



Original Paper

Intelligent responsive self-assembled micro-nanocapsules: Used to delay gel gelation time



Chuan-Hong Kang, Ji-Xiang Guo*, Dong-Tao Fei, Wyclif Kiyangi

Unconventional Petroleum Research Institute, China University of Petroleum, Beijing, 102249, China

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ABSTRACT

In the application of polymer gels to profile control and water shutoff, the gelation time will directly determine whether the gel can “go further” in the formation, but the most of the methods for delaying gel gelation time are complicated or have low responsiveness. There is an urgent need for an effective method for delaying gel gelation time with intelligent response. Inspired by the slow-release effect of drug capsules, this paper uses the self-assembly effect of gas-phase hydrophobic SiO₂ in aqueous solution as a capsule to prepare an intelligent responsive self-assembled micro-nanocapsules. The capsule slowly releases the cross-linking agent under the stimulation of external conditions such as temperature and pH value, thus delaying gel gelation time. When the pH value is 2 and the concentration of gas-phase hydrophobic SiO₂ particles is 10%, the gelation time of the capsule gel system at 30, 60, 90, and 120 °C is 12.5, 13.2, 15.2, and 21.1 times longer than that of the gel system without containing capsule, respectively. Compared with other methods, the yield stress of the gel without containing capsules was 78 Pa, and the yield stress after the addition of capsules was 322 Pa. The intelligent responsive self-assembled micro-nanocapsules prepared by gas-phase hydrophobic silica nanoparticles can not only delay the gel gelation time, but also increase the gel strength. The slow release of cross-linking agent from capsule provides an effective method for prolongating the gelation time of polymer gels.

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1. Introduction

With the development of water flooding in oil fields, formation heterogeneity is enhanced, and injected water flows along high-permeability channels, resulting in a large amount of irreducible oil in low-permeability areas (El-Hoshoudy et al., 2019). Current enhanced oil recovery (EOR) technologies, such as polymer flooding, can increase contact between the waterflood and oil and, consequently, the swept area. However, the polymer can break through and flow to production wells, resulting in polymer loss and reduced oil displacement efficiency (Zareie et al., 2019; Chen et al., 2018). In the EOR method, polymer gels act as the blocking agent of high-permeability channels, which can divert the injected liquid into the low-permeability area, expand the swept volume, and effectively improve oil recovery (Kang et al., 2021; You et al., 2018).

The cross-linked polymer gel produced during oil production is a common chemical system for profile control, and water shutoff

(Bai B. et al., 2022). The system is based on polymer and cross-linking agent, and the polymer is generally partially hydrolyzed polyacrylamide. Cross-linking agents include metal chromium ion, aluminum ion, zirconium ion, phenolic resin, polyvinylimide, and composite cross-linking agent, etc. (Amir et al., 2019; Zhu et al., 2019; Singh et al., 2018a). Generally, the gel gelation time at high temperatures is short, especially for metal cross-linked systems (Cao et al., 2020; Yang et al., 2019; Zhang H. et al., 2020). The gel gelation time and gel strength of the gel system are affected by temperature, salinity, pH, crosslinker concentration, and other factors (Liu and Liu, 2022; Lu et al., 2023; Han et al., 2020; Yin et al., 2022). Too fast gelation ratio is not conducive to deep profile control, especially in high-temperature oil reservoirs, which greatly limits the application of gel systems, so it is very important to delay the gel gelation time. Metal cross-linking agent gel system is widely used in medium and low-temperature reservoir conditions, but when the temperature is too high, the gelation time of the system is sharply shortened, which quickly leads to wellbore blockage or plugs the area around the well; thus, delaying the gelation time of polymer gel has become a major research focus. At present,

* Corresponding author.

E-mail address: guojx003@126.com (J.-X. Guo).

common methods of delaying the gelation time of gel include: forming metal ion complexes, preparing solid cross-linking agents, preparing multiple emulsions, packaging technology, and adding chemical retarders to delay gelation time of the gel system (Sun et al., 2016; Koilraj et al., 2019; Xu et al., 2017; Cordova et al., 2008; Ghriga et al., 2019; Xie et al., 2021). However, it is difficult to control the gelation time of the gel system formed by different metal ions and different coordination ions, and the addition of chemical retarders may affect the gel strength (El Karsani et al., 2014), and the stability of multiple emulsions is poor, and there are many restrictions in application. At present, nanoparticles are widely used in the petroleum industry (Peng et al., 2018; Fakoya and Shah, 2017). Nanoparticles have also been applied in delayed gels. Polymer electrolyte composite nanoparticles capture Cr(III) ions and control their release to delay cross-linking (Cordova et al., 2008). Dai et al. (2016) showed that the addition of silica nanoparticles as gel enhancer made the gel exhibit excellent stability under high temperature and high salt conditions. At the same time, the addition of nanoparticles can enhance the strength and storage modulus of the gel (Lashari et al., 2018; Zareie et al., 2019; Fadil et al., 2020).

In order to solve the problem that polymer solution is difficult to inject due to its high viscosity in polymer flooding technology, Gong et al. (2022), using polyurethane as shell material, synthesized encapsulated polymers with different shell-core ratios to achieve delayed thickening of polymer microcapsules. Varkey et al. (2018) used polyelectrolyte complex (PEC) microcapsules composed of xanthan and chitosan polymers to encapsulate rhodococcus. Under the stimulation of changing pH value, cells were released statically in microcapsules with significant vitality, indicating their feasibility in oil recovery (Varkey et al., 2018). Some scholars used hydrophobic silica coated acid as an alternative delayed acid system, and the microencapsulation of acid has a certain intelligent response (Singh et al., 2018b). Compared with ordinary capsules, intelligent responsive capsules have higher intelligent responsiveness, which can control the capsule system to release internal wrapped substances by changing external conditions. At the same time, intelligent responsive self-assembled micro-nanocapsules have the advantage of self-assembly, that is, assembly can be realized through simple operation, which greatly improves the encapsulation efficiency compared with ordinary capsule systems. Pu et al. (2023) successfully prepared nanocapsule by precipitating controllable nano-inclusions of hydrophobic polymers, polymethyl methacrylate (PMMA) and Pluronic®P-123, onto stable Cr³⁺ water nanodroplets, achieving precisely controlled release of Cr³⁺. However, the capsules require a certain temperature to trigger release, and the effect at low temperatures is unclear (Pu et al., 2023). The purpose of Pu et al. was to shorten the interval of gel gelation time, but the metal cross-linking agent gel system formed by Cr³⁺ and HPAM formed too fast, which could easily cause oil well blockage in actual oil well plugging operations and could not go deep into the formation. The purpose of the self-assembled micro-nanocapsule in this research was to delay the gel gelation time, so as to realize the deep profile control of gel in the deep formations. For reservoirs with formation water salinity of 2.4×10^5 mg/L and pH value of 7.53, in this paper, a kind of intelligent responsive self-assembled micro-nanocapsule was prepared using gas-phase hydrophobic silica nanoparticles. The cross-linking agent solution was encapsulated in the capsule, and then the capsule was added to the polymer solution. The self-assembled micro-nanocapsules release the crosslinker solution slowly under the stimulation of external conditions such as temperature and pH value, thus greatly delaying the gel gelation time, the effect of delaying gel gelation time is more obvious at medium and low temperatures. At the same time, the influence of pH value,

temperature, concentration of gas-phase hydrophobic silica nanoparticles on the self-assembly effect of micro-nanocapsule was studied, and the influence of the above factors on the strength, viscoelasticity and delay gelation time of the gel system was evaluated.

