Synthesis and characterization of high temperature resistant thermal expansion microspheres with P(acrylonitrile/methacrylic acid/*N,N*-dimethylacrylamide/*n*-butylacrylate) shell

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Abstract

High temperature resistant microspheres were prepared via Pickering suspension polymerization. Acrylonitrile (AN), methacrylic acid (MAA) and *N,N*-dimethylacrylamide (DMAA) were used as monomers, and *n*-butylacrylate (BA) was used as modified monomer to improve the expansion properties of the microspheres. Morphology of the microspheres was characterized by scanning electron microscopy (SEM) and polarizing optical microscope (POM) respectively. The average diameter of the prepared microspheres was 51.9 μm , and the maximum expansion volume was 4 times of the original volume. The expansion performance and blowing agent content of the microspheres were characterized by thermal mechanical analysis (TMA) and thermogravimetric analysis (TGA) respectively. The onset expansion temperature of the microspheres was 159.5 $^{\circ}\text{C}$, the maximum expansion temperature was 213.9 $^{\circ}\text{C}$, and the encapsulation content of the blowing agent was 14.62%. Fourier transform infrared (FTIR) showed that the adjacent chains of AN and MAA form imide ring structure during the thermal expansion process of the microspheres.

Keywords High temperature resistant · Expandable microspheres · Suspension polymerization · Imide ring structure

1 Introduction

Thermal expansion microspheres (TEMs) are polymer particles with core-shell structure, which are generally composed of thermoplastic polymer shell encapsulated with low boiling hydrocarbons [1]. Upon heating, the polymer shell softens, and the vapor pressure generated by the internal blowing agent causes microspheres to expand, the diameter of the expanded microspheres can be increased by 3–5 times [2]. After cooling, the microspheres still can maintain its expanded state. Due to the unique properties, TEMs were widely used in various fields, such as printing ink, ceramics, composite materials, etc. [3, 4].

Pickering emulsion is a kind of emulsion stabilized by nano solid particles (such as nano-silica) [5]. TEMs are

generally prepared by Pickering suspension polymerization to disperse the oil phase in the water phase containing a nano inorganic dispersant [6]. According to the maximum expansion temperature, TEMs can be divided into three categories: low temperature ($< 120^{\circ}\text{C}$), medium temperature (between 120 and 180°C) and high temperature (higher than 180°C) TEMs [7–9]. At present, there are few reports on the preparation of high temperature resistant TEMs. Kawaguchi et al. [10] successfully prepared TEMs with excellent heat resistance by using acrylonitrile (AN), methacrylonitrile (MAN) and methacrylic acid (MAA) as monomers, and the maximum expandable temperature can reach 195°C . Jonsson et al. [11] synthesized TEMs with poly (AN–MAN) copolymer as a shell. The maximum expandable temperature of the microspheres can reach

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224 °C by adjusting the type and content of blowing agent and cross-linker.

In current reports, high temperature resistant TEMs are usually prepared by monomers such as AN and MAN, or by adding a third monomer with high glass transition temperature [12]. However, MAN is expensive, and only a few countries like Japan and Germany can produce it in large quantities [13]. Therefore, using cheaper monomers instead of MAN to prepare high temperature resistant TEMs has good economic value.

In this study, MAA was used to substitute MAN, thermal expansion microspheres were successfully prepared by Pickering suspension polymerization using AN and MAA as the major monomers, DMAA as the third monomer to control the polymerization rate, BA as modified monomer to improve the plasticity of the microsphere shell and *n*-pentane as blowing agent. The shell structure and expansion properties of the prepared microspheres were characterized.

2 Experimental procedure

2.1 Materials

Silicon dioxide (20 nm diameter, Hydrophilic) was offered by Jiangsu TianXing New Materials Co., Ltd. (China), Polyvinyl pyrrolidone (PVP K17, $M_w = 8000$ g/mol) was made in Shanghai Xushuo Biotechnology Co., Ltd. (China). Hydrochloric acid (HCl) was provided by Nanjing Chemical Reagent Co., Ltd. (China). Acrylonitrile (AN) was bought from Sinopec QiLu Petrochemical Company (China). Methacrylic acid (MAA), *N,N*-Dimethylacrylamide (DMAA), sodium chloride (NaCl), ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Sodium nitrite (NaNO_2), *n*-Butylacrylate (BA), ethyleneglycol dimethacrylate (EGDMA), *n*-Pentane, 2,2'-Azobisisobutyronitrile (AIBN) provided by Shanghai Macklin Biochemical Co., Ltd. (China).

