

Preparation of heat resisting poly(methyl methacrylate)/silica fume composite microspheres used as ultra-lightweight proppants

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Ultra-lightweight heat resisting poly(methyl methacrylate) (PMMA)/silica fume microspheres were successfully prepared via in-situ suspension polymerisation. Scanning electron microscopy indicated that PMMA/silica fume composite microspheres had good sphericity and the silica fume particles were evenly dispersed in microspheres and formed lots of macroporous material. Furthermore, density analysis illustrated that the density of composites was about 1.06–1.24 g/cm³ with good suitability for water carrying. Thermal stability of the PMMA/silica fume composite particles was significantly better than pure for PMMA. Therefore, PMMA/silica fume composite microspheres possess an entirely feasible application in oil exploitation as ultra-lightweight proppants.

1. Introduction: Hydraulic fracturing is an effective and commonly used way to enhance petroleum or gas operation in oilfields [1, 2]. Proppants are required in hydraulic fracturing operations to ensure support to the hydraulic fractures and keep them open against the application of closure stresses to ensure conduction of oil and gas to the borehole [3]. The ideal proppant would be as strong as diamond, as light as water and as cheap as earth. However, it is difficult to obtain one product having all these ideal properties [4]. Proppants used in the art include sand and ceramics, with their corresponding apparent specific gravity (ASG) ranging from 2.65 to 3.40 g/cm³. Difficulty with proppant transport and reducing fracture conductivity stems from increasing ASG [5, 6]. More recently, ultra-lightweight (ULW) materials have been used as proppants since they reduce the required fluid velocity for proppant transport within the fracture [7–9], which provides a greater number of fracture areas to increasing fracture conductivity.

Poly(methyl methacrylate) (PMMA) microsphere is a kind of functional material, which has high sphericity and is ULW (close to 1 g/cm³). However, PMMA has poor thermal stability and high cost, which limits its application. On the contrary, silica fume (SF) exhibits excellent thermal stability because of the high Si–O bond energy. Furthermore, SF is cheap and available [10, 11]. Hence, the introduction of SF into the PMMA matrix is an efficient approach to obtain the merits of both organic and inorganic phases. Some early studies, involving PMMA/SiO₂ composite particles and their performances, have been reported [12, 13]. However, so far there have been no publications on perfect composite particles of spherical millimetre size, light weight and having excellent thermal stability to be used as proppants.

In the work reported in this Letter, we aimed at producing new composites that have good thermal properties, and could be applied to oilfield exploitation as proppants. Therefore, PMMA/SF composite particles with high SF content were synthesised via in-situ suspension polymerisation. ULW microspheres with good thermal stability were obtained, which exhibit promising application as water carrying fracturing proppants.

2. Experimental: The silica fume (SF, ϕ 50–500 nm) was provided by the Shanghai Aikai Silica Fume Material Co. Ltd and modified by APTES and SA. First, SF, APTES ($m_{\text{SF}}: m_{\text{APTES}} = 100:4$) and toluene were poured into a 250 ml flask, then reacted at 90°C with stirring for 2 h. Then, SA ($m_{\text{SF}}: m_{\text{SA}} = 100:4$) was dissolved

in the mixture and continued to react for 2 h. The product was purified by centrifugations and dried at 60°C for 8 h. Finally, the modified SF was obtained.

The PMMA/SF composite particles were synthesised via in-situ suspension polymerisation. 1.6 g sodium hydroxide (NaOH) and 4.0 g six hydrated magnesium chloride (MgCl₂·6H₂O) were replaced into 120 ml of deionised water at 60°C with vigorous stirring. Then, 0.3 g benzoyl peroxide (BPO) and 3.0 g divinyl benzene (DVB) were dissolved in 20.0 g of MMA, to which 10.0 g modified SF was added. Then the mixture was poured into the flask, heated to 80°C, and kept for 2 h. Finally, the expected composite particles were obtained. For comparison, pure PMMA was fabricated under the same condition.

A three-phase contact angle, θ , was measured by a contact angle meter (JC2000Y, Shanghai Zhongchen Digital Technology Apparatus Co. Ltd). Fourier transform infrared spectroscopy (FTIR) spectra were verified by means of a Nicolet Avatar 360 FTIR spectrometer in the range 400–4000 cm⁻¹. The microstructure and morphology were tested under a field emission scanning electron microscope (FESEM, Hitachi SU8010, Japan) and energy-dispersive spectroscopy (EDS, Genesis, EDAX, USA). Density was measured using a MDMDY-300 automatic density meter. Simultaneous thermal analysis was recorded using a Netzsch STA409 PG/PC instrument, which was used in the TGA configuration under nitrogen atmosphere with a heating rate of 10 °C/min from 30 to 700 °C.

3. Results and discussion: Fig. 1 illustrates the process for the preparation of ultra-lightweight proppants. One of the key technologies is modification SF.

