAM are of vital importance.

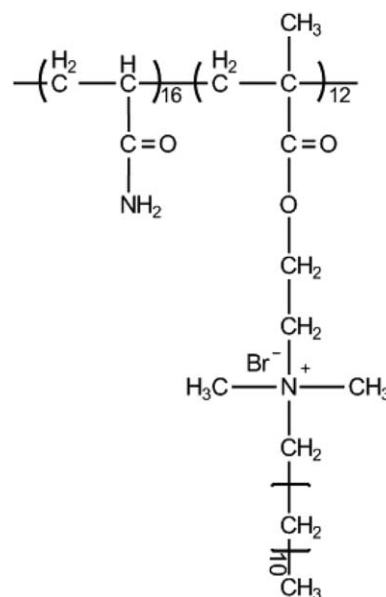
It is well recognized that hybridization of nanoparticles with the bulk polymers can improve the mechanical, optical, thermal, magnetic, and electric properties of the polymers.^{21,22} Recently, hybrid hydrogels formed by water-soluble polymers and nanoparticles have attracted considerable attention and achieved significant advancement.^{23–29} When thermoresponsive polymers, poly(*N*-isopropylacrylamide) (PNIPAM) or poly(ethylene oxide-*co*-propylene oxide) (PEO-PPO), are mixed with hydrophilic silica nanoparticles, homogeneous thermoresponsive hybrid aqueous dispersions can be obtained where particles act as physical linkages through physic-sorption of the lower critical solution temperature (LCST) chains.²⁴ PNIPAM or polyethers can interact specifically with nanoparticles, the specific binding of these polymers to inorganic surfaces can also be used to reinforce the mechanical properties of polymer networks and control the rheological properties.^{24,25} For PNIPAM and its derivatives, the inorganic silica particles act as physical crosslinks in PNIPAM/silica hydrogels and the viscoelastic properties are controlled by the loading of silica.²⁶ PEO is able to be adsorbed onto silica surfaces, and the viscosity increases with addition of silica particles which physically crosslink the macromolecular chains, the storage moduli of PEO/silica hybrids changes obviously as compared to PEO solutions.²⁷ The strong interactions between these polymers and silica are generally attributed to the formation of hydrogen bonds between carbonyl or ether groups of NIPAM or PO, EO units and silanol functionalities of nanoparticle surfaces.^{23,28,29} Based on these preliminary results, it is concluded that silica nanoparticles can effectively interact with water-soluble polymers which have carbonyl groups and act as physical crosslinkers between macromolecules. Hence, the carbonyl groups of amide and hydrophobic group in HAPAM molecule show the possibility to interact with silanol groups at the surface of silica. By this way, the network structures of HAPAM could be reinforced and the poor thermal stability is expected to be improved to some extent. Nevertheless, to our knowledge, no such HAPAM/nanoparticle hybrids have been reported to date.

In this work, silica nanoparticles were introduced into HAPAM aqueous solution to strengthen the network structure of HAPAM, and the steady and dynamic rheological behaviors of the hybrid aqueous solutions in both pure water and brine were examined in comparison with HAPAM alone. The thickening ability of the hybrid solutions has also been investigated with respect to the silica concentration, shear rate, temperature, and aging time.

EXPERIMENTAL

Materials

The detailed synthesis and characterization of HAPAM copolymer (Scheme 1) used in this work have been reported previously.³⁰ HAPAM was prepared via inverse suspension copolymerization of the hydrophilic comonomer, acrylamide (AM), and the hydrophobic comonomer, 2-methacryloyloxyethyl *n*-alkyl dimethyl ammonium bromide. Its weight-average molecular weight (M_w) is $5.89 \times 10^6 \text{ g mol}^{-1}$ determined by gel permeation chromatographic (GPC), and the mass percentage of



Scheme 1. The molecular structure of HAPAM.

hydrophobic monomer along the polymer chain is 0.75 wt % in final composition.

Silica nanoparticles (TM-50, Ludox) were obtained from Sigma-Aldrich. The crude silica suspension (50 wt %) was purified by continuous ultrafiltration (membrane cutoff = 10 kDa) with water at pH 8 in order to remove small molecules and surfactants used as conditioners to stabilize the dispersion. A stable suspension of negatively charged nanoparticles was finally conditioned at 16.8 wt % (pH = 8). The average diameter of these particles is 22 nm, and the corresponding specific area is $S_{\text{spe}} = 140 \text{ m}^2 \text{ g}^{-1}$ considering a specific weight $\rho = 1.4 \text{ g m}^{-3}$, obtained by dynamic light scattering.

