

Storage Stability and Solubility of Poly(urea-formaldehyde) Microcapsules Containing α -Olefin Drag Reducing Polymer

Bing Li, Guilin Dong, Changqiao Zhang

School of Chemistry and Chemical Engineering, Shandong University, Jinan, Shandong, China

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ABSTRACT: Microcapsules containing α -olefin drag reducing polymer were prepared by *in situ* and interfacial polymerization with urea, formaldehyde, and styrene as shell materials, respectively. IR spectrums of prepared shells indicated the formations of poly(urea-formaldehyde) and polystyrene in the microencapsulating process. The morphologies of uncoated particles and microcapsules were observed by scanning electron microscopy (SEM) which proved that the α -olefin drag reducing polymer particles were effectively coated. For the purpose of determining the stability of microcapsules in transportation and storage, the static pressure experiment was carried out and lasted for 6 months. In this process, microcapsules with polystyrene as shell material stuck together after 3 months; however, those with poly(urea-formaldehyde) kept the state of particles. The thermal characteristics of

uncoated particles (core), poly(urea-formaldehyde) (shell), and microcapsules with that as shell material were characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) which proved that thermal stable temperature of microcapsules containing α -olefin drag reducing polymer with poly(urea-formaldehyde) as shell material was below 225°C, and the mean heat absorbed by microcapsules in the temperature increasing process was 1.5–2.0 W/g higher than that by cores. The evaluation of drag reducing rate of microcapsules showed that the microencapsulating process had no influence on the drag reduction of α -olefin drag reducing polymer. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1450–1456, 2011

Key words: microcapsule; α -olefin drag reducing polymer; particle

INTRODUCTION

Pipeline transportation is one of the five primary transportation ways (railway, road, water, airway, and pipeline). Pipeline transportation is also the main transportation type in commercial application of transporting of oil and natural gas. Oil conveyed with pipeline worldwide accounts for about 94% gross production of it. Drag reducing technology of pipeline transportation is a key factor that controls the pipeline construction and operation cost, and even the pipeline security. Up to now, this technology is applied widely in the oil transportation domain through adding of drag reducing agent (DRA) in oil pipeline.^{1–5}

High molecular polymer drag reducing agents, e.g., poly α -olefin, play a dominant role in the drag reducing technology scheme of oil pipeline transportation. The acting constituent of this drag reducing agent is α -olefin polymer which is commonly prepared by random copolymerization of more than

three types of long chain α -olefins,^{6–11} and the molecular weight of it exceeds 6×10^6 .¹² Because of van der Waals forces and entanglements between molecules, α -olefin polymer is in viscoelastic state and there is no crystallinity.¹³ So it cannot be injected into oil pipelines with a mechanical pump directly to play drag reducing role. For the purpose of ejection, α -olefin polymer must be made into suspension by using dispersion technology. The main method of dispersion technology widely adopted at present is to make α -olefin polymer cool to glass state, then ground into powders and scattered into dispersant in which the isolation agent is added in low temperature environment.^{14,15} The acting content of α -olefin polymer in suspension is about 25%. But this method cannot solve the key problem about isolation of particles, and the poly α -olefin particles in suspension often stick together along with the prolongation of storage time. This problem often causes that the suspension cannot be used stably for long term on the field of ejection, and the transportation cost of suspension in which there is only 25% acting content is increased. Based on this point, it becomes a hot spot that viscoelastic α -olefin polymer is microencapsulated and stored for a long time in solid state.¹⁶ In addition, the microcapsules can be

Correspondence to: C. Zhang (zhangchqiao@sdu.edu.cn).

scattered in suspension and used directly, so the transportation cost of the drag reducing agent is reduced obviously. Based on the above opinions, the research of microencapsulation of α -olefin polymer plays a dominant role in the drag reducing technology of pipeline transportation.

EXPERIMENTAL

Materials

Massive drag reducing polymer was prepared by bulk polymerization of α -olefins. First, the polymer was soaped in -173°C liquid nitrogen for 5 h until it was cooled to glass state, then was ground in a ball mill for several times until the average diameter of particles used as core materials was about 200 μm . Urea, formaldehyde solution (37 wt %), and styrene used as shell materials were purchased from Tianjin Chemical Plant, China. Potassium persulfate and sodium bisulfite used as oxidant and reductant were purchased, respectively, from Linyi Tianke Chemical Co. Ltd., and Shanghai Jinmaotai Chemical Co. Ltd., China. Dodecyl sulfate sodium used as surfactant was purchased from Wuxi Duolijia Commercial Co. Ltd., China. All materials were used directly without further purification.

