

Preparation of Polymer Microspheres in Supercritical Carbon Dioxide and Their Evaluation as Cold-Flow Improvers in Diesel

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ABSTRACT: Polymeric microspheres were synthesized by the precipitation copolymerization of methacrylic acid and styrene in supercritical carbon dioxide. Scanning electron microscopy showed that the products were spherical microparticles. The mean diameter of the particles was 0.2–2 μm . The synthesis conditions affecting the particle size and morphology were examined in detail. The well-

distributed copolymer microspheres were applied as low-temperature improvers for diesel. The results showed excellent performance for high-paraffin diesel at low temperatures. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2749–2753, 2010

Key words: additives; processing

INTRODUCTION

The copolymerization of styrene and methacrylic acid (MAA) has attracted great concern recently. This copolymerization, used as a polytemplate (2-vinylpyridine), was reported by Frisch.¹ Styrene–MAA block copolymer micelle-doped polypyrrole films were researched by Kapui² with scanning electron microscopy (SEM). Ruckenstein³ and Chaiyasat⁴ synthesized copolymers of styrene and MAA in concentrated emulsions. Li and Kan⁵ reported that they prepared this copolymer in the presence of alcohol and alcohol–water mixtures. We aimed to synthesize styrene–MAA copolymer through a novel polymerization process, which was conducted in supercritical carbon dioxide (SC-CO₂).

It is well known that SC-CO₂ possesses interesting solvent properties, which have been applied to a range of separation and extraction processes, as well as organic reactions and the polymer industry;^{6–12} SC-CO₂ can be used as an environmentally benign solvent substitute, which is nontoxic and nonflammable and has easily accessible critical conditions, that is, $T_c = 304$ K and $P_c = 7.37$ MPa, where T_c is temperature copolymerization and P_c is pressure copolymerization. Recently, polymerization in SC-CO₂ has attracted much attention as an environmen-

tally benign procedure. New polymerization technologies with zero-waste production in SC-CO₂ have been developed,^{13–15}; for example, Romack et al.¹⁶ reported the preparation of poly (acrylic acid) microparticles in SC-CO₂ without fluorinated surfactants; Xu et al.¹⁷ investigated the effects of acetic acid and ethanol as cosolvents on the product morphology by the precipitation polymerization of acrylic acid in SC-CO₂; Otake¹⁸ reported the copolymerization of acrylic acid and MAA in SC-CO₂. The copolymerization of styrene/MAA can be used as a low-temperature improver for diesel. Low-temperature operability is a big problem for diesel, especially for high-paraffin diesel in cold winters; a lot of additives, such as pour-point depressants, antigel additives, and cold-flow improvers, have been developed to improve the low-temperature tolerance of diesel. Compared to polymer microspheres and common additives, polymer microspheres perform better.

Various factors in the synthesis process, such as the copolymerization pressure, temperature, and initial MAA/styrene concentration ratio, which may affect the particle size and morphology were researched in detail.

EXPERIMENTAL

Materials

Styrene and MAA were obtained from Kewei Co., Ltd. (Tianjin, China). Their purities were believed to be greater than 98%.

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TABLE I
Copolymerization Conditions, Yields, and Particle Distributions

Number	ADV N (g)	MAA (g)	Styrene (g)	Temperature (K)	Pressure (MPa)	EM (g)	Time (h)	Dp (μm)	Geometric standard deviation (—)	Yield (%)
1	0.03	0.43	0	338	20	0	6	0.5	0.34	95
2	0.03	0.43	0.02	338	20	0	6	0.28	0.24	97
3	0.03	0.43	0.05	338	20	0	6	0.35	0.28	96
4	0.03	0.43	0.105	338	20	0	6	0.66	0.32	95
5	0.03	0.43	0.05	338	15	0.01	6	0.48	0.3	97
6	0.03	0.43	0.05	338	25	0.02	6	0.32	0.28	96
7	0.03	0.43	0.05	338	30	0.03	6	0.3	0.28	97
8	0.03	0.43	0.05	348	20	0.04	6	0.4	0.3	95
9	0.03	0.43	0.05	368	20	0	6	0.42	0.28	96
10	0.03	0.43	0.05	338	10	0	6	0.66	0.34	96
11	0.03	0.43	0.05	338	15	0	6	0.56	0.36	97
12	0.03	0.43	0.05	338	25	0	6	0.32	0.28	97
13	0.03	0.43	0.05	338	30	0	6	0.28	0.24	95
14	0.03	0.43	0.05	348	20	0	6	0.38	0.3	96
15	0.03	0.43	0.05	358	20	0	6	0.45	0.4	96
16	0.03	0.43	0.05	368	20	0	6	0.54	0.46	96

EM, ethyl mercaptan; Dp, particle diameter; Standard deviation, $\ln \sigma = \sqrt{(1/\sum n)(\sum n(\ln D - \ln D_p))^2}$ where n is the number of particle, D is the particle diameter.