2.2 Process

2.2.1 Preparation of water phase

Silicon dioxide (7 g), sodium chloride (45 g), PVP K17 (0.1 g), sodium nitrite (0.03 g) ethanol (0.06 g) and deionized water (150 g) were added to a 250 mL glass beaker successively and homogenized using emulsification machine at 10,000 rpm for 3 min. Then, the pH of the mixed solution was adjusted to 3 with hydrochloric acid. After that, the mixture was injected into a 500 mL boiling three-necked flask placed in an ice-water bath for reserve.

2.2.2 Preparation of oil phase

AN (15 g), MAA (4.6 g), DMAA (2.3 g) and BA (1.15 g) were added to a 100 mL glass beaker to obtain the monomer mixture. EGDMA (0.09 g), AIBN (0.127 g, 0.55 wt% based on the monomer) and *n*-Pentane (8 g, 25.8 wt% of the oil phase) was dissolved into the monomer mixture and mixed with magnetic stirred.

2.2.3 Suspension polymerization

The oil phase mixture was slowly injected into a three-necked flask containing prepared aqueous phase at 800 rpm/min and stirred for 30 min to give an oil-in-water suspension. The polymerization was conducted in a 500 mL stainless steel reactor with the inside diameter of 35 mm and equipped with an agitator and nitrogen protection. The suspension mixture was injected into the reactor through the feeding device. The reactor was purged with nitrogen for 2 min to remove air and then increase pressure to 0.5 MPa with nitrogen. The stirring rate was set at 240 rpm/min and the reaction temperature was raised to 60 °C. After 24 h of constant temperature and pressure reaction, the reactor was cooled to room temperature, and then the pressure in the reactor was removed. The products were washed three times with water and separated using circulating water vacuum pump with qualitative filter paper. Thermal expansion microspheres were dried in a blast drying oven at 50 °C for 24 h.

2.2.4 Measurements

The micromorphology and particle size of microspheres were studied by tungsten-filament scanning electron microscope (SEM, JEOL, JSM-6480). The expandable properties of microspheres were tested by thermal mechanical analysis (TMA, PerkinElmer, 4000). The sample (1 mg) was put into a quartz crucible and heated from 50 to 350 °C at a heating rate of 15 °C/min under air atmosphere with applying a load of 0.06 N to the probe. The onset expansion temperature (T_s), maximum expansion temperature (T_{max}) and maximum expansion displacement (D_{max}) of the microsphere were obtained by the displacement of the probe. The expansion process of microspheres was monitored by polarizing optical microscope (POM, Nikon, DS-Fi2) coupled to a hot stage, the samples were heated from room temperature to 250 °C at a set speed (15 °C/min). The content of blowing agent and thermal stability of microspheres was measured by thermogravimetric analysis (TGA, PerkinElmer, 8000) and heated from 50 to 500 °C at the rate of 3 °C/min under nitrogen atmosphere. The chemical composition of the unexpanded and expanded microspheres were characterized by Fourier transform

Fig. 1 SEM images of the **a** several microspheres and **b** single microsphere

Fig. 2 Particle size distribution of TEMs

infrared spectrometer (FTIR, NICOLET, iS10) in the wave-range of $4000\text{--}400\text{ cm}^{-1}$ with 32 scans.

2.2.5 Results and discussion

2.3 Particle micromorphology

Figure 1 shows SEM images of the microspheres, the shape of particles was spherical and there are many creases on the surface, which may be due to insufficient uniformity of polymer deposition and uneven cross-linking density of the microsphere shell during suspension polymerization [14]. The particle size of the microspheres displayed in Fig. 1(a) was measured and counted by metallographic size analysis software. The particle size of the microspheres was mainly distributed at $38.6\text{--}80.2\text{ }\mu\text{m}$. The maximum particle size distribution area was $45\text{--}50\text{ }\mu\text{m}$, and the average diameter of microspheres was $51.9\text{ }\mu\text{m}$ (Fig. 2).