2. Experimental methods

2.1. Raw materials

Gas-phase hydrophobic silica nanoparticles (particle size: 7–40 nm), chromium acetate, and D-isoascorbic acid (99%) were provided by the Macklin Biochemical Co. Ltd., China. Partially hydrolyzed polyacrylamide (HPAM, molecular weight 8.0×10^6 , hydrolysis degree 25%) was purchased from the Yaanda Biotechnology Co. Ltd., China. The water used in the experiment was self-prepared simulated formation water (salinity 2.4×10^5 mg/L, pH 7.53).

2.2. Preparation of self-assembled micro-nanocapsules and their gel systems

2.2.1. Preparation of self-assembled micro-nanocapsules

The chromium cross-linking agent solution with a concentration of 0.4% was prepared with chromium acetate and simulated formation water, and then the solution of chromium cross-linking agent and the gas-phase hydrophobic nano-silica were successively added to a waring agitator at a mass ratio of 10:1. The mixture was stirred at a speed of 1000 r/min for 3 min. That is, self-assembled micro-nanocapsules wrapped with cross-linking agent solution were obtained. The encapsulation of self-assembled micro-nanocapsules is shown in Fig. 1(a)–(c).

2.2.2. Preparation of self-assembled micro-nanocapsules gel system

A 1.5% HPAM solution was prepared by dissolving HPAM powder in simulated formation water. 10 mL of 1.5% HPAM solution was taken and added to 2 mL of 0.20% D-isoascorbic acid and 5 mL of self-assembled micro-nanocapsules. After being stirred with glass rod at room temperature for 5 min, a delayed cross-linking gel system containing self-assembled micro-nanocapsules was obtained. The delayed cross-linking gel system was placed in glass bottles under different temperature conditions and then periodically took out to observe the gelation time of gel. The gelation of gel is shown in Fig. 1(d) and (e).

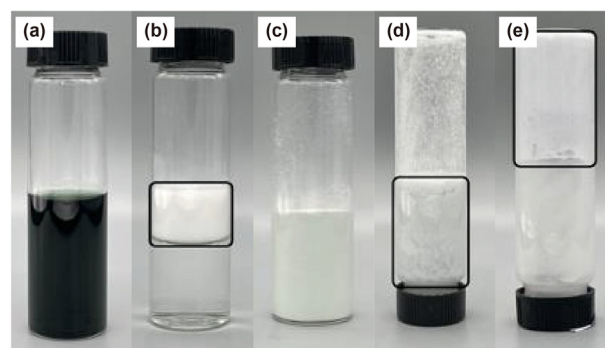


Fig. 1. Preparation of self-assembled micro-nanocapsules with delayed cross-linking gel. (a) Solution of chromium cross-linking agent; (b) The upper part is gas-phase hydrophobic SiO₂ nanoparticles, and the lower part is deionized water; (c) Self-assembled micro-nanocapsules (containing chromium cross-linking agent); (d) The state of ungelatinized delayed cross-linking gel system; (e) The state of delayed cross-linking gel system after gel gelation.

2.3. Evaluation method of gelation time and gel strength

Gelation time and gel strength were evaluated using gel strength code method (Sydansk, 1993). Gel gelation time was determined by observing the flow state of gel in the upside down glass bottle with time. The gel was divided into 10 grades according to different flow, suspension and tongue spitting states. The initial gelation time of a gel is defined as the time it takes for the gel to transition from the solution state to the strength code D (see Table 1).

2.4. Thermal stability measurement for self-assembled micro-nanocapsules

The self-assembled micro-nanocapsules were put into a measuring cylinder, and then the cylinder was placed in an oven at 30, 50, 70, 90, 110, 130, and 150 °C. The capsule was taken out every 2 h to observe the volume of the cross-linking agent solution released, and the thermal stability of the capsule was evaluated using the diversion ratio (defined as the ratio of the volume of the cross-linking agent released to the initial volume).

2.5. Rheological property measurements for self-assembled micro-nanocapsules gel system

The rheological properties of the gel system, such as yield stress, viscoelastic and creep recovery, were measured by the MARSIII rheometer (HAAKE, Germany) (Azimi et al., 2019). The experimental temperature was 30 °C and the shear ratio of the yield stress ranged from 1 to 100 Pa. The storage modulus (G') and the loss modulus (G'') of the sample were tested at the scanning frequency of 0.1 Hz and the stress was scanned in the range of 0.1–100 Pa. The linear viscoelastic region of the gel should be determined for viscoelastic testing and creep recovery performance testing. A stress value should be selected as the test stress in the linear viscoelastic region (Zhang S. et al., 2020). The test frequency range is 0.01–1 Hz, and the creep time of the creep recovery performance test is 100 s, the recovery time is 100 s.

2.6. Microstructure analysis of self-assembled micro-nanocapsules

Optical microscope observation: A drop of assembled micro-nanocapsules was placed on a slide, and the structure of micro-nanocapsules under the microscope was observed with an optical microscope.

Scanning electron microscope observation: The prepared self-assembled micro-nanocapsules were placed on a glass dish and freeze-dried with liquid nitrogen. Then, the frozen-dried micro-nanocapsules were placed in a vacuum freeze-drying machine for 24 h, and the dried samples were sprayed with gold. Finally, the samples were placed in an observation table for observation (Bai Y.

et al., 2022).

Observation by laser scanning confocal microscopy (CLSM): The aqueous solution of the crosslinker was added with a Nile blue dye with an excitation wavelength of 633 nm, and then the labeled cross-linking agent aqueous solution was encapsulated to form a capsule. The capsules were placed on a slide, and the micro-nanocapsules were observed under fluorescence mode using a Zeiss LSM710 confocal microscope (10× objective lens, 10× eyepiece).

3. Results and discussion

3.1. Mechanism of self-assembled micro-nanocapsules delaying gel gelation

The preparation of self-assembled micro-nanocapsules and their mechanism to delay gelation are shown in Fig. 2. In the presence of air, silica nanoparticles with hydrophobic properties can self-assemble on water droplets to form a capsule containing a cross-linking agent solution, the water phase of which is encapsulated in a hydrophobic silica capsule. Under the stimulation of external conditions such as high temperature and pH change, the capsule becomes unstable, breaks, and the cross-linking agent solution is released. At this time, the cross-linking agent can contact the polymer solution for cross-linking reaction, thus greatly delaying the gelation time between the cross-linking agent and the polymer.

3.2. Self-assembled micro-nanocapsules structure

The microstructure of self-assembled micro-nano sustained-release capsules was observed by an optical microscope, a scanning electron microscope, and a laser scanning confocal microscope, and the results are shown in Fig. 3. It can be clearly seen from Fig. 3(a) that the cross-linking agent aqueous solution is encapsulated by micro-nano particles to form a self-assembled micro-nano capsule, and Fig. 3(b) is the SEM image of the micro-nano particles after the cross-linking agent aqueous solution is lost after the self-assembled micro-nanocapsule sample is freeze-dried with liquid nitrogen. The self-assembled micro-nanocapsules are formed by observing the micro-nanoparticle encapsulated in the cross-linking agent aqueous solution, and their self-assembly capability is characterized. Confocal laser scanning microscopy (CLSM), which does not require vacuum conditions, was selected, and the aqueous solution was labeled by adding Nile blue reagent stain to the cross-linker solution, and then the aqueous solution was encapsulated with gas-phase hydrophobic SiO₂. Finally, the “quicksand” state of the package was observed by CLSM under fluorescence mode. In Fig. 3(c), it can be seen that the “quicksand” coated with fluorescent dye labeling of the crosslinker aqueous solution is magenta in color, which confirms that the gas-phase hydrophobic SiO₂ can be used as

Table 1
Gel strength code.