Preparation of Hybrid Samples

The hybrid samples were prepared by mixing silica suspension with HAPAM solution at the designed recipe following a previously reported procedure for mixing silica nanoparticles with graft copolymer solution.³¹ The inorganic/organic mixtures were gently stirred for 3 days and left to stand for 1 day prior to rheological studies.

CHARACTERIZATIONS

Infrared Spectroscopy

The Fourier transform infrared spectra (FT-IR) of HAPAM and HAPAM/silica hybrid were registered in solid state using a KBr pellet method in the transmittance mode. A Nicolet MX-1E FT-IR spectrophotometer (USA) was used to record the spectra within the scanning range of $4000\text{--}400 \text{ cm}^{-1}$.

Cryo-TEM Observation

The specimens for Cryo-TEM observation were prepared in a controlled environment vitrification system. The climate chamber temperature was $25\text{--}28^\circ\text{C}$, and the relative humidity was kept close to saturation to prevent evaporation from the sample during preparation. Five microliter of sample solutions at room temperature was placed on a carbon-coated holey film supported by a copper grid, and gently blotted with filter paper to

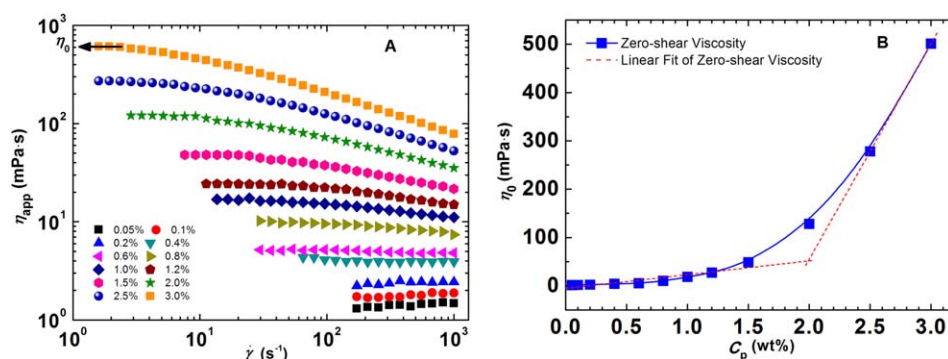


Figure 1. (A) Apparent viscosity plotted as a function of shear rate for various concentrations of HAPAM and (B) zero-shear viscosity (η_0) plotted as a function of polymer concentration for HAPAM in pure water at 25°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

obtain a thin liquid film (20–400 nm) on the grid. The grid was quenched rapidly into liquid ethane at -180°C and then transferred into liquid nitrogen (-196°C) for storage. Then the vitrified specimen stored in liquid nitrogen was moved into a JEM2010 cryo-microscope using a Gatan 626 cryo-holder and its workstation. The acceleration voltage was 200 kV, and the working temperature was kept below -170°C . The images were recorded digitally with a charge-coupled device camera (Gatan 832) under low-dose conditions with an under-focus of $\sim 3 \mu\text{m}$.

Rheological Measurements

Rheological measurements were made on a Physica MCR 301 (Anton Paar, Austria) rotational rheometer equipped with concentric cylinder geometry CC27 (ISO3219) with a measuring bob radius of 13.33 mm and a measuring cup radius of 14.46 mm. Samples were equilibrated at the temperature of interest for no <20 min prior to experiments. The rheological behavior of samples was determined under both steady and oscillatory shear to obtain the steady and dynamic viscoelastic properties. Dynamic frequency spectra were conducted in the linear viscoelastic regimes, as determined from dynamic stress-sweep measurements. All experiments were carried out using stress-controlled mode, and Cannon standard oil was used to calibrate the instrument before the measurements. The temperature was set to $\pm 0.1^\circ\text{C}$ accuracy by a Peltier temperature control device, and a solvent trap was used to minimize water evaporation during the measurements.