Preparation

Based on previous experiments and for purpose of cost saving, poly(urea-formaldehyde) and polystyrene, which were chosen as shell materials of microcapsules containing α -olefin drag reducing polymer, were synthesized by *in situ* and interfacial polymerization, respectively.

In situ polymerization of urea and formaldehyde was carried out in suspension in which α -olefin drag reducing polymer particles were the dispersed phase, and water was the continuous phase. This system was similar to oil-in-water emulsion in which oil drop was the dispersed phase. But the α -olefin drag reducing polymer particles prepared before microencapsulation were bigger than oil drops generally. In an optimal procedure, 5 g urea and 11 g formaldehyde solution (37 wt %) were dissolved in deionized water (70 g) with mechanical stirring (300 rpm) at room temperature. In most cases it may be desirable to use surfactant to keep the stability of suspension, so 0.1 g sodium dodecyl sulfate (SDS) was added. Because of adhesion between α -olefin drag reducing polymer particles, they could not be stored in room temperature for long time. So 15 g α -olefin drag reducing polymer powders must be quickly added in water at high stirring speed (500 rpm) before the particles stuck together and the stirring was kept for 15 min. Then the pH of suspension was adjusted to 1.0

with sulfuric acid. After reaction for 20 min, the particles were separated with vacuum filtration, purged with deionized water for three times to adjust pH to 7.0. Then the particles were dried at 60°C for 24 h and stored in a drying bottle.

In the process of microencapsulation of α -olefin drag reducing polymer by interfacial polymerization of styrene, about 85 g water and 0.1 g dodecyl sulfate sodium were mixed and the stirring speed was kept at 500 rpm for 5 min. Then 0.1 g potassium persulfate and 0.1 g sodium bisulfite was added. After 30 min stirring, about 9.5 g styrene was dropped in and 15 g drag reducing polymer powders were added quickly. Then the stirring speed was slowed down to 100 rpm and temperature was increased to 80°C . After reaction for 60 min, the particles were separated with vacuum filtration until temperature was decreased to 25°C . Then the particles were dried at 60°C for 24 h and stored in drying bottle.

Characterization

For purpose of asserting formation of poly(urea-formaldehyde) and polystyrene, the structures of molecular functional groups in shell materials were analyzed by IR spectrometer (Nicolet 380, Thermo Electron Corporation, USA). The effect of microencapsulation can be estimated through observation of morphology of microcapsules, so the morphologies of α -olefin drag reducing polymer particles without shell protection and microcapsules were obtained with a scanning electronic microscope (SEM, JEOL JSM-7600F, Japan). Prior to being observed, the samples were metalized with a gold layer.

When microcapsules are packed with boxes in practical application, the shells of them may be cracked by extruding them, so the storage stability should be concerned. Static pressure experiment was carried out and had lasted for 6 months. The microcapsules were stored in a cylindrical vessel which simulated the practical box style and the depth of packed microcapsules was 1 cm. The round surfaces of microcapsules were pressed by different weights which were equivalent to those of 12, 24, 36, 48, and 60 cm thickness of microcapsules, respectively. These cylindrical instruments were stored at 25°C for 6 months. Morphologies of microcapsules sampled in every month were detected.

Packed microcapsules containing α -olefin drag reducing polymer were usually stored in outdoor environment. The temperature might be more than 60°C in summer at some low latitudes. Whether the shell of microcapsules has thermal stability that stores heat and keeps the drag reducing effect of core materials on this extreme circumstance is very important. So the thermal properties of α -olefin drag reducing polymer particles (core), poly(urea-formaldehyde)

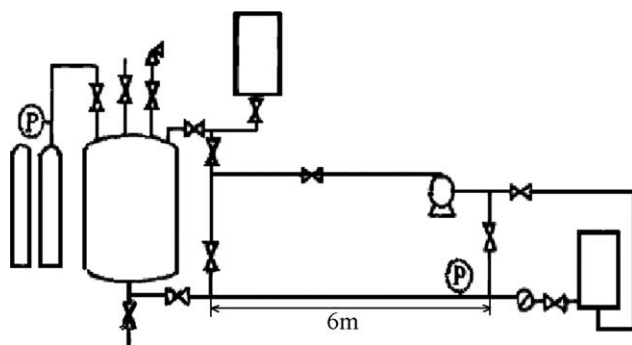


Figure 1 Drag reduction efficiency evaluating system.