Strength code	Gel name	Intensity description
A	Non-detecting gel	The viscosity of the system is comparable to that of the polymer
B	High fluidity gel	The gel viscosity is slightly higher than the polymer viscosity
C	Liquid gel	Most of the gel can flow to the other end of the bottle
D	Medium flow gel	A small portion cannot flow to the other end, and is tongue shaped
E	Almost no flow gel	A small amount can flow slowly to the other end, most are not liquid
F	High deformation non-flowing gel	The gel should not run to the top of the bottle when the glass is turned over
G	Medium deformation does not flow gel	It only reaches the middle of the glass when flipped
H	Slight deformation does not flow gel	Only the surface of the gel deforms when flipped over
I	Rigid gel	The gel surface does not deform when turned over
J	Ringing gel	When the glass bottle is shaken, the mechanical vibration like a tuning fork can be felt

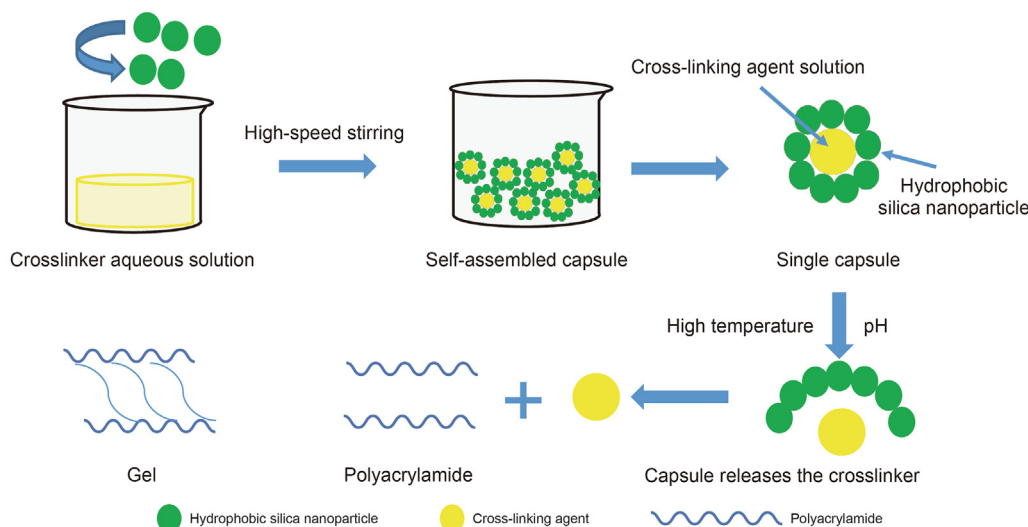


Fig. 2. Mechanism of micro-nanocapsules delaying gel gelation time.

a coating to wrap the crosslinker aqueous solution to form a capsule.

3.3. Effect of pH on self-assembly effect of micro-nanocapsules

In order to study the effect of pH value on the self-assembly effect of micro-nanocapsules, the self-assembly effect of micro-nanocapsules under different pH values was evaluated by adjusting the pH value of the cross-linking agent aqueous solution. The self-assembly effect of micro-nanocapsules was mainly evaluated by the diversion ratio of micro-nanocapsules. The experimental results are shown in Fig. 4. Fig. 4(a) shows the self-assembly effect of micro-nanocapsules with a mass ratio of 1:10 of gas-phase hydrophobic SiO₂ to cross-linking agent aqueous solution. “Quicksand” is formed after the assembly of gas-phase hydrophobic SiO₂ particles and cross-linking agent aqueous solution with pH values of 2, 4, 7, 10, and 12. In other words, self-assembled micro-nanocapsules can be obtained under the mass ratio of gas-phase hydrophobic SiO₂ to crosslinker is 1:10. When the mass ratio of gas-phase hydrophobic SiO₂ to crosslinker aqueous solution is 1:50, as shown in Fig. 4(b), “quicksand” can be formed after assembly of gas-phase hydrophobic SiO₂ and crosslinker aqueous solutions with pH values of 2, 4, 7, and 10, and self-assembled micro-nanocapsules can be obtained. However, after the assembly of gas-phase hydrophobic SiO₂ and the cross-linking agent aqueous solution with pH 12, the cross-linking agent solution separation phenomenon is obvious, and the self-assembly effect of micro-nanocapsules is poor. A large number of cross-linking agent aqueous solutions are not encapsulated, and a complete micro-nanocapsules cannot be formed. It is confirmed that pH value and the concentration of gas-phase hydrophobic silica will affect the self-assembly effect of self-assembled micro-nanocapsules.

Micro-nanocapsules with mass ratios of 1:5, 1:10, 1:25, and 1:50 of gas-phase hydrophobic SiO₂ to cross-linking agent aqueous solution were prepared at different pH values in the laboratory. The effect of pH value on self-assembled of micro-nanocapsules was evaluated by observing the diversion ratio of micro-nanocapsules. Fig. 5 shows the micro-nanocapsules formed at different mass ratios of gas-phase hydrophobic SiO₂ to crosslinker aqueous solution (pH of 2, 4, 7, 10, 12). When the mass ratio of gas-phase hydrophobic SiO₂ to crosslinker aqueous solution is 1:5 and the pH values are 2 and 12, the diversion ratio of micro-nanocapsules formed after

300 h is 3% and 100%, respectively. The experimental results show that with the increase in pH value, the diversion ratio of micro-nanocapsules increases, and the self-assembly effect worsens. Acidic conditions are conducive to the formation of micro-nanocapsules between gas-phase hydrophobic SiO₂ and aqueous solution and enhance their stability. The effect of pH value on the self-assembly effect of micro-nanocapsules is mainly analyzed because the increase in pH value will increase the number of charges on the surface of hydrophobic silica nanoparticles and reduce its hydrophobic performance. As a result, the self-assembly capacity of micro-nanocapsules decreases and separation occurs, so changing pH value can adjust the self-assembly capacity of micro-nanocapsules (Singh et al., 2019; Panthi et al., 2017). When the pH value is 2 and the mass ratios of gas-phase hydrophobic SiO₂ to aqueous solution of crosslinker are 1:5 and 1:50, the diversion ratio of micro-nanocapsules formed after 300 h is 3% and 20%, respectively. The experimental results show that with the increase in the concentration of gas-phase hydrophobic SiO₂, the diversion ratio of micro-nanocapsules decreases and the stability increases. This is because the increase in particle concentration is conducive to more particles participating in the self-assembly process, forming a stable self-assembled micro-nanocapsule.

3.4. Influence of temperature on self-assembly effect of micro-nanocapsules

In order to study the effect of temperature on the self-assembly effect of micro-nanocapsules, micro-nanocapsules prepared with different concentrations of hydrophobic SiO₂ in the gas phase were placed in a constant temperature oven at 30, 50, 70, 90, 110, 130, and 150 °C, and the diversion ratio of micro-nanocapsules under different time conditions was observed. To evaluate the effect of temperature on the self-assembly of micro-nanocapsules. Fig. 6 shows the diversion ratio curves of micro-nanocapsules formed by the mass ratio of gas-phase hydrophobic SiO₂ and crosslinker aqueous solution of 1:5, 1:10, 1:25, and 1:50 under different temperature conditions, respectively. The experimental results show that under the same time conditions, the higher the temperature, the larger the diversion ratio; the higher the concentration of gas-phase hydrophobic SiO₂, the lower the water diversion ratio. The analysis is that with the increase in temperature, micro-nanocapsules begin to break and the cross-linking agent aqueous