Long-Term Thermal Stability Measurement

The samples for long-term thermal stability experiment were prepared in pure water and distributed into 100-mL specially designed glass bottles which were purchased from Schott AG, and then sealed with screw-caps, followed by placing them into an oven and aged at 85°C . The oxygen residing in the solutions was not removed. At consecutive time intervals, the samples were taken out for viscosity monitoring at 85°C with the MCR rheometer mentioned above.

RESULTS AND DISCUSSION

Concentration Dependence of HAPAM

To investigate the interaction between silica nanoparticles with HAPAM at different concentration domains, the concentration dependence of HAPAM was studied firstly so as to determine the CAC. Figure 1(A) shows the concentration-dependent flow curves of HAPAM aqueous solutions between 0.05 and 3.0 wt %. When

polymer concentration (C_p) is lower than 0.8 wt %, the HAPAM solutions behave as Newtonian fluids; that is, viscosity is independent of shear rate. While at higher polymer concentration, the flow curves are composed of two parts: Newtonian behavior at low shear rates and shear-thinning response with increasing shear rates. In the Newtonian fluid region, zero-shear or plateau viscosity (η_0) can be obtained by extrapolating the shear rate to zero.

The variation of η_0 as a function of polymer concentration is plotted in Figure 1(B), where two parts can be separated at around 2.0 wt %. Below this concentration, η_0 increases linearly with increasing polymer concentration; above 2.0 wt %, η_0 increases drastically. This suggests that 2.0 wt % is the CAC of HAPAM, above which a transient network is formed via intermolecular hydrophobic associations.

Effect of Polymer Concentration on HAPAM/Silica Hybrids

For the HAPAM/silica hybrid, the interaction between HAPAM and silica nanoparticles largely depends on the concentration of HAPAM and silica. First, the influence of polymer concentration on HAPAM/silica hybrid was examined. Compared in Figure 2 are the flow curves of pure HAPAM aqueous solutions and HAPAM/silica hybrids with a fixed silica concentration of 1.5 wt % but at varied HAPAM concentrations: 1.5 wt % (<CAC), 2.0 wt % (=CAC), and 2.5 wt % (>CAC). When $C_p < \text{CAC}$,

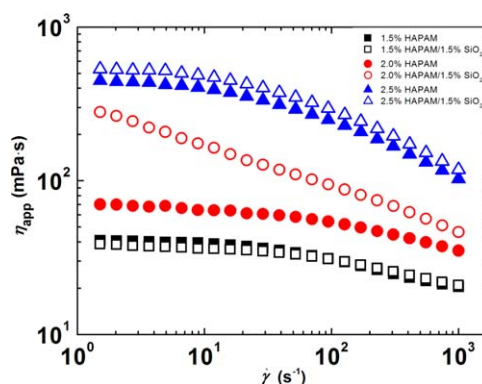


Figure 2. Apparent viscosity plotted as a function of shear rate for HAPAM aqueous solutions and HAPAM/silica hybrids with fixed silica loading but different polymer concentrations ($T = 25^\circ\text{C}$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