A three-phase contact angle and FTIR spectra were employed to observe the changes of SF before and after modification, respectively, as shown in Fig. 2. Owing to the abundant hydroxyl on the surface, the SF was hydrophilic and the contact angle was about 32.5°. After modification by APTES, the contact angle increased to 72.5° because of the hydrophobicity groups. This result also confirmed by FTIR that the characteristic absorption peaks at about 800 and 1100 cm⁻¹ enhanced obviously because of the increase in Si–O content and the formation of Si–O–Si in the surface of the APTES-modified SF. Meanwhile, the peak intensities at about 3460 and 1460 cm⁻¹ were increased. This was because of the presence of the –NH₂ bond in the APTES, which indicated that the SF was successfully modified by APTES [14].

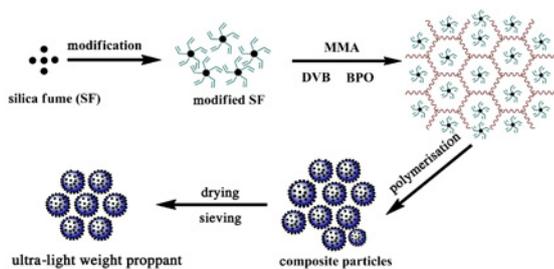


Figure 1 Schematic illustration of the synthesis of ultra-light weight proppants

To obtain excellent hydrophobic SF, the SF was modified by APTES/SA and the contact angle increased to 139.5°. The result was also verified by FTIR in that the C=O stretching vibration peak and the N–H bending vibration peak of amide bond (–CONH–) was enhanced at 1715 and 1530 cm⁻¹, respectively. In addition, the vibration peak at 2925 cm⁻¹ was observed, which was attributed to the C–H bond of methylene, indicating that the SF was successfully modified by APTES/SA [15]. As a result, the SF was translated into a hydrophobic state and had good compatibility with monomers, thus the SF could be introduced into PMMA as much as possible.

The FESEM images of pure PMMA and PMMA/50 wt% SF composite particles are shown in Figs. 3a and b, respectively. The composite spherical particles presented a 0.8–1.0 mm size and a rougher surface than pure PMMA because of the addition of SF. It can be seen from the sections of pure PMMA (Fig. 3c) and PMMA/SF composite particles (Fig. 3d) that the internal structure of pure PMMA was compact, while abundant macroporous and SF particles were observed inside the composite particles with the high addition of SF. These microporous particles made a great contribution to the lightweight characteristic of composite particles. According to the experiments, the reason for the formation of the microporous particles may be explained by the residual toluene on the surface of the SF, which was a pore-foaming agent during polymerisation.

To confirm the chemical composition of particles, EDS spectrum was employed for samples, shown in Figs. 3c and d. The results showed that besides the C, O and Au peaks, the Si appeared in composite particles (Fig. 3f) while it could not be observed in pure PMMA (Fig. 3e). Meanwhile, the C/Si ratio was about 2/1, which

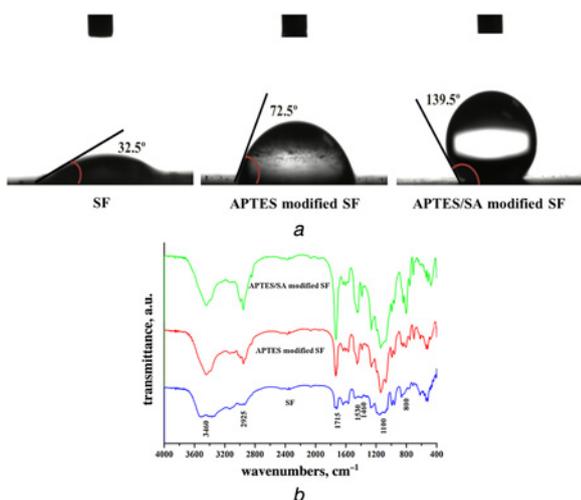


Figure 2 Three-phase contact angle determination photograph and FTIR spectra of SF-, APTES-modified SF and APTES/SA-modified SF
 a Three-phase contact angle determination photograph
 b FTIR spectra