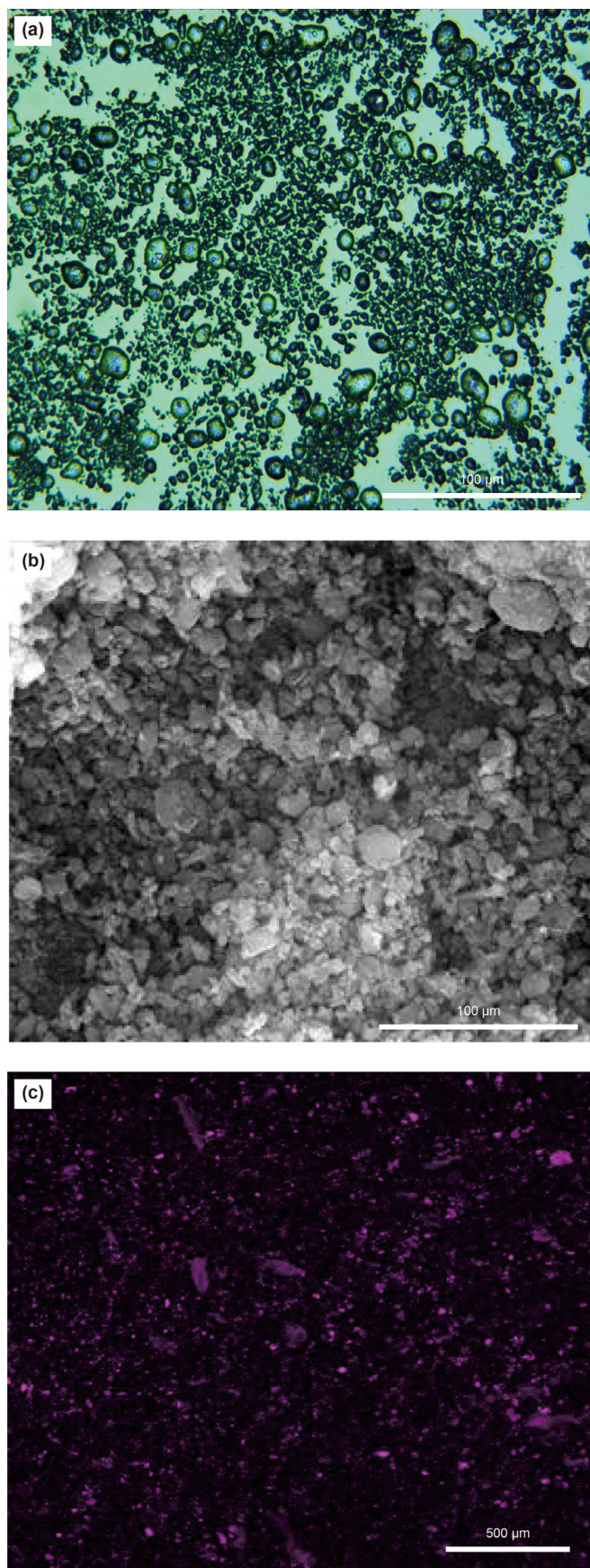


Fig. 3. Microscope (a), SEM (b) and CLSM (c) images of micro-nanocapsules.

solution encapsulated in micro-nanocapsules flows out, increasing the diversion ratio. As the concentration of hydrophobic particles increases, more hydrophobic particles participate in the self-assembly process, and the cross-linking agent aqueous solution is encapsulated inside the hydrophobic particles, reducing the diversion ratio.

3.5. Influence of stirring speed on self-assembly effect of micro-nanocapsules

In the process of self-assembly of gas-phase hydrophobic SiO_2 particles, agitation is an essential external condition. In order to investigate the influence of agitation speed on the self-assembly effect of micro-nanocapsules, the self-assembly effect of different gas-phase hydrophobic SiO_2 particle concentrations was evaluated at a stirring speed of 1000–5000 r/min. The experimental results are shown in Fig. 7. The diversion ratio of micro-nanocapsules decreases first and then increases with the increase in stirring speed. The optimal stirring speed of micro-nanocapsules formed with 1:5 gas-phase hydrophobic SiO_2 /cross-linking agent mass ratio is 3500 r/min, but when the mass ratio is less than 1:5, the optimal stirring speed can be less than 3500 r/min. It can be seen that the higher the concentration of gas-phase hydrophobic SiO_2 particles, the greater the corresponding optimal stirring speed. As the concentration of gas-phase hydrophobic SiO_2 particles increases, the number of hydrophobic particles participating in self-assembly behavior in the system increases, and a larger stirring speed is required to help encapsulate the crosslinker aqueous solution inside the gas-phase hydrophobic SiO_2 particles.

3.6. Particle size analysis of self-assembled micro-nanocapsules

The particle size distribution of micro-nanocapsules is shown in Fig. 8. The particle size of micro-nanocapsules gradually increases with the increase in the amount of gas-phase hydrophobic SiO_2 . The D_{50} values of micro-nanocapsules are 1124, 1196, 1264, and 1341 nm when the mass ratios of gas-phase hydrophobic SiO_2 to cross-linking agent aqueous solution are 1:50, 1:25, 1:10, and 1:5, respectively. With the increase in the concentration of gas-phase hydrophobic SiO_2 nanoparticles, more gas-phase hydrophobic SiO_2 particles participate in the self-assembly process, and the particle size of the formed micro-nanocapsules also gradually increases, basically reaching the micron level.

3.7. Effect of self-assembled micro-nanocapsules on the delay gel gelation time

Under the condition that the polymer concentration is 1.5% and the concentration of the cross-linker of chromium acetate solution is 0.2%, the effects of micro-nanocapsules (different concentrations of gas-phase hydrophobic SiO_2 particles, different pH values of cross-linking agent solution) on the gel gelation time were studied, and the results are shown in Fig. 9. As can be seen from Fig. 9, the gel gelation time of the gel system increases with the decrease in the pH value of the micro-nanocapsules, and gradually increases with the increase in the concentration of gas-phase hydrophobic SiO_2 particles in the micro-nanocapsules. Under the condition of 30 °C and the pH value of the cross-linking agent solution of 2, the gel gelation time of the self-assembled gel system without the addition of gas-phase hydrophobic SiO_2 particles is 14 h, and the gel gelation time of the micro-nanocapsular gel system with 2.0% gas-phase hydrophobic SiO_2 particles is 68 h, which extends the gel gelation time by 4.86 times. The gel gelation time of the micro-nanocapsule gel system with the concentration of 10.0 wt% of gas-phase hydrophobic SiO_2 particles was 175 h, and the gel

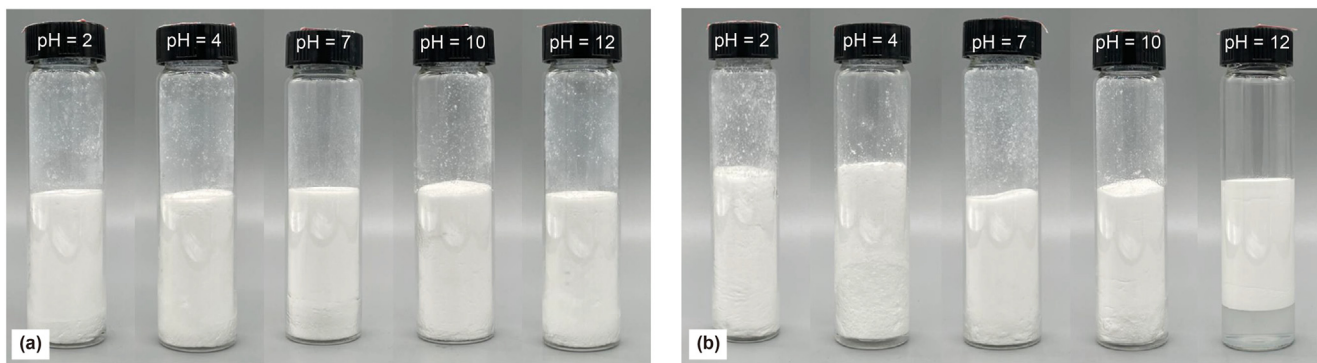


Fig. 4. Self-assembly of silica nanoparticles in solutions with different pH values. The mass ratios of hydrophobic particles to cross-linking solution are 1:10 (a) and 1:50 (b), respectively.