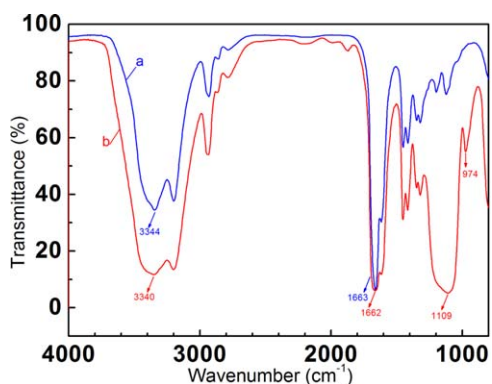


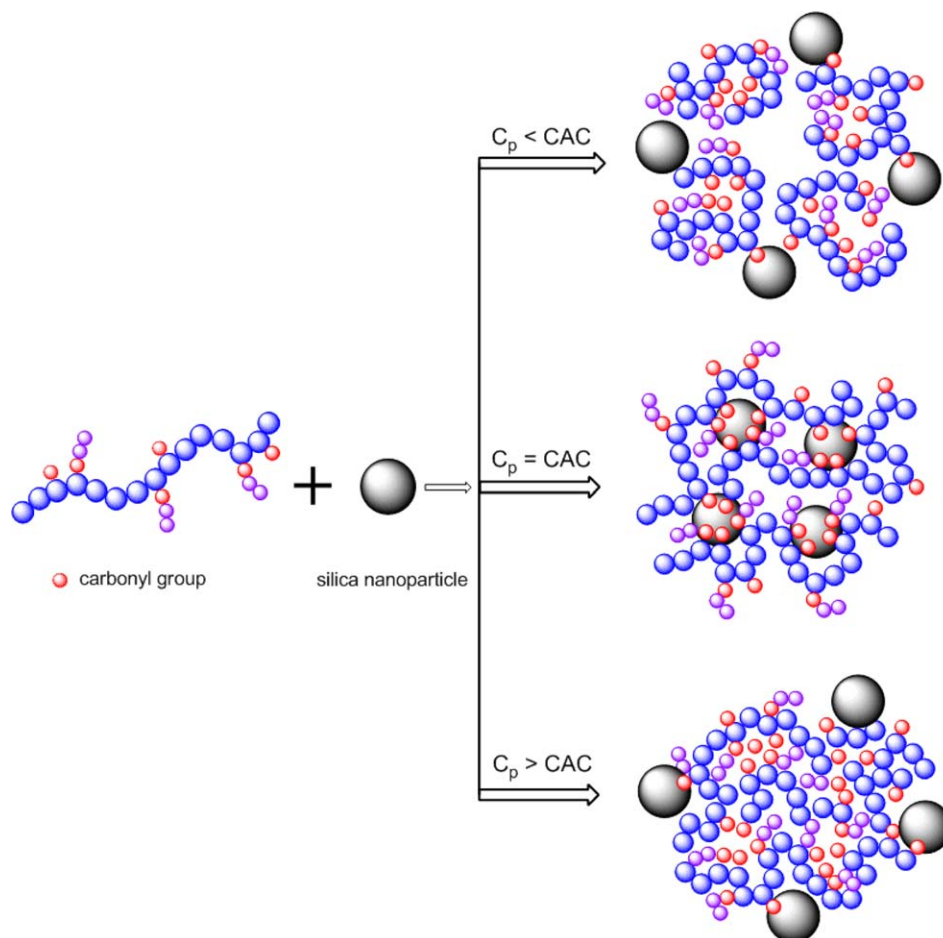
Figure 3. Comparison of FT-IR spectra of (a) 2.0% HAPAM and (b) 2.0% HAPAM/1.5% SiO₂. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

introduction of silica imparts little effect on the viscosity—the curves of hybrid and HAPAM solution nearly superimposed; when $C_p > CAC$, minor enhancement in viscosity is observed but the shape of flow curves does not change; nevertheless, Newtonian plateau disappears and shear-thinning begins at low shear rates when $C_p = CAC$. In this case, shear viscosity of the hybrid apparently increases in comparison with the pure poly-

mer solution. For example, the viscosity of “2.0% HAPAM/1.5% SiO₂” at 10 s⁻¹ is three times larger than that of 2.0% HAPAM solution.

To see why the viscosity increases upon addition of silica nanoparticles at critical polymer association concentration, FT-IR spectroscopy was employed to check if there are some hydrogen bonds formed between silica and the polymer. As depicted in Figure 3, the peaks in the wavenumber range of 1200–4000 cm⁻¹ are nearly the same for both HAPAM and HAPAM/silica hybrid, both of which show strong stretching vibration peaks at 3344 and 1663 cm⁻¹ attributing to amino group and carbonyl group of amides, respectively. However, a new peak appears at 1109 cm⁻¹ in the spectrum of HAPAM/silica hybrid sample, which is ascribed to the Si–O–Si asymmetric band stretching vibration. In addition, the peak at 3344 cm⁻¹ becomes broader and a peak at 974 cm⁻¹ is found due to combination of hydrogen bonded amide with hydroxyl on silica surface,^{32,33} suggesting the formation of hydrogen bonds between polymer and nanoparticles in the hybrid.