1,2,2'-Azobis(2,4-dimethyl-valeronitrile) (ADV N) used as an initiator was purchased from Kewei and recrystallized twice from methanol before use. Its purity was believed to be greater than 95%.

Carbon dioxide (CO₂), with a 99.9% minimum purity, was purchased from Beifang Co., Ltd. (Fushun, China).

The distilled diesel was supplied by Daqing Refinery Factory (Heilongjiang, China) and redistilled in our laboratory. The boiling characteristics were determined according to ASTM D 86, the cold filter plugging point (CFPP) value was determined according to ASTM D 4539, and the cloud point value was determined according to ASTM D 2500. The distribution of n -paraffin was determined by GC 102.

Polymerization procedure

All copolymerization reactions occurred in a 100-mL stainless steel high-pressure cell equipped with a stirrer. A certain amount of initiator (ADV N), as shown in Table I, was added to the cell. Then, we injected CO₂ for 15 min. We deoxygenated the monomer by purging with nitrogen for 15 min, and the monomer was then loaded into the cell in a CO₂ atmosphere. The cell was then sealed, and enough liquid CO₂ was added with a CO₂ pump. First, the temperature was gradually increased to the desired reaction temperature. The pressure was increased to the desired reaction pressure by the gradual addition of CO₂. The polymerization reaction lasted for 6 h. After the polymerization, the cell was immersed in a cold-water bath, and the sample of polymer particles was collected from the bottom of the cell.

Characterization

The particle morphologies were analyzed and imaged with SEM, as shown in Figure 1. The particle size and size distribution were determined by SEM and with a SALD laser diffraction particle-size analyzer (Shimadzu Co., Ltd., Tokyo, Japan). To analyze the particle size and distribution with the SALD analyzer, the sample was dispersed in water with surfactant and sonicated before the analysis. The geometric standard deviation of the sample particle diameter was within $\pm 5\%$, as shown in Figure 2.

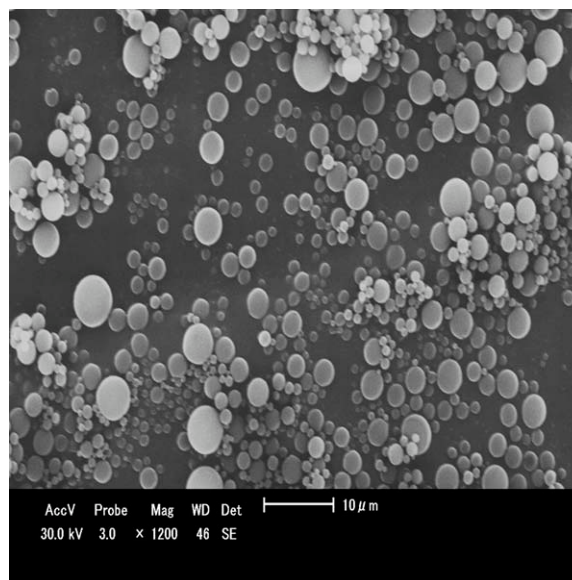


Figure 1 SEM photograph of microparticles obtained by precipitation copolymerization at 338 K and 20 MPa with an MAA/styrene molar ratio of 5 : 1.

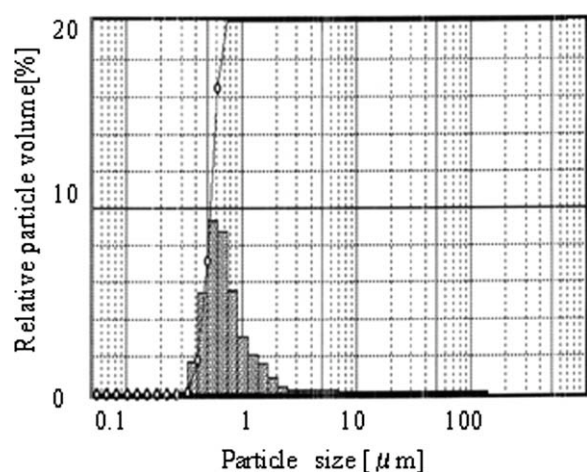


Figure 2 Distribution of the MAA–styrene copolymer particles.