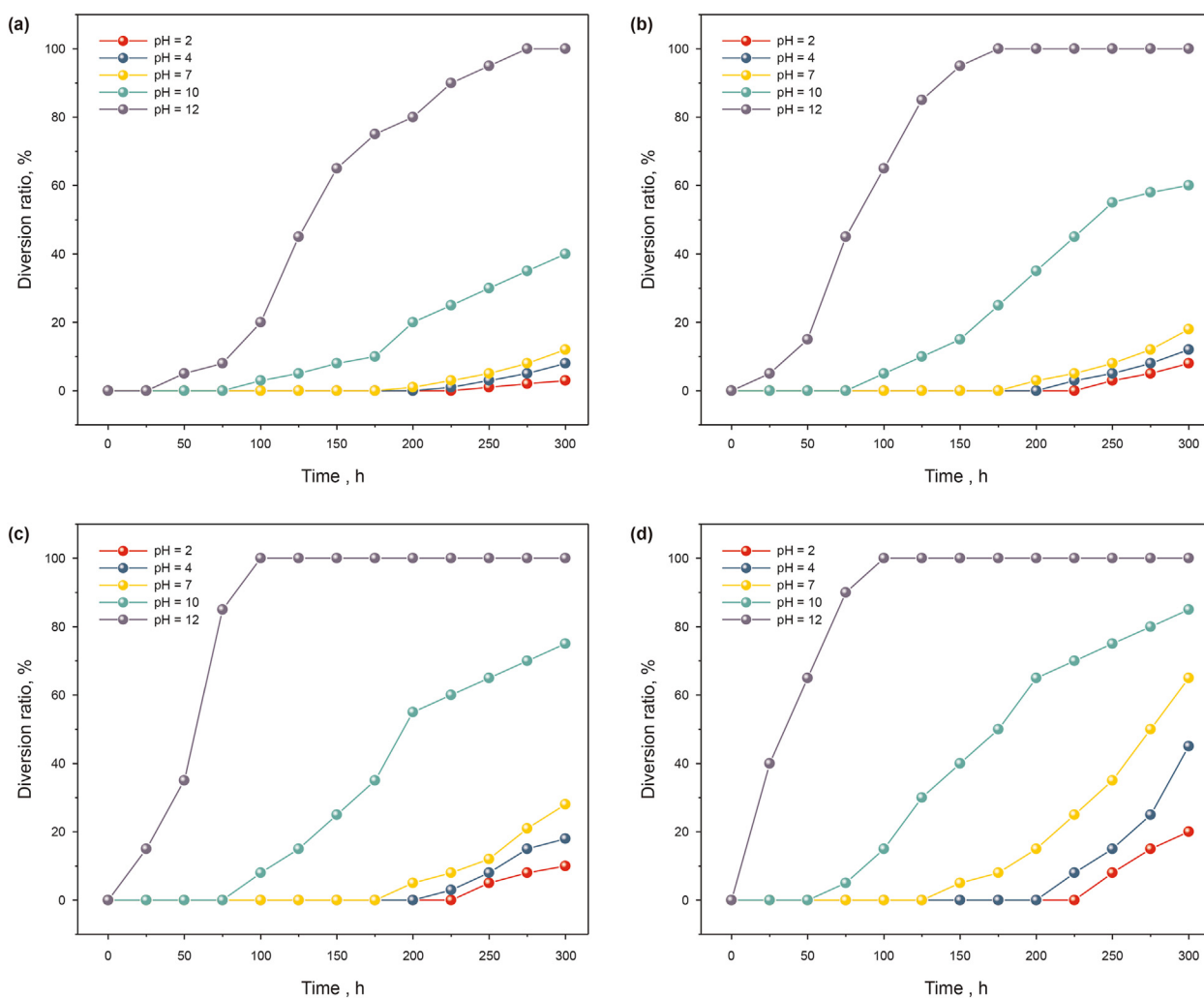


Fig. 5. Influence of pH value of the cross-linking agent solution on the self-assembly effect of micro-nanoparticles when the mass ratios of hydrophobic particles to cross-linking agent solution are 1:5 (a), 1:10 (b), 1:25 (c), and 1:50 (d), respectively.

gelation time was extended by 12.5 times. The results show that under the same temperature and pH value, the higher the concentration of gas-phase hydrophobic SiO₂ particles, the better the effect of delaying the gel gelation time, because more gas-phase hydrophobic SiO₂ particles participate in the self-assembly process, and the cross-linking agent solution in the capsule is difficult

to be released, so the gel gelation time of the gel system becomes longer. Under the condition of 30 °C and the pH value of the cross-linking agent solution of 12, the gel gelation time of the micro-nanoparticle gel system with the concentration of 2.0 wt% of gas-phase hydrophobic SiO₂ particles is 30 h, and the gel gelation time is 2.14 times longer; the gel gelation time of the micro-

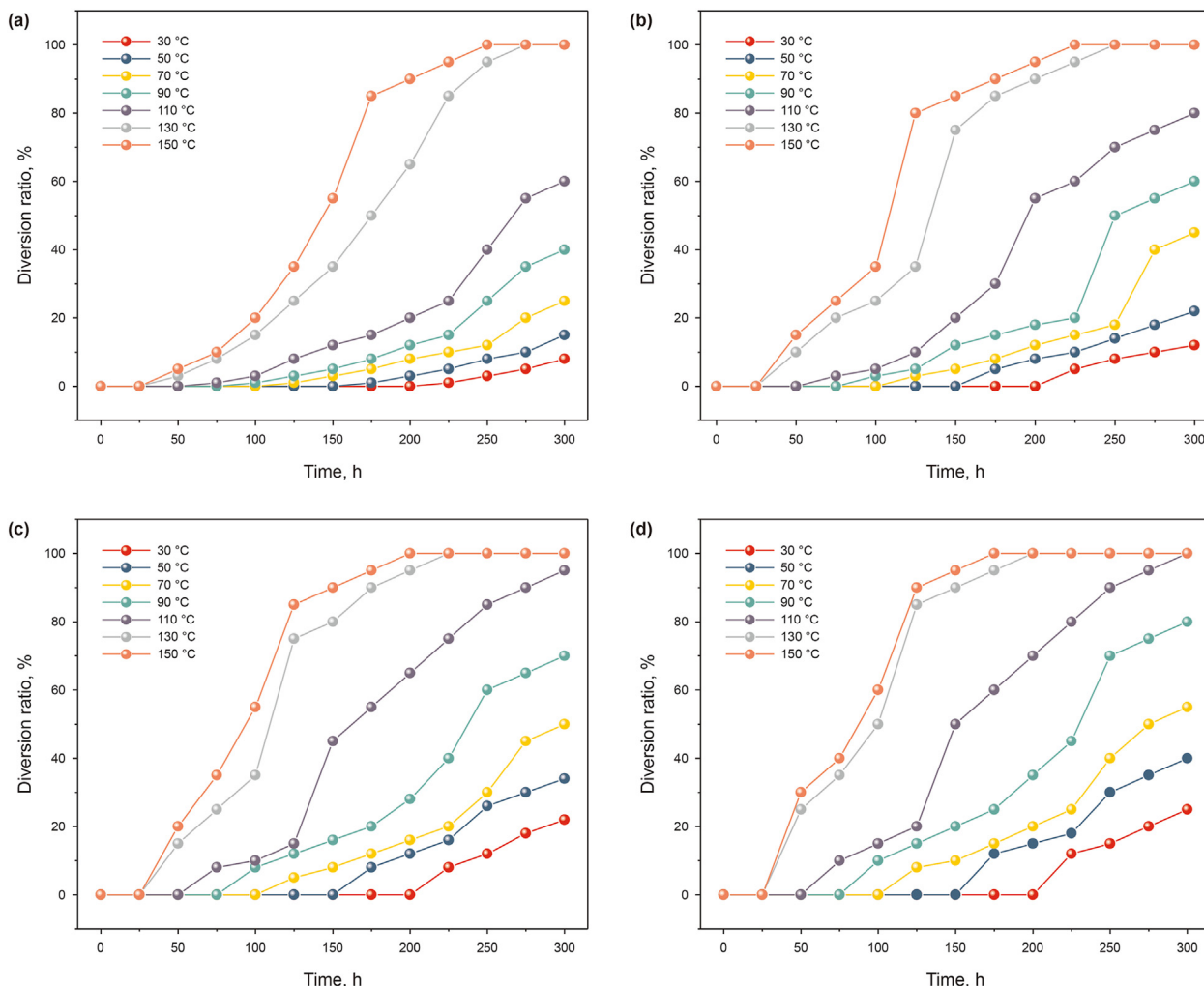


Fig. 6. Influence of temperature on the self-assembly effect of micro-nanoparticles when the mass ratios of hydrophobic particles to cross-linking agent solution are 1:5 (a), 1:10 (b), 1:25 (c), and 1:50 (d), respectively.