The interaction between HAPAM and silica particles is schematically illustrated in Scheme 2. At low polymer concentration (<CAC), intramolecular hydrophobic association is dominant in HAPAM solution, leading to the formation of small



Scheme 2. Schematic illustration of the interaction between HAPAM and silica nanoparticles at different polymer concentrations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 4. Appearances of HAPAM (A) and HAPAM/silica hybrid (B) in pure water ($T = 25^\circ\text{C}$) with different silica loading: (B1) 0.5 wt %, (B2) 1.0 wt %, (B3) 1.5 wt %, (B4) 2.0 wt %, and (B5) 2.5 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

aggregates. Thus, macromolecular chains have little chance to interact with silica nanoparticles. As the polymer concentration increases to CAC, inter-molecular hydrophobic association becomes predominant, giving rise to a network structure of polymer chains by approaching each other. When silica nanoparticles are added, the carbonyl groups in HAPAM molecule interact with silanol groups at the surface of the particles and hydrogen bonds form between silica and the polymer. Silica nanoparticles act as physical crosslinkers between macromolecules. The organic/inorganic interaction not only reinforces the network structures of HAPAM, but also promotes the formation of hybrid networks. At high polymer concentration ($> \text{CAC}$), strong associations caused by a large number of hydrophobic groups play against the interaction between HAPAM and silica particles. Meanwhile, only part of the carbonyl groups in HAPAM molecule can effectively interact with silica nanoparticles. The number of hydrogen bonds formed in the hybrid is limited. As a result, silica particles show little influence on the property of HAPAM solutions in semidilute polymer concentration regime.

Effect of Nanoparticle Loading on Apparent Viscosity of HAPAM/Silica Hybrids

In the above sections, we found a transient network of HAPAM chains is formed when the polymer concentration is at CAC, and the apparent viscosity further increases upon addition of 1.5 wt % of silica nanoparticles. It is interesting to see what will happen higher loading of silica particles is introduced. The initial HAPAM aqueous solution at room temperature is transparent [Figure 4(A)], while the HAPAM/silica hybrid aqueous solution turns into translucent [Figure 4(B)]. These samples are stable and homogeneous and no visible macroscopic phase separation is observed over time at room temperature.

Thus, the effect of silica nanoparticle concentration on HAPAM/silica hybrid was further studied at a fixed polymer concentration of 2.0 wt %. Presented in Figure 5 is the dependence of silica concentration on the aqueous solution viscosity of HAPAM/silica hybrid. It is apparent that the viscosity of hybrid systems is enhanced gradually with increasing silica concentra-

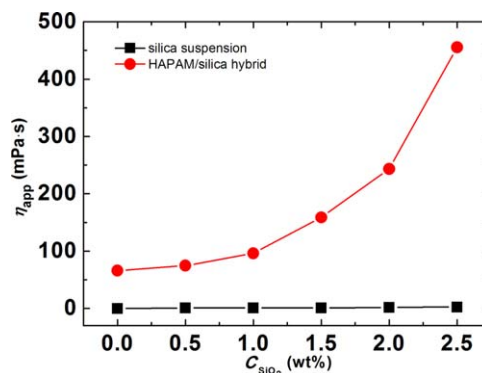


Figure 5. Dependence of apparent viscosity on silica nanoparticle concentration for HAPAM/silica hybrid in pure water and silica suspension ($T = 25^\circ\text{C}$, $\dot{\gamma} = 10 \text{ s}^{-1}$, $C_p = 2.0 \text{ wt } \%$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tion, and exhibits a sharp increase as the silica concentration reaches to 2.0 wt %. It is worth noting that the viscosity of silica suspension remains just a few mPa s^{-1} independent of the concentration used (Figure 5). Thus, the viscosity enhancement of the hybrid system cannot be regarded as the superposition of viscosity of HAPAM solution and that of silica suspension.

Similar to the formation of hydrogen bonds between carbonyl groups of NIPAM units and silanol functions of the surfaces in the PNIPAM/silica system,²⁴ the incremental viscosity of HAPAM/silica hybrid is also attributed to the strong interactions between HAPAM and silica particles caused by the formation of hydrogen bonds between carbonyl groups of HAPAM and silanol functions of silica. With increasing concentration of silica, the fraction of carbonyl groups interacted with nanoparticles becomes stronger, consequently, the movement of polymer chains is limited, and the hydrodynamic volume increases, resulting in the increase of the aqueous solution viscosity of HAPAM/silica hybrid.