Fig. 3 The TMA curve of TEMs

2.4 Expansion performance analysis

The TMA curve of TEMs is shown in Fig. 3. The onset expansion temperature of the microspheres was $159.5\text{ }^{\circ}\text{C}$. The onset expansion temperature was mainly determined by the glass transition temperature (T_g) of the microsphere shell and the boiling point of the blowing agent. When the temperature gradually reached $213.9\text{ }^{\circ}\text{C}$ (T_{max}), the microspheres expand to the maximum. When the temperature was further increased, the strength of polymeric shell was not enough to endure the vapor pressure of n-Pentane and burst. Figure 4 shows the Polarizing microscope images of before and after expansion. After expansion, the average diameter of the expanded microspheres was about $159\text{ }\mu\text{m}$. In order to obtain more intuitive foaming properties, the test tube with 0.42 g of the microspheres was placed in an oven at $210\text{ }^{\circ}\text{C}$ for 10 min, and the volume after expandable was about 4 times that before expandable (Fig. 5).

Fig. 4 Polarizing microscope images of the **a** unexpanded microspheres and **b** expanded microspheres (214 °C)

Fig. 5 A picture of 0.42 g of TEMs. **a** Unexpanded **b** expanded (210 °C for 10 min)

2.5 Thermal stability analysis

Figure 6 shows the TG and DTG curves of the expandable microsphere. At 205 °C, the weight loss of microspheres was about 4.4%. This may be caused by the small amount of residual monomer and trace water in the shell of microspheres. The weight loss of microspheres was about 14.62% from 202 to 295 °C. This can be attributed to the burst of the shell and the escape of *n*-pentane during the expansion of the microspheres [15]. It can be concluded that the encapsulated amount of *n*-pentane in microspheres was 14.62%, which was lower than the added amount of raw materials (25.8%). At 214.8 °C, the maximum escape rate of blowing agent was 3.34% min⁻¹. The polymeric shell begins to decompose gradually after 295 °C and the maximum decomposition rate was 1.32% min⁻¹ when the temperature reached 323.7 °C.

Fig. 6 The TG and DTG curves of TEMs

Fig. 7 FTIR curves of the (a) unexpanded microspheres and (b) expanded microspheres

Scheme 1 The formation of imide ring structure during expansion

2.6 Shell structure analysis

Infrared spectroscopy analysis was performed on the unexpanded and expanded thermal expansion microspheres respectively, and the obtained spectrum is shown in Fig. 7. For the unexpanded microspheres, the sharp peak at 2243 cm^{-1} was clearly the absorption peak of $\text{C}\equiv\text{N}$. At 1729 cm^{-1} , the peak shape was strong and sharp, which can be judged as the absorption peak of $\text{C}=\text{O}$ in carboxyl group. 1635 cm^{-1} should be the absorption peak of $\text{C}=\text{O}$ in amide group. The peak at about 1223 cm^{-1} can be identified as the absorption peak of $\text{C}-\text{N}$. The peak at 940 cm^{-1} was the bending vibration absorption peak of $-\text{OH}$ of carboxyl group. Compared with the unexpanded microspheres, the shell structure of the expanded microspheres was analyzed. The intensity of the peak of $\text{C}\equiv\text{N}$ decreased. At 940 cm^{-1} , the bending vibration peak of $-\text{OH}$ disappeared, and at 1728 cm^{-1} , the $\text{C}=\text{O}$ absorption peak moved slightly to the low frequency field and split, the low wave number subpeak was slightly enhanced, which was the result of the transformation of $\text{C}=\text{O}$ of carboxyl group to $\text{C}=\text{O}$ of imide. The absorption peak of $\text{C}-\text{N}$ at 1211 cm^{-1} was greatly enhanced [16]. The result of infrared spectroscopy indicated that the adjacent AN and MAA formed a six-membered imide ring structure (Scheme 1) during the expansion of the microspheres [17].