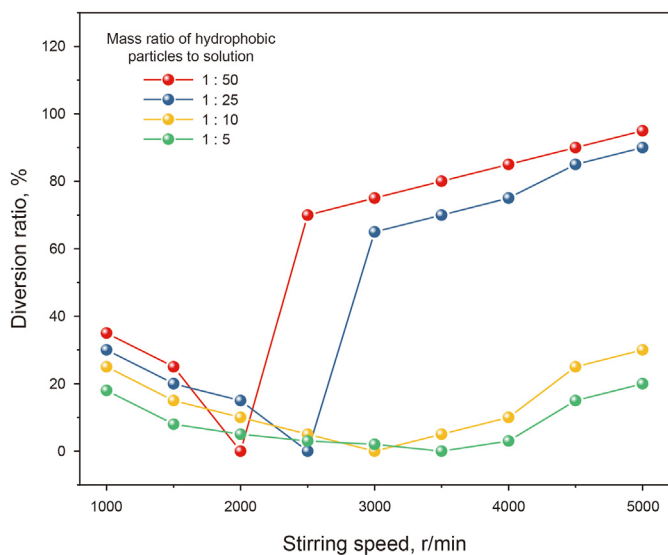


Fig. 7. Influence of stirring speed on the self-assembly effect of micro-nanoparticles.

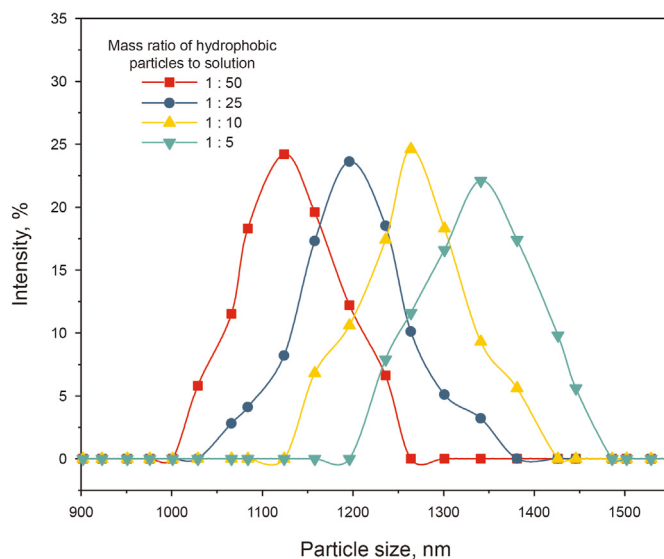


Fig. 8. Particle size distribution of micro-nanocapsules formed at different mass ratios of hydrophobic particles to cross-linking agent solution.

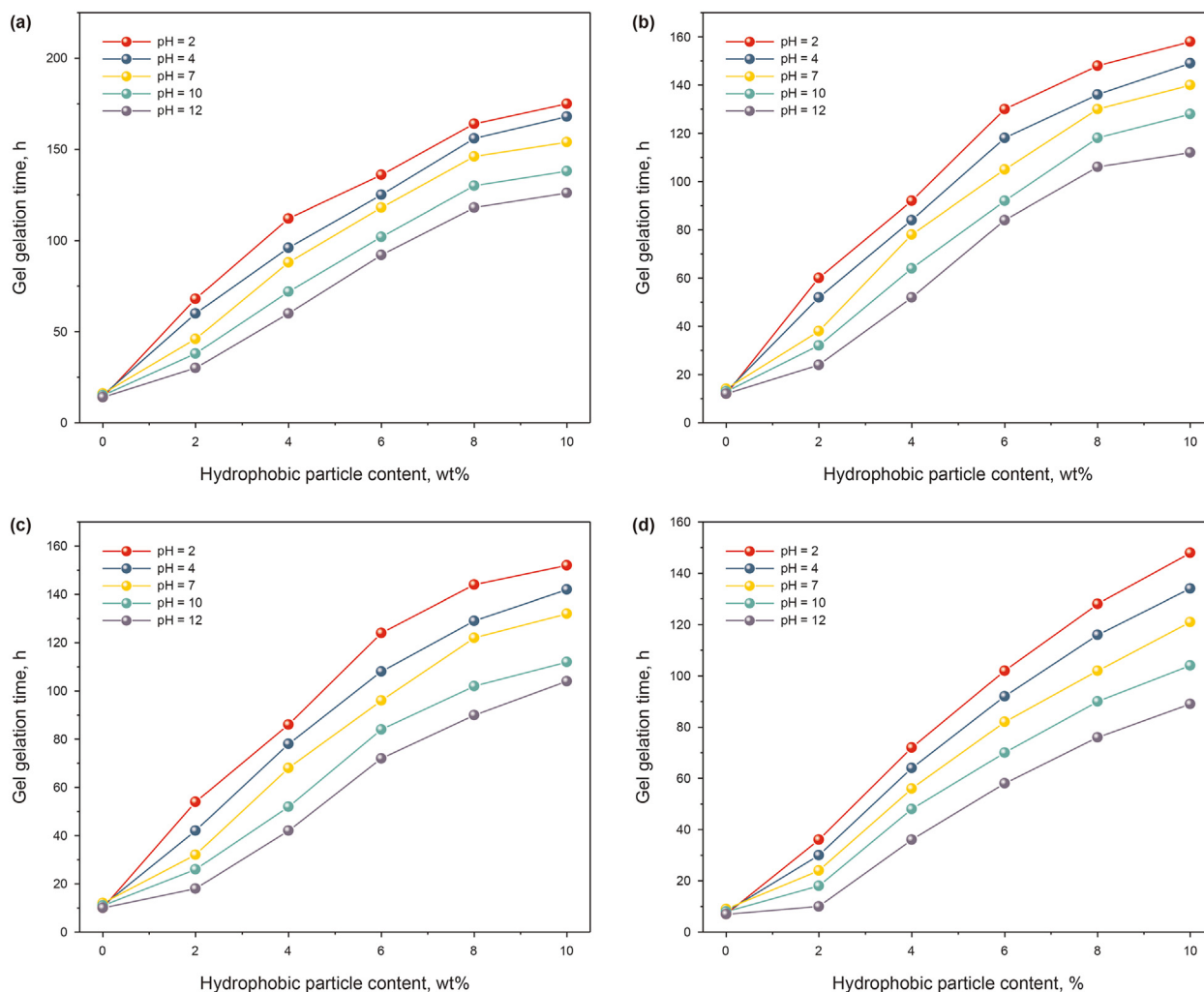


Fig. 9. Effects of different self-assembly ratios on gel gelation time at different temperatures. (a) 30 °C; (b) 60 °C; (c) 90 °C; (d) 120 °C.

nanocapsule gel system with 10.0 wt% gas-phase hydrophobic SiO₂ particles is 126 h, and the gel gelation time is 9.0 times longer. It can be seen that under the same temperature and the same concentration of gas-phase hydrophobic SiO₂ particles, the greater the pH value, the worse the effect of delayed gelation time. This is because the increase in pH value will increase the charge number on the surface of hydrophobic silica, resulting in a decline in its hydrophobic performance. Part of the gas-phase hydrophobic SiO₂ particles dissolve in aqueous solution, resulting in a decline in the self-assembly ability of micro-nanocapsules, and the cross-linking agent in the capsules is released in advance, accelerating the formation of gel, resulting in poor delayed gel time, which confirmed the results of the previous study that the diversion ratio of micro-nanocapsules increased with the increase in pH value. At the same time, the above experimental conclusions can be obtained at 60, 90, and 120 °C.