Effect of Temperature on Apparent Viscosity of HAPAM/Silica Hybrid

As stated in the “Introduction” part, the poor heat tolerance represents one of the notorious drawbacks of HAPAM polymers when considering its applications in oilfield industry. Therefore,

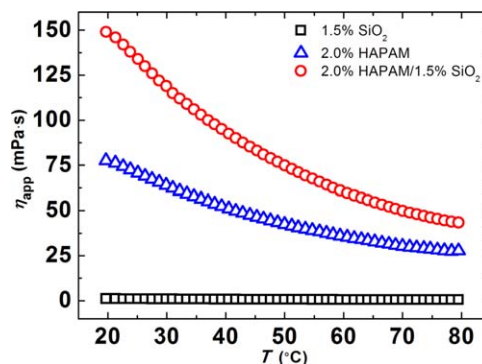


Figure 6. Apparent viscosity plotted as a function of temperature for HAPAM, silica, and HAPAM/silica hybrid in pure water ($\dot{\gamma} = 10 \text{ s}^{-1}$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

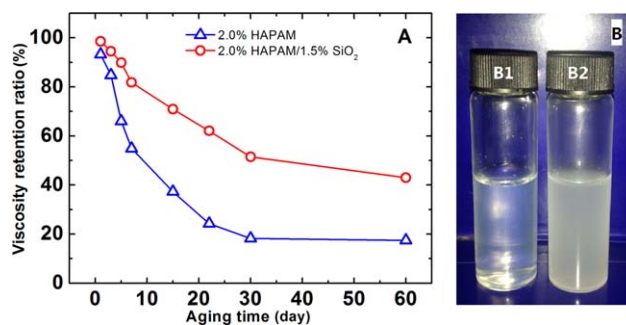


Figure 7. (A) Viscosity retention ratio plotted as a function of aging time for both HAPAM and HAPAM/silica hybrid in pure water ($T = 85^{\circ}\text{C}$, $\dot{\gamma} = 10 \text{ s}^{-1}$); (B) the appearance of the HAPAM/silica hybrid before (B1) and after (B2) 60 days of aging at 85°C . $\eta_b/\eta_a \times 100\%$ is the viscosity retention ratio. η_a is the apparent viscosity before aging while η_b is the apparent viscosity after aging. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

we studied the effect of temperature in the aqueous solution viscosity of “2.0% HAPAM/1.5% silica” hybrid (Figure 6). For comparison, pure 2.0 wt % HAPAM solution and 1.5 wt % silica suspension were also studied as well. With increasing temperature, the viscosity of silica suspension keeps constant, but both HAPAM solution and HAPAM/silica hybrid show typical thermo-thinning behavior. Compared with pure HAPAM aqueous solution, the HAPAM/silica hybrid has twofold higher viscosity in the whole temperature range studied.

Such an improvement against heating could be interpreted by the physical crosslink of the macromolecular chains with the silica nanoparticles. As discussed above, the hydrogen bonds between HAPAM and silica particles reinforce the network structures of HAPAM and promote the formation of hybrid networks. These interactions reinforced the network structures of HAPAM and improved the thermal stability of polymers. The decreased solution viscosity with increasing temperature for aqueous solutions of HAPAM/silica hybrid could be attributed as follows: the hydrophobic effect is impaired which increasing copolymer solubility as the temperature increases,^{15–19} and the amide pendant group in HAPAM molecule is readily hydrolyzed into carboxylic group at high temperature,^{5,20} leading to the

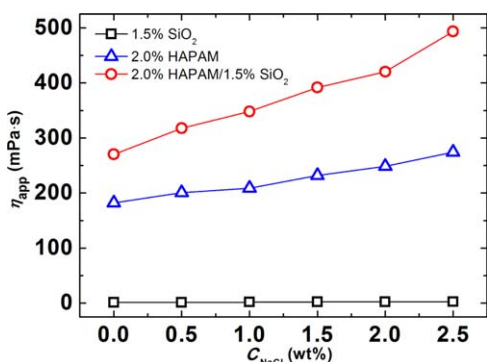


Figure 8. Apparent viscosity plotted as a function of NaCl concentration for HAPAM, silica, and HAPAM/silica hybrid ($T = 25^{\circ}\text{C}$, $\dot{\gamma} = 10 \text{ s}^{-1}$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