(shell), and microcapsules were detected with simultaneous thermal analyzer (SDTQ600, USA) at a heating rate of 20°C/min from 20 to 500°C in nitrogen atmosphere. The TGA and DSC diagrams were obtained with analysis software (TA Universal Analysis).

For purpose of observing the drag reducing effect of coated particles, the shell of microcapsules should be dissolved in oil easily. So the drag reducing rate was detected. Before measuring, different samples including α -olefin drag reducing polymer particles without shell protection (blank sample) and microcapsules after 6 months' static pressure experiment were dissolved in diesel (about 17.4 g sample was dissolved in 2.5 L diesel) with stirring (500 rpm), respectively. The stirring time was 120 min and the solutions were sampled every 10 min for drag reduction efficiency evaluation. The drag reducing rates were detected on a drag reduction efficiency evaluating system. The measuring part of this system is a stainless steel pipe which is 6-m length with a 2-cm inside diameter and there is a pressure meter fixed on the outlet of it. About 250 mL of solution in which the sample was dissolved was added in 100 L of diesel and impressed in the circular pipeline with air compressor. The drag reduction efficiency can be calculated through eq. (1).

$$DR\% = 100(\Delta P_0 - \Delta P_{DR})/\Delta P_0 \quad (1)$$

where DR% is confined as drag reducing rate, ΔP_0 is pressure drop with solvent, and ΔP_{DR} is pressure drop with solution of drag reducing agent. The drag reduction efficiency evaluating system was shown in Figure 1.

RESULTS AND DISCUSSION

IR spectrum analysis

Figure 2 showed the functional groups IR spectrums of poly(urea-formaldehyde) and polystyrene. As seen in Figure 2(a), the spectrum of poly(urea-formaldehyde) showed absorption bands at 3350 and

2960 cm^{-1} for —OH and C—H stretching. Because of affection of N, the absorption frequency of C=O decreased to 1640 cm^{-1} and that of N—H increased to 1550 cm^{-1} and overlapped at the characteristic zone. This also was the result of overlapping of I spectrum band and II spectrum band of amides. The middle absorption peak at 1247 cm^{-1} was the in-plane bending vibration of O—H. Bending of N—H was observed at 640 cm^{-1} . The most important is that absorbing at 1440 and 1390 cm^{-1} were mixing frequencies of C—N and N—H bending vibrations, as well as the bending vibration of C—H. This confirmed formation of poly(urea-formaldehyde).

The spectrum of poly styrene showed in Figure 2(b) presented that stretching vibration of =C—H in benzene was reflected from 2800 to 3000 cm^{-1} . The vibration of C=C in benzene was shown in the field of 1400–1600 cm^{-1} . The in-plane bending vibrations of =C—H and C=H were shown from 900 to 1200 cm^{-1} and from 700 to 760 cm^{-1} . Compared with the standard spectrum of polystyrene, it was very obvious that polystyrene was the final product.

Morphologies

Figure 3 presented the morphologies of drag reducing particles and two kinds of microcapsules. The