3.8. Influence of micro-nanocapsule particles on rheological properties of gel system

The addition of nanoparticles will affect the rheological properties of the gel system (Shehbaz and Bera, 2023; Elhaei et al., 2021). The effects of the concentration of gas-phase hydrophobic SiO₂ particles in micro-nanocapsules on the storage modulus (G'),

loss modulus (G''), creep recovery properties, and yield stress (τ_0) of the gel are shown in Fig. 10. Fig. 10(a) shows that the storage modulus (G') increases with the increase in the concentration of gas-phase hydrophobic SiO₂ particles in the micro-nanocapsules. In the linear viscoelastic region, the storage modulus values of the micro-nanocapsules systems with different mass fractions of gas-phase hydrophobic SiO₂ particles are in a range of 0.2–25 Pa, which are basically unchanged with shear stress, indicating that the strain changes with the change of stress. Therefore, this region is the linear viscoelastic region of the gel system and the linear viscoelastic region is presented as a rectangle in Fig. 10(a).

Fig. 10(b) shows that the loss modulus increases with the increase in the concentration of gas-phase hydrophobic SiO₂ particles in micro-nanocapsules. However, unlike the elastic modulus, the linear viscoelastic region of the gel system with the addition of micro-nanocapsules is not rectangular. As the concentration of gas-phase hydrophobic SiO₂ particles in micro-nanocapsules increases, as shown in Fig. 10(b), the linear viscoelastic region also increases, showing a trapezoid shape. The results show that the addition of gas-phase hydrophobic SiO₂ particles can significantly increase the storage modulus (G') and loss modulus (G'') of the gel system.

Fig. 10(c) shows the test results of the creep recovery performance of the gel system. According to Fig. 10(c), during the creep stage of the gel system (0–100 s), under the influence of stress, the

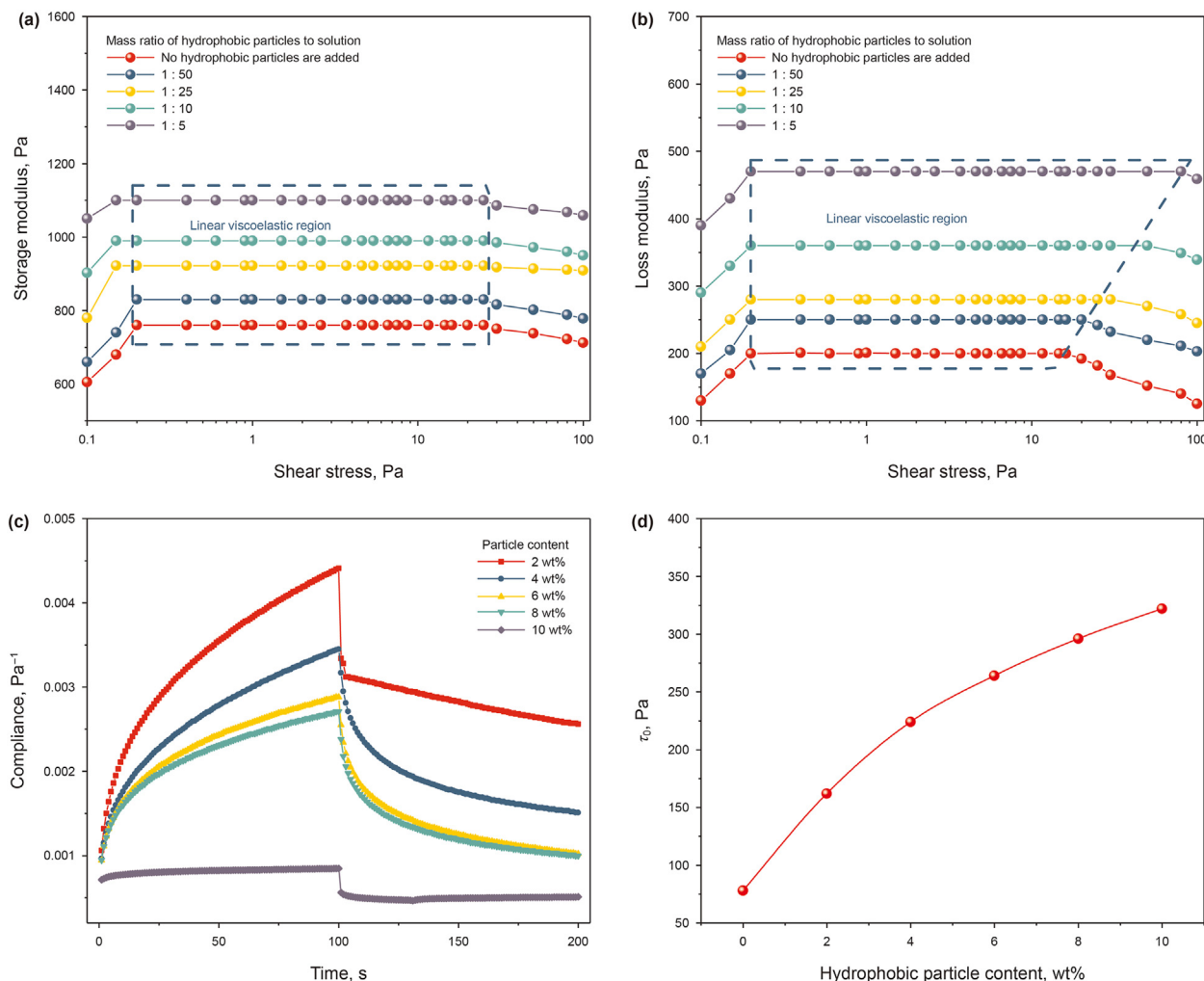


Fig. 10. Effects of different self-assembly ratios on the rheological properties of gels.

compliance values of the gel system containing gas-phase hydrophobic SiO₂ particles with different mass fractions show an increasing trend. In the recovery stage (100–200 s), after the stress is removed, the gel system with 2.0 wt% gas-phase hydrophobic SiO₂ particles cannot completely recover, and when the concentration of gas-phase hydrophobic SiO₂ particles added is greater than 2.0 wt%, the gel system can completely recover. As the concentration of hydrophobic particles increases, the flexibility value of the system decreases, which means that its strength is relatively high, so it is not easy to deform, and it is easier to return to the original state after deformation, which is close to the ideal solid response.

Fig. 10(d) shows that the yield stress of the system increases with the increase in the concentration of gas-phase hydrophobic SiO₂ particles in the micro-nanocapsules. The yield stress of the system is 78 Pa when hydrophobic particles are not added, and 162 Pa when 2.0 wt% gas-phase hydrophobic SiO₂ particles are added. The yield stress is 322 Pa after adding 10.0% gas-phase hydrophobic SiO₂ particles. The higher the yield stress is, the higher the strength of the gel formed and the harder it is to be destroyed. Therefore, increasing the concentration of the gas-phase hydrophobic SiO₂ particles in the micro-nanocapsules can prevent the gel system from being destroyed. The results showed that adding micro-nanocapsules could improve the strength of the gel.