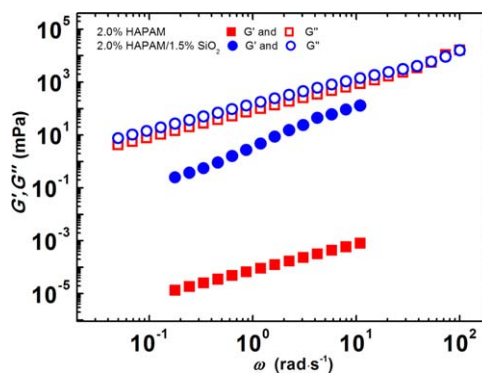


Figure 9. Frequency dependence of G' and G'' for HAPAM and HAPAM/silica hybrid in pure water ($T = 25^{\circ}\text{C}$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decreased viscosity; in addition, the hydrogen bonds of HAPAM/silica hybrid are sensitive to temperature, and gradually dissociate when temperature is increased.³⁴

Long-Term Thermal Stability of HAPAM/Silica Hybrid

To check the temperature tolerance of the HAPAM and HAPAM/silica hybrid solutions, long-term thermal stability experiment of the samples was performed. Figure 7(A) presents viscosity retention ratio as a function of aging time for the HAPAM and HAPAM/silica hybrid aqueous solutions after aging at 85°C . One can clearly find that the viscosity retention ratio of the HAPAM/silica hybrid is much higher than that of pure HAPAM at same aging time. For instance, after aging for 60 days, the viscosity retention ratio of HAPAM at 85°C is only 17.47% while that of the hybrid is 43%. Meanwhile, as shown in Figure 7(B), although the HAPAM/silica hybrid turns into opaque after aging at 85°C for 60 days, no visible macroscopic phase separation is observed.

Effect of Electrolyte on Apparent Viscosity of HAPAM/Silica Hybrid

Salt tolerance is another consideration of HAPAM when considering its applications. So we examined the influence of NaCl on solution viscosity of HAPAM, silica and “2.0% HAPAM/1.5% silica” hybrid (Figure 8). Still, the viscosity of silica suspension is independent of salt content, while both HAPAM and HAPAM/silica hybrid show viscosity increase upon increasing NaCl content.

On the one hand, intra-molecular hydrophobic associations are enhanced by NaCl due to electrostatic screening of the small charged groups, leading to reduction of hydrodynamic volume, thus decreasing the solution viscosity.³⁰ On the other hand, with the increase of NaCl concentration, the polarity of the solvent increases correspondingly, resulting in reinforced intermolecular associations of the hydrophobic groups, thus higher apparent viscosity is obtained.^{4,35} When intermolecular associations prevail over electrostatic screening, the apparent viscosity of HAPAM aqueous solutions increases. For HAPAM/silica hybrid, silica nanoparticles are negatively charged as described in experimental section, while the hydrophobic part of HAPAM

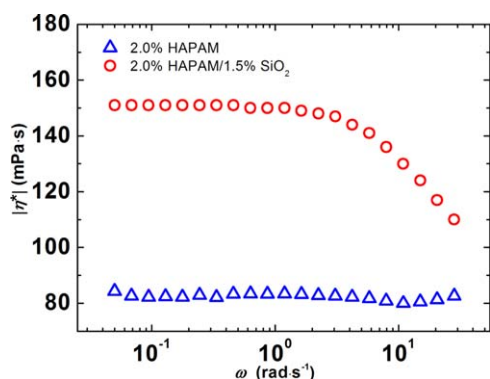


Figure 10. Frequency dependence of complex viscosity ($|\eta^*|$) for HAPAM and HAPAM/silica hybrid in pure water ($T = 25^\circ\text{C}$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

is positively charged. The electrostatic attraction caused between HAPAM and silica forces the amide groups of HAPAM to interact with silica nanoparticles, thus promoting the formation of hybrid networks and showing enhanced viscosity incremental.

Viscoelastic Behavior of HAPAM/Silica Hybrid

Viscoelastic properties of polymer solutions were used extensively to gain insight into the structure and conformation of polymers in solution. A polymer or hybrid solution responds to angular frequency under the influence of a constant oscillatory strain, and the characteristic viscoelastic parameters such as the storage (G') and loss (G'') modulus are measured. Compared in Figure 9 is the viscoelastic response of 2.0% HAPAM aqueous solution and “2.0% HAPAM/1.5% silica” hybrid in pure water. G' and G'' of both samples increase with increasing angular frequency in the range of 0.05–100 rad s^{-1} , but those of the hybrid sample increase significantly. However, it should be noted that the increase for G' is more remarkable than that for G'' , indicating silica nanoparticles deeply influence the elastic properties of the polymer network. Complex viscosity ($|\eta^*|$) is normally used to express the total contribution of viscous and elastic character to the solution viscosity and to characterize the viscoelastic behavior of a polymer solution. The angular frequency dependence of $|\eta^*|$ for both HAPAM and HAPAM/silica hybrid in pure water is displayed in Figure 10. The

HAPAM aqueous solution shows Newtonian behavior independent of frequency in the investigated range. After addition of silica nanoparticles, $|\eta^*|$ increases with apparent shear-thinning behavior in the range of 1–30 rad s^{-1} , indicative of reinforcement of hydrophobic associating structure.