Cloud points, pour points, and low-temperature filterability (LTFT) were used to characterize the cold-flow performance of the diesel fuels. At the cloud point, long-chain hydrocarbons begin to form small wax crystals, and when enough wax crystals, whose diameters exceed 0.5 μm , precipitate, the fuel appears cloudy. If temperature decreases below the cloud point, the crystals continuously grow and agglomerate. When the crystals are large enough, they will plug fuel filter systems. At the pour point, the fuel can eventually gel up and cease to pour, although much of the fuel has not been frozen. The pour point is useful for characterizing the suitability of a fuel for large storage and pipeline transportation.^{19,20} If the diameters of wax crystals become 50–250 μm , the fuel will gel up or plug the filter and make it impossible for the fuel system to deliver fuel to the engine, which could be evaluated by LTFT at a certain temperature.^{21,22} These properties were evaluated with the following standard test methods: ASTM D 97, ASTM D 4539, and ASTM D 2500.^{23–25} Among these properties, LTFT is the most important for characterizing whether a fuel can be used at low temperatures for a vehicle

RESULTS AND DISCUSSION

Effect of the monomer concentration ratio on the particle morphology

The copolymerization proceeded at 338 K and 20 MPa with various concentration ratios of MAA to styrene in the range 5.0–1.0 mol/mol. No fine polymer particles were obtained in the MAA/styrene molar ratio range of 1 : 1 to 4 : 1. At an MAA/styrene ratio of 5 : 1, a desirable result was obtained. The concentration of MAA played a key role in the particle morphology. This was because MAA acted as not only a monomer but also as a stabilizer dur-

ing the copolymerization of styrene with MAA in SC- CO_2 .²⁶ The minor addition of styrene helped to decrease the mean diameter of the particles, as shown in numbers 1 and 2 in Table I. This proved that trace styrene modified the copolymers and made them more stable. However, with increasing styrene, the diameter increased, as shown in numbers 2, 3, and 4 in Table I, and the obtained copolymers were more difficult to precipitate; this resulted in a viscous copolymer solution. The SEM photograph for the copolymer synthesized at 338 K and 20 MPa (MAA/styrene = 5 : 1; Fig. 1) indicated that the polymeric particles had a spherical shape whose diameter was several hundred nanometers. The copolymers were polydispersed because of the aggregation of the copolymer during the precipitation polymerization. The particle size distribution was determined with the SALD laser diffraction particle-size analyzer. To analyze the particle size and distribution with the SALD analyzer, the sample was dispersed in water with surfactant and sonicated before the analysis. The reproducibility of the primary particle diameter and geometric standard deviation of the sample particle diameter was within $\pm 5\%$. The particle-size distribution of the polymer microsphere of MAA–styrene was fairly monodispersed, as shown in Figure 2.

Effect of the copolymerization temperature on the particle morphology

Temperature is an important parameter for the copolymerization reaction. The effect of the copolymerization temperature was considered with a specific monomer ratio (MAA/styrene = 5 : 1) at 20 MPa, as shown in numbers 3, 14, 15, and 16 in Table

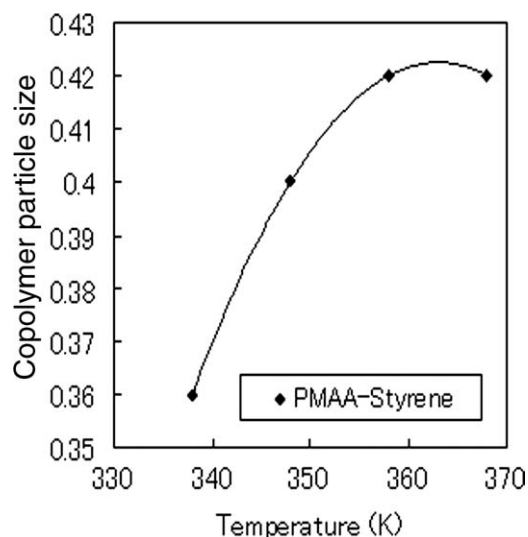


Figure 3 Effect of temperature at 20 MPa with an MAA/styrene molar ratio of 5 : 1 [PMAA–styrene = poly(methacrylic acid-*co*-styrene)].