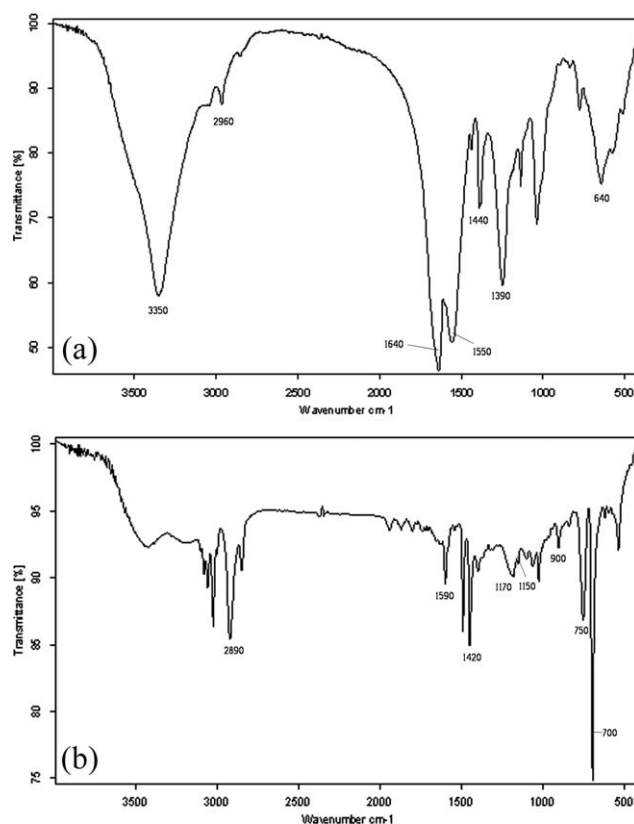


Figure 2 IR spectrums of (a) poly(urea-formaldehyde) and (b) poly styrene.

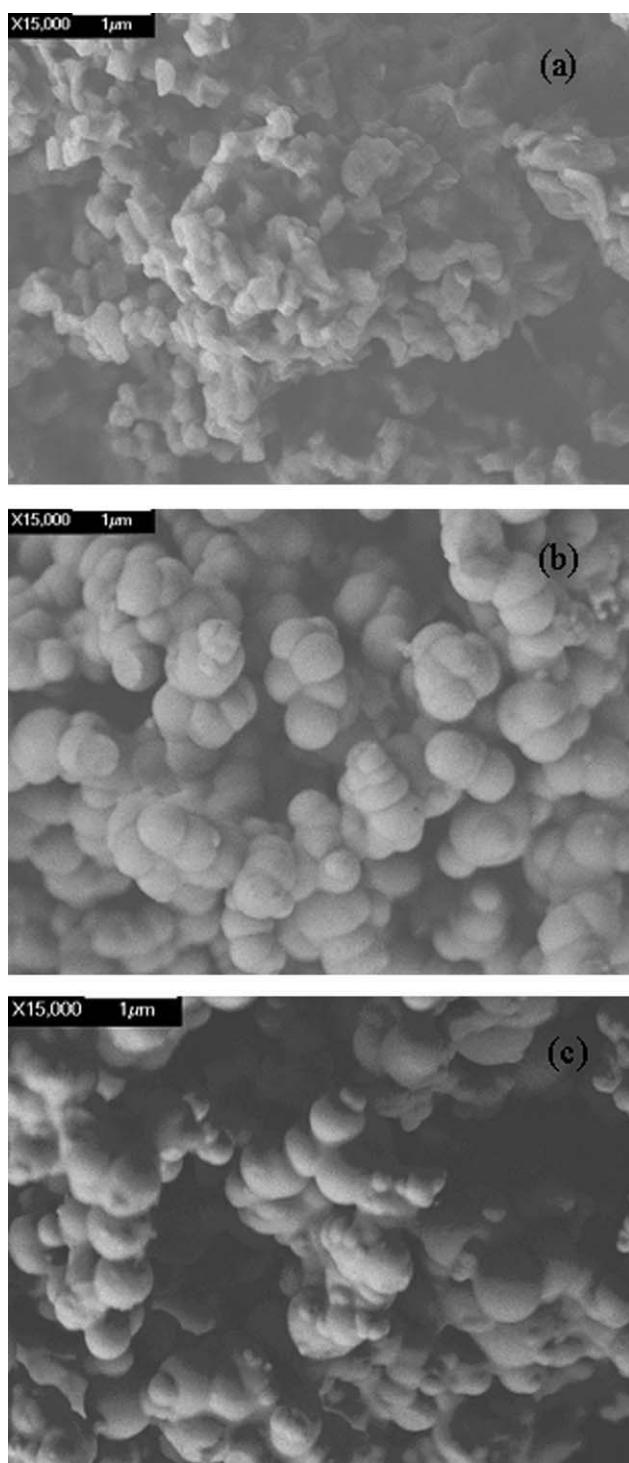


Figure 3 SEM photographs of (a) α -olefin drag reducing polymer particle, (b) oil drag reducing polymer microcapsule with poly (urea-formaldehyde) layer, and (c) oil drag reducing polymer microcapsule with poly styrene layer.

surface of uncoated drag reducing particles was jagged. But that of microcapsules with poly(urea-formaldehyde) as shell material changed greatly. The jagged surface was substituted by upheaped small balls. Although the morphology of microcapsules with polystyrene as shell material changed

obviously, the size uniformity was lower than that with poly(urea-formaldehyde).