These results demonstrate the considerable influence of the interfacial interactions of silica nanoparticles on the viscoelastic behavior of HAPAM. With addition of silica, the effective interactions between carbonyl groups of HAPAM and silanol functions of silica occurred, increasing the number and strength of the network junctions. Therefore, in the HAPAM/silica hybrid, the network structure of HAPAM is strengthened and the elasticity of hybrid becomes more pronounced.

Cryo-TEM Observation of HAPAM/Silica Hybrid

To corroborate the above findings, the microstructures formed in both HAPAM and HAPAM/silica hybrid aqueous solutions were further observed by cryo-TEM. Transient networks are formed via intermolecular hydrophobic associations of HAPAM when the polymer concentration is 2.0 wt % and no spherical particle is observed in Figure 11(A). After introduction of silica nanoparticles, they appear in spherical particles (ca. 22 nm) and a three-dimensional network structure is formed as exhibited in Figure 11(B). In the HAPAM/silica hybrid, silica nanoparticles did not aggregate in large area and HAPAM molecules were absorbed on the surface of nanoparticles. Because of the hydrogen bonds between organic and inorganic phase, silica nanoparticles interact with HAPAM and act as physical cross-links throughout the hybrid. Thus, the transient networks of HAPAM are effectively reinforced by silica nanoparticles, resulting in improved rheological properties as the above findings.

CONCLUSIONS

We demonstrate that HAPAM/silica hybrid can be readily formed at critical association concentration of HAPAM. The solution properties of HAPAM/silica hybrid were studied under different conditions. With addition of silica, hybrid networks were formed and polymer networks were effectively reinforced in aqueous solutions because of hydrogen bonds formed between macromolecular chains of HAPAM and silica nanoparticles. From the comparison between HAPAM and HAPAM/silica hybrid, it was found that the apparent viscosity, heat-

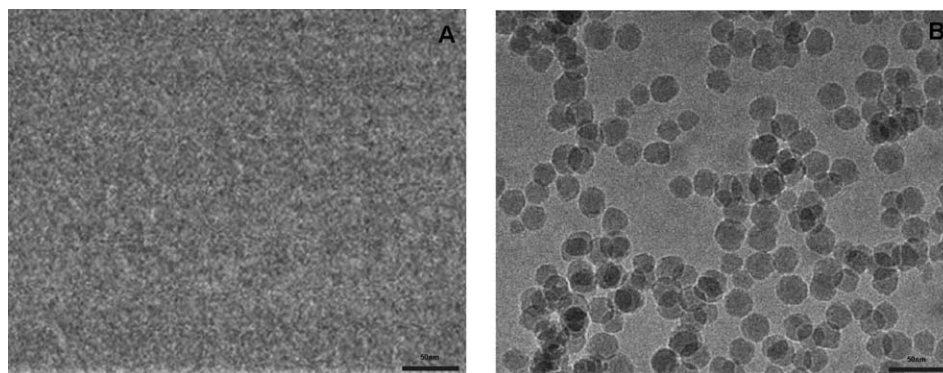


Figure 11. Cryo-TEM observations of 2.0% HAPAM (A) and 2.0% HAPAM/1.5% SiO₂ hybrid (B) in pure water ($T = 25^\circ\text{C}$). Bars in A and B are 50 nm.

resistance, salt-tolerant capability, and storage modulus are all enhanced by adding silica nanoparticles. Moreover, the HAPAM/silica hybrid formed at critical polymer association concentration can achieve the property of HAPAM solutions in semidilute concentration, and exhibits much better long-term thermal stability than the pure HAPAM. These properties may make HAPAM/silica hybrid of potential technological interest in oil recovery or drilling applications and other important commercial applications.

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