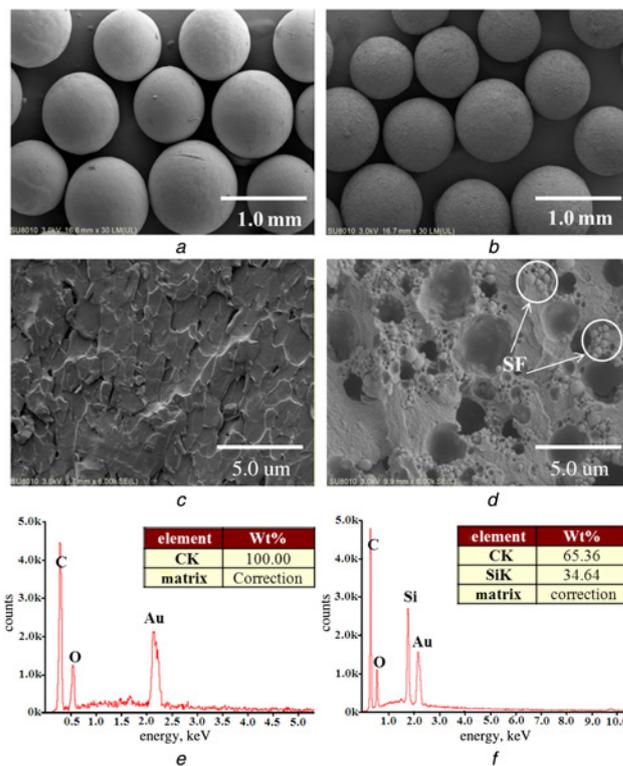


Figure 3 SEM images of pure PMMA (the surface (Fig. 3a) and section (Fig. 3c)) and PMMA/50 wt% SF composite particles (the surface (Fig. 3b) and section (Fig. 3d)); EDS spectrum of pure PMMA (Fig. 3e) and PMMA/50 wt% SF composite particles (Fig. 3f)

further proved that 50 wt% SF had been successfully blended into the composite particles.

The density test was performed to analyse the lightweight characteristic of composite particles. The results of the theoretical values and measurements of the apparent densities are shown in Fig. 4. It could be seen that the incorporation of SF (about 2.32 g/cm³ at room temperature) to the PMMA system caused the increase of apparent density with increasing SF content. Furthermore, the measurements of apparent density (1.06–1.24 g/cm³) were obviously lower than the theoretical values (1.06–1.34 g/cm³). This result was because of the abundant micron-sized pores inside the PMMA/SF composite particles shown in Fig. 3d. This macroporous structure occupied a lot of volume of composite particles, thus influencing the lower apparent density obviously [16, 17]. From the above results, it was found that the composite

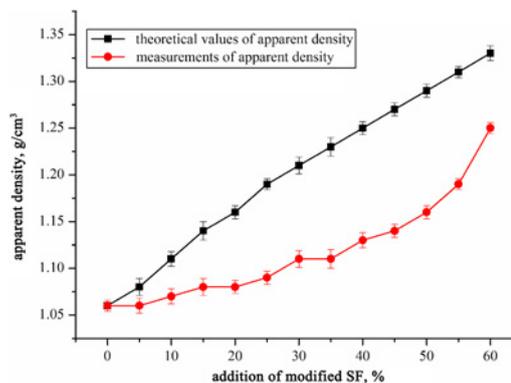


Figure 4 Apparent density curves of PMMA/SF composite particles with different SF contents

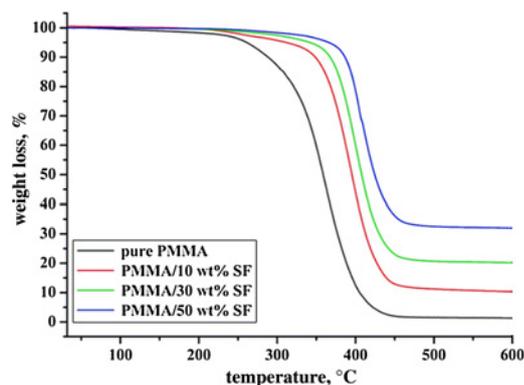


Figure 5 TGA curves of pure PMMA and PMMA/SF composite particle with different SF contents

particles possessed lightweight characteristics and had potential application as ULW proppants.

The thermal properties of these composites were examined by TGA. The results provided in Fig. 5 show the TGA curves of pure PMMA and PMMA/SF hybrid copolymers heated in nitrogen. From the TGA curve, pure PMMA was initially stable up to 140°C (2.73% mass loss, probably because of physisorbed water evaporated at this temperature). The thermal stability of the PMMA/SF composite particles were significantly better than pure PMMA. The temperature at which the weight drastically decreased and the plateau region appeared increased with increasing SF content of the composite. Moreover, around 400°C, at which temperature residual PMMA was completely degraded, the PMMA/SF composite particles showed higher residual weights than the SF content. This phenomenon might be attributed to the interpenetration of polymer chains with an inorganic scaffold of SF which could restrain the mobility of the polymer chains [18]. In view of these results, the high SF content of the composite particles could enhance the thermal stability of composite particles dramatically.

4. Conclusion: Millimetre-sized, lightweight and heat resisting PMMA/SF composite particles were successfully prepared via in-situ suspension polymerisation. The results suggested that these composite particles had a uniform 0.8–1.0 mm size and high sphericity. The density of the composite particles was much lower than its theoretical value because of the abundant 1.0–4.0 μm macroporous material formed inside the particles. Furthermore, the thermal stability of the PMMA/SF composite particles was initially better than that of pure PMMA because of the homogeneous distribution of SF into the composite particles. Therefore, such composite particles have been considered as excellent candidates for ULW proppants in petroleum and gas exploration.

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6 References

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