Storage stability

Figure 4 showed SEM photographs of microcapsules pressed by weight which was equivalent to that of 60 cm thickness microcapsules and experiencing 0, 3, and 6 months' static pressure experiment. It was obvious that after 3 months, microcapsules with polystyrene as shell material could not maintain the microcapsule's status, and there was partial adhesion between microcapsules. After 6 months' experiment, these microcapsules completely stuck together and were no longer suitable for practical application. The microcapsules with poly(urea-formaldehyde) as shell material, however, still kept the state of upheaped small balls and there was no adhesion between them.

Thermal stability

Because microcapsules with polystyrene as shell material were unstable in static pressure experiment, they were not suitable for commercial application. Based on this point, thermal stability was measured only to microcapsules with poly(urea-formaldehyde) as shell material.

The TGA diagrams of α -olefin drag reducing polymer particles (core), poly (urea-formaldehyde) (shell), and microcapsules are shown in Figure 5. The weight loss from 50 to 225°C shown on the curve of shell might be attributed to water evaporation or oligomer of urea and formaldehyde decomposition. From 225 to 300°C, there was a sharp weight loss which might be resulted from the decomposition of poly(urea-formaldehyde). On the curve of the core, there was an obvious weight loss from 375 to 475°C. This might be the decomposition of α -olefin drag reducing polymer. It also can be seen from the curve of the microcapsule that there was a great weight loss from 375 to 475°C that resulted from decomposition of the microcapsule, though there was little loss from 225 to 375°C. By contrast the curve of the core and microcapsule, they almost coincided with each other below 225°C, but after 225°C, the microcapsule exhibited mild weight loss from 225 to 375°C. The integration of weight loss of microcapsules was about 3.36% in this field, which was approximately the shell constituent percent in microcapsules. This obviously confirmed that the constituent of shell in microcapsules was too small to affect the thermal stability of microcapsules. Through comprehensive analysis of the three curves, it can be understood that the thermal stable temperature of microcapsules containing α -olefin drag reducing polymer with poly(urea-formaldehyde) as