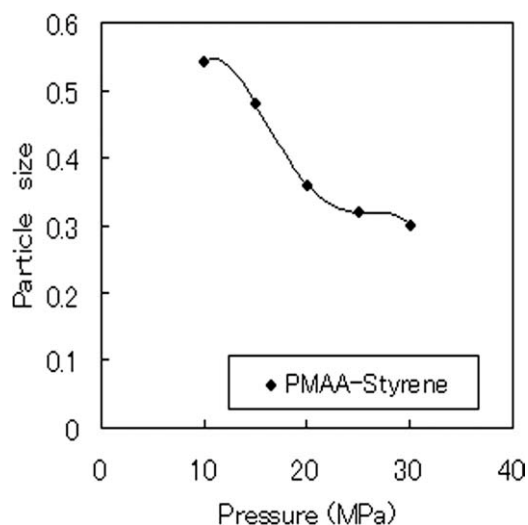


Figure 4 Effect of pressure at 343 K with an MAA/styrene molar ratio of 5 : 1 [PMAA-styrene = poly(methacrylic acid-*co*-styrene)].

I. The polymer particles' mean diameters of the copolymer are displayed versus the temperature in Figure 3. The mean diameter of the particles increased with the temperature in the range 338–368 K. This was because the temperature affected the polymerization mainly through changing SC-CO₂ density. The density of SC-CO₂ decreased from 0.68 to 0.49 g/cm³ with increasing temperature from 338 to 368 K at 20 MPa. Thus, the monomer mass concentration increased by 40%; this resulted in larger polymer particles being produced.

Effect of ethyl mercaptan on the particle morphology

Ethyl mercaptan was used as a chain-transfer agent in the copolymerization reaction to control the molecular weight. The particle sizes were compared with and without the addition of ethyl mercaptan, as shown in numbers 5–8 and 11–14 in Table I, but there was no obvious effect on the particle size or morphology.

Effect of the copolymerization pressure on the particle morphology

The pressure was researched with a fixed monomer ratio (MAA/styrene = 5 : 1) at 338 K. The analysis

TABLE II
Characteristics of the Sample Oils

	Test oil 1	Test oil 2	Test oil 3
Initial boiling point (°C)	145	140	150
20% (°C)	235	230	231
90% (°C)	360	355	360
Cloud point (°C)	+5	+3	+8
CFPP (°C)	0	-1	+3
<i>n</i> -Paraffins (C ₂₂)	2.3%	2.0%	2.5%

TABLE III
CFPP Efficiency for the MAA-Styrene Copolymer

Sample oil	Addition (ppm)			
	100	150	200	250
Oil 1	0	-2	-5	-11
Oil 2	0	-3	-7	-10
Oil 3	1	-2	-5	-9

results are shown in Figure 4. The copolymer particle mean diameter decreased with increasing copolymerization pressure. This was because the SC-CO₂ density increased from 0.25 to 0.8 g/m³ with increasing pressure from 10 to 30 MPa at 338 K; this resulted in a lower monomer mass concentration in the copolymerization system. So, the copolymerization temperature and pressure affected the synthesized polymer particle morphology, mainly through the SC-CO₂ density and monomer mass concentration.

Performance as a low-temperature flow improver

Low-temperature flowing property (LTFP) is the most important parameter for a low-temperature flow improver.^{27–29} The MAA-styrene copolymer microspheres were used as flow improver for diesel; LTFT was tested according to an ASTM D 4539 low-temperature flow test procedure. The sample was observed starting from a temperature that was at least 5°C above the cloud point of the sample, and the sample was cooled at a rate of 1°C/h and filtered through a 17-mm screen under a 20-kPa vacuum (150 mmHg). The minimum temperature, at which 180 mL of sample oil could be filtered just in 60 s, was recorded. LTFT could be quantified by this minimum temperature. LTFT data of the high-paraffin sample oils 1, 2 and 3, whose characteristics are shown in Table II, are displayed in Table III. LTFT was not significantly affected by a 0.01% additive concentration, but with increasing additive concentration, LTFT obviously decreased. Compared with a commercial low-temperature flow improver called T1804 (a vinyl acetate/ethylene copolymer), whose performance is shown in Table IV, the copolymer

TABLE IV
CFPP Efficiency for T1804

Sample oil	Addition (ppm)			
	100	150	200	250
Oil 1	1	0	-2	-7
Oil 2	0	0	-3	-7
Oil 3	1	-2	-3	-5

additives were better than T1804 in improving LTFT of fuel.

CONCLUSIONS

Polymeric MAA–styrene copolymer microspheres were successfully synthesized in SC-CO₂ through a zero-waste method. SEM showed that the products were the expected spherical microparticles. The mean diameter of the particles was 0.2–2 μm. The lower temperature and higher pressure helped to produce fine microspheres. These copolymer microspheres can be used as low-temperature improvers for diesel and showed excellent performance for improving the cold-flow properties of high-paraffin diesel.

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