3 Conclusions

In this study, thermal expansion microspheres were synthesised via Pickering suspension polymerization with AN (65 wt%), MAA (20 wt%), DMAA (10 wt%) and BA (5 wt%) as shell and *n*-pentane (25.8 wt%) as blowing agent. The average diameter of the prepared microspheres was $51.8\text{ }\mu\text{m}$. TMA showed the onset expansion temperature (T_g) and the maximum temperature (T_{max}) were $159.5\text{ }^\circ\text{C}$ and $213.9\text{ }^\circ\text{C}$, respectively. The maximum expansion volume was about 4 times of the original volume. The encapsulation amount of blowing agent in microspheres was 14.62 wt% by TGA. FTIR characterization confirmed that the formation of imide ring structure in the shell of expanded TEMs during expansion.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

- Jonsson M, Nordin O, Malmström E, Hammer C (2006) Suspension polymerization of thermally expandable core/shell particles. *Polymer* 47:3315
- Jeoung SK, Han IS, Jung YJ et al (2016) Fabrication of thermally expandable core-shell microcapsules using organic and inorganic stabilizers and their application. *J Appl Polym Sci*. <https://doi.org/10.1002/app.44247>
- Chen B, Tang J, Zhang G, Chen S, Zhang J (2017) Properties and morphologies of epoxy resin based composites reinforced by polyurethane and graphene oxide. *Mater Trans* 58:842
- Zhang J, Li P, Zhang Z et al (2019) Solvent-free graphene liquids: promising candidates for lubricants without the base oil. *J Colloid Interface Sci* 542:159
- Kim JG, Ha JU, Jeoung SK, Lee K, Baek S-H, Shim SE (2015) Halloysite nanotubes as a stabilizer: fabrication of thermally expandable microcapsules via Pickering suspension polymerization. *Colloid Polym Sci* 293:3595
- Zhang J-X, Liu S, Yan C et al (2017) Abrasion properties of self-suspended hairy titanium dioxide nanomaterials. *Appl Nanosci* 7:691
- Zhou S, Li Z, Zhou Z, Xu W, Ma H, Ren F (2018) Simple method for preparation of thermally expandable microspheres of PMMA encapsulating NaHCO_3 via thermally induced phase separation. *J Appl Polym Sci*. <https://doi.org/10.1002/app.46179>
- Ji LJ, Jiang YS, Liang G et al (2017) Thermally expandable microspheres of poly(acrylonitrile)/ethyl methacrylate/methacrylic acid) with fast thermal response property. *Pigment Resin Technol* 46:115
- Chen SY, Sun ZC, Li LH (2016) Preparation and characterization of thermally expandable microspheres. *Mater Sci Forum* 852:596
- Kawaguchi Y, Itamura Y, Onimura K, Oishi T (2005) Effects of the chemical structure on the heat resistance of thermoplastic expandable microspheres. *J Appl Polym Sci* 96:1306
- Jonsson M, Nordin O, Kron AL, Malmström E (2010) Thermally expandable microspheres with excellent expansion characteristics at high temperature. *J Appl Polym Sci*. <https://doi.org/10.1002/app.31543>
- Kawaguchi Y, Oishi T (2004) Synthesis and properties of thermoplastic expandable microspheres: the relation between crosslinking density and expandable property. *J Appl Polym Sci* 93:505

13. Gao Y, Zhang N, Zhu L, Hou Z (2018) Preparation and properties of thermoplastic expandable microspheres with P(AN-MMA) shell. *Russ J Appl Chem* 90:1634
14. Rheem MJ, Jung H, Ha J, Baeck S-H, Shim SE (2016) Suspension polymerization of thermally expandable microspheres using low-temperature initiators. *Colloid Polym Sci* 295:171
15. Hou Z-S, Kan C-Y (2014) Preparation and properties of thermo-expandable polymeric microspheres. *Chin Chem Lett* 25:1279
16. Liu T-M, Zhang G-C, Liang G-Z, Chen T, Zhang C (2007) In situ cyclization reactions during the preparation of high-performance methacrylic acid/acrylonitrile/acrylamide ternary copolymer foam. *J Appl Polym Sci* 106:1462
17. Zhang J, Ye R, Zou J, Tang J, Wang H (2015) A study of isothermal curing of PMI using DMA. *Adv Mater Sci Eng* 2015:1

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