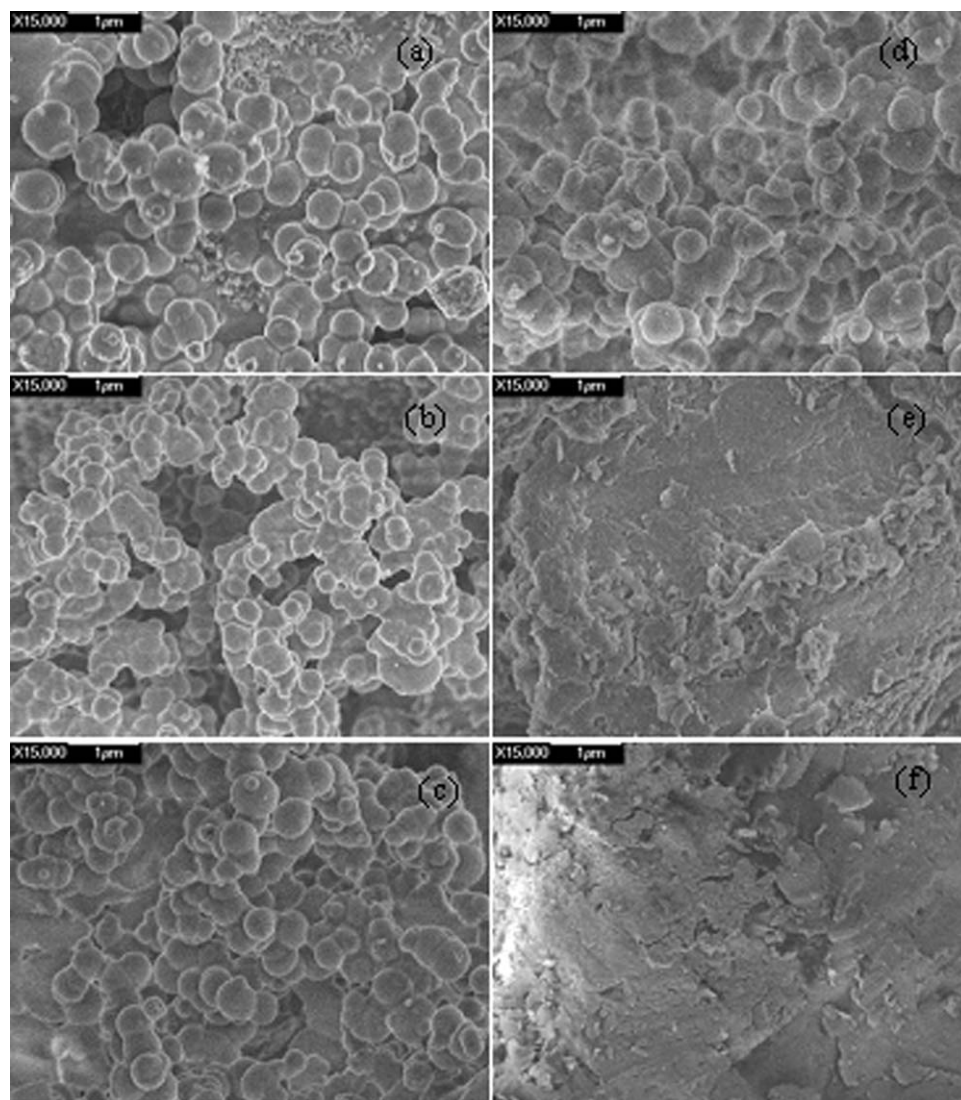


Figure 4 SEM photographs of microcapsules pressed by weight which was equivalent to that of 60 cm thickness microcapsules: (a)–(c) microcapsules with poly (urea-formaldehyde) as shell material experiencing 0, 3, and 6 months' static pressure experiment; (d)–(f) microcapsules with poly styrene as shell material experiencing 0, 3, and 6 months' static pressure experiment.

shell material is below 225°C. But in practical application, environmental temperature is too low to affect the stability of them.

Figure 6 presented the DSC diagrams of α -olefin drag reducing polymer particles (core), poly(urea-formaldehyde) (shell), and microcapsules which were clear for distinguishing heat adsorption of core from that of shell. From 50 to 300°C on the curve of shell, there were three endothermal peaks which were bound to water evaporation, oligomer of urea and formaldehyde decomposition, and poly (urea-formaldehyde) decomposition, respectively. The curve of the microcapsule was under that of the core, and the mean heat absorbed by microcapsules in temperature increasing process was 1.5–2.0 W/g higher than that by cores. This confirmed that the

heat effectively accumulated in the process of evaporation and decomposition of shell.

Solubility

Generally speaking, with the increase of static pressure on packed microcapsules, they will solve more quickly in diesel and the solution will show a higher drag reducing rate. The relationship between drag reducing rate distribution and stirring time is shown in Figure 7. Blank sample, 12 cm, 24 cm, 36 cm, 48 cm and 60 cm represented solutions of α -olefin drag reducing polymer particles without shell protection and different microcapsule samples pressed by different weights which were equivalent to those of 12, 24, 36, 48, and 60 cm thickness

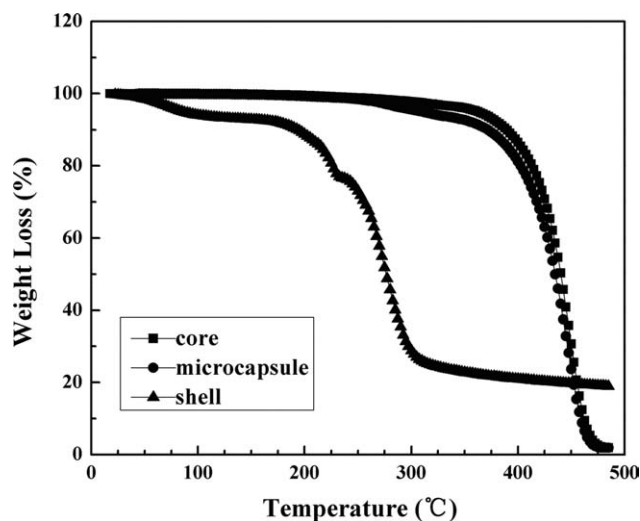


Figure 5 TGA diagrams of α -olefin drag reducing polymer particle (core), poly (urea-formaldehyde) (shell), and microcapsule.

microcapsules. It was obvious that drag reducing rates of different samples were close to that of the blank sample. The drag reducing rate of samples pressed by higher pressure was more close to that of uncoated polymer particles. This phenomenon may be attributed to the fact that the airtight structures of microcapsules were broken to different degrees along with the increase of static pressure. Microcapsules pressed by higher pressure solved more quickly, so the effective constituent to play drag reducing role was higher. When drag reducing rate reached a peak value which was about 35%, there was a little decline. This might be the result that drag reducing polymer degraded along with the increase of stirring time.