3.9. Influence of micro-nanocapsule particles on the gel microstructure

In order to explore the effects of the addition of gas-phase hydrophobic SiO₂ particles on the gel microstructure, a Quanta 200F field emission environmental scanning electron microscope was used to observe the effects of gas-phase hydrophobic SiO₂ particles on the microstructure, and the experimental results are shown in Fig. 11. SEM images of the gel systems without gas-phase hydrophobic SiO₂ particles are shown in Fig. 11(a) and (b). The results show that the gel system without gas-phase hydrophobic SiO₂ particles has only a small part of the network structure, and the overall state is relatively loose, indicating that the cross-linking density between polymer molecular chains in the system is insufficient, the gel strength is low. The structure after the addition of gas-phase hydrophobic SiO₂ particles is shown in Fig. 11(c). At the same multiples under environmental scanning electron microscopy, a dense cross-linked network structure is formed inside the system, which can firmly support the gel structure and the cross-linked structure makes the system not easily damaged. Compared with the gel without addition gas-phase hydrophobic SiO₂, the addition gas-phase hydrophobic SiO₂ gel has a higher strength on the macro level, which is consistent with the rheological viscoelastic measurement results. The gel system with gas-phase hydrophobic SiO₂ particles added was further enlarged, and its

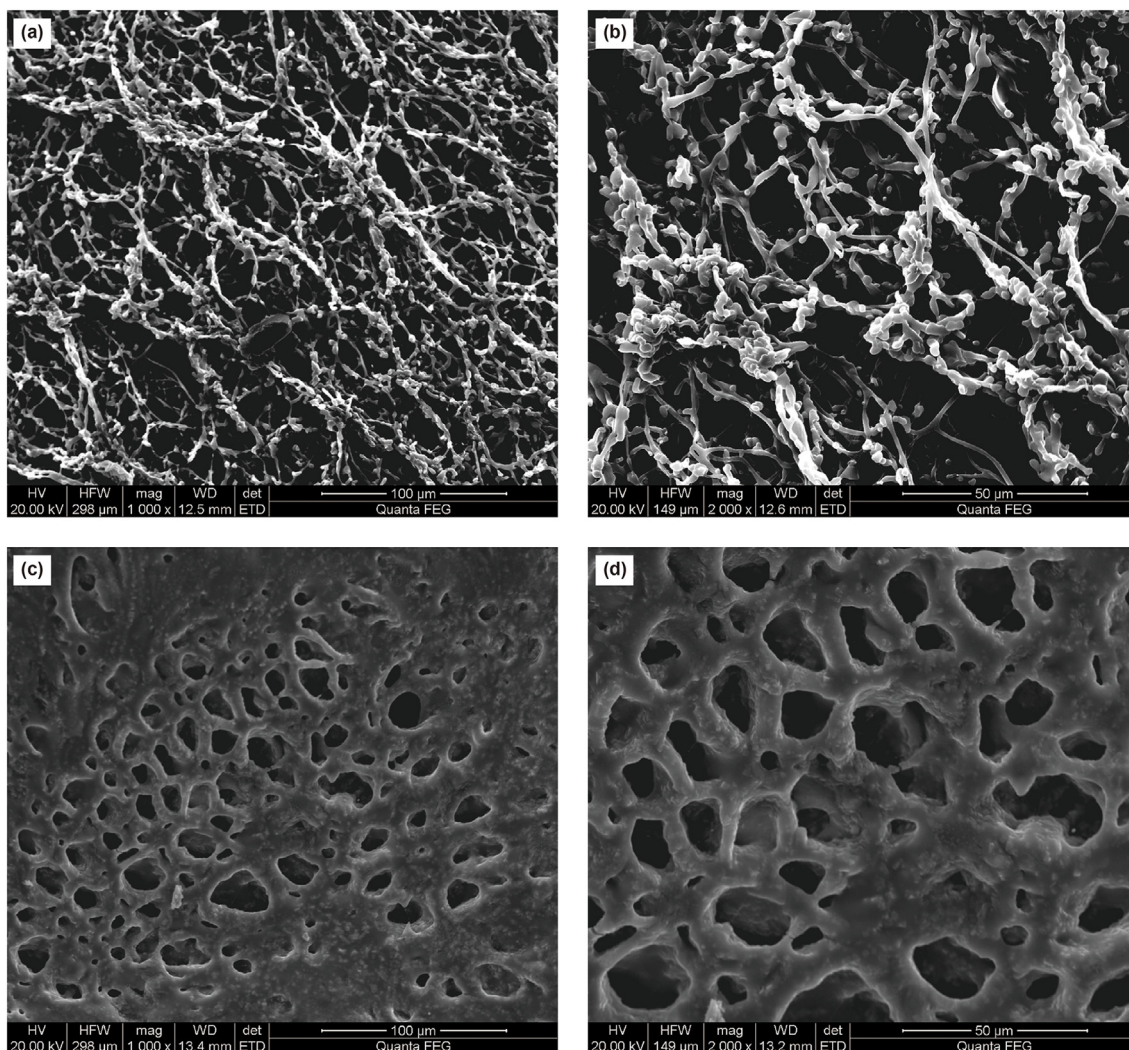


Fig. 11. SEM images of the gel systems without (a, b) and with (b, c) addition of gas-phase hydrophobic SiO₂ particles.

structure was observed at 2000 \times , as shown in Fig. 11(d). It can be seen that in the mesh structure, particle pellets are attached to the mesh structure, which means that hydrophobic particles play a skeleton-supporting role in the mesh structure, thus improving the overall strength of the gel system.

4. Conclusions

A kind of intelligent responsive self-assembled micro-nanocapsules was prepared by using gas-phase hydrophobic SiO₂ particles as raw material. The self-assembly capacity of intelligent responsive self-assembled micro-nanocapsule is affected by temperature, pH value and concentration of gas-phase hydrophobic SiO₂ particles, reducing pH value and increasing the concentration of atmospheric hydrophobic SiO₂ particles can enhance the encapsulation ability of self-assembled micro-nanocapsules. The applicable solution pH value of self-assembled micro-nanocapsules is 2–10, pH value is 2, the mass ratio of gas-phase hydrophobic SiO₂ particles to aqueous solution of cross-linking agent is 1:5, and the diversion ratio of micro-nanocapsules is 3.0% after heat treatment at 150 °C for 300 h, which indicates that self-assembled micro-nano slow-release capsules have good thermal stability. In terms of delayed gelation time, the gelation time of the self-assembled

nano-capsule gel system with pH value of 2 and the concentration of gas-phase hydrophobic SiO₂ particles of 10% is extended by 12.5, 13.2, 15.2 and 21.1 times at 30, 60, 90 and 120 °C, respectively, compared with the gel system without hydrophobic particles added. The results showed that the self-assembled micro-nanocapsules had a better effect of prolongating gel gelation time under high temperature conditions. The gas-phase hydrophobic SiO₂ particles not only have the effect of delaying the gelation time of self-assembled package crosslinker solution, but also the addition of gas-phase hydrophobic SiO₂ improves the storage modulus, loss modulus and yield stress of the gel system, greatly enhancing the strength of the gel system. This kind of efficient and intelligent responsive capsule prepared by simple stirring method using the self-assembly of gas-phase hydrophobic SiO₂ provides a new practical method for delaying the gelation time of polymer gel.

CRediT authorship contribution statement

Chuan-Hong Kang: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Ji-Xiang Guo:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization. **Dong-Tao Fei:** Writing – original draft, Methodology,

Investigation, Formal analysis, Conceptualization. **Wyclif Kiyangi:** Writing – review & editing, Writing – original draft, Supervision, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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