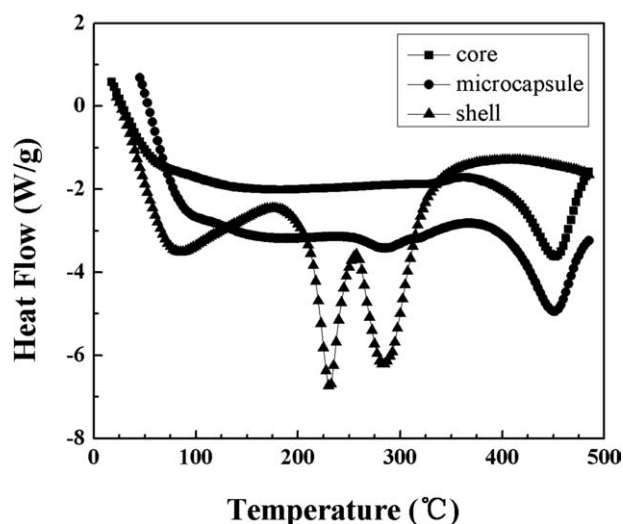


Figure 6 DSC diagrams of α -olefin drag reducing polymer particle (core), poly (urea-formaldehyde) (shell), and microcapsule.

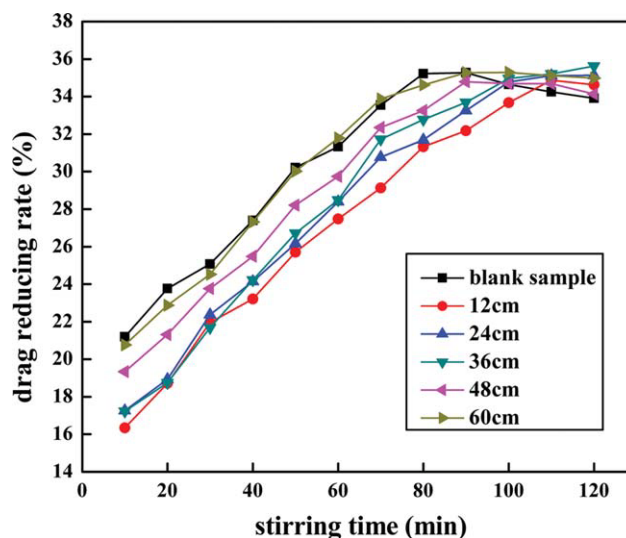


Figure 7 Relations between drag reducing rate distribution and stirring time [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

CONCLUSIONS

1. Microcapsules that contain α -olefin drag reducing polymer were prepared by *in situ* polymerization of urea and formaldehyde and interfacial polymerization of styrene. These two kinds of microcapsules could effectively protect α -olefin drag reducing polymer particles from adhesion. But the morphologies of the two kinds of microcapsules were obviously different from each other.
2. Through 3 months' static pressure experiment, the shell of microcapsules with polystyrene as shell material had been broken and part of them stuck with each other. After 6 months, these microcapsules have been adhered together. The microcapsules with poly(urea-formaldehyde) as shell material, however, remained the state of unheaped small balls after 6 months' static pressure experiment and met the requirement of long time storage in practical application.
3. Thermal stable temperature of microcapsules containing α -olefin drag reducing polymer with poly(urea-formaldehyde) as shell material was below 225°C. The mean heat absorbed by microcapsules in temperature increasing process was 1.5–2.0 W/g higher than that of core.
4. Drag reducing rates of different samples were close to that of blank sample. Along with prolongation of stirring time, the drag reducing rates of different samples reached a peak value, i.e., 35%. After the peak value, there was a little decline. This might be the result that the drag reducing polymer degraded along with the increase of stirring time.

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