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Thermally expandable microspheres with excellent high-temperature expansion property

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Abstract. Core-shell thermally expandable microspheres (TEMs) were prepared via Pickering suspension polymerization. Acrylonitrile (AN), methacrylic acid (MAA) and *N,N*-dimethylacrylamide (DMAA) were used as the comonomers, the 2,2′-azobisisobutyronitrile (AIBN) was used as the initiator and the ethyleneglycol dimethacrylate (EGDMA) was used as the crosslinker. The effects of initiator concentration, cross-linking agent concentration and modified monomer type on the morphology, thermal properties and encapsulation content of TEMs were investigated. The results show that the small change in initiator concentration had a significant effect on the properties of TEMs. When the initiator concentration was 0.55%, the microspheres showed core-shell structure and the maximum expansion ratio was 3.06 times. According to the scanning electron microscope (SEM) image, the heat resistance of the microspheres increased with the increase of the content of crosslinking agent. The lower the water solubility of the modified monomer, the more stable the foaming of the TEMs. When methyl acrylate (MA) was used as a modified monomer, the initial expansion temperature of the microspheres was 163.2 °C, the maximum expansion temperature was 223.5 °C, and the encapsulation content of the blowing agent was 14.70%.

Keywords: thermal properties, polymer composites, industrial applications, initiator, crosslinker

1. Introduction

Thermally expansion microspheres (TEMs) are polymer particles with core-shell structures, which are generally composed of thermoplastic polymer shells encapsulated with low boiling hydrocarbons. When microspheres are heated to 80–190 °C, which is above the glass transition temperature (T_g) of the polymeric shell, the shell softens and the liquid hydrocarbon evaporates, resulting in the expansion of the microspheres [1, 2]. The density of the microspheres under these conditions decreases from 1100 to 30 kg/m^3 [3]. Upon heating, the volume of the microspheres maintains to contain hydrocarbon prior to cooling, and the expansion is irreversible because of the plastic

deformation of the shell [4]. The ability to increase the volume makes TEMs suitable in a wide range of industrial applications, such as a filler to reduce the weight of materials [5, 6], to increase heat, corrosion and acoustic resistances [4, 7, 8], to create surface textures on wallpaper and textile [1], pressure sensors for pressure-sensitive equipment in smart robots [9]. The properties of TEMs are mainly affected by the T_g of polymeric shell, the type of foaming agent, and the composition of polymeric shell [3]. Because of gas-barrier properties of acrylonitrile (AN) and methacrylonitrile (MAN), they are mainly used in production of TEMs [1, 10]. However, the high toxicity and expensive price of MAN are the main

disadvantages [11]. Methyl methacrylate (MMA) with good barrier properties, low toxicity and low price can be an appropriate alternative for MAN monomer [12]. Nowadays, TEMs usually use thermoplastic polymer as core-shell structure [13]. Once shell layer breaks during heating, it is easy to cause collapse of TEMs. Monomers used for preparing TEMs are generally slightly soluble or insoluble in water, such as styrene (St), acrylonitrile (AN), *etc*. In addition, TEMs are easy to dissipate heat, products are easy to purify, and can produce particles of 10 μm to several millimeters [2, 14]. So, suspension polymerization is currently used [15]. On the other side, for monomers with high water solubility, such as MAA, the preparation of TEMs by Pickering suspension polymerization should be considered. Pickering emulsion is a kind of emulsion that stabilizes the water-oil interface by using nano solid particles instead of traditional organic surfactants [16, 17]. At present, most inorganic dispersants used in preparation of TEMs by Pickering suspension polymerization are nano SiO_2 and nano $Mg(OH)_2$ [12, 18]. In the past ten years, researchers have prepared TEMs with excellent properties by Pickering suspension polymerization [12, 17, 19].

According to the maximum expansion temperature, TEMs can be divided into three categories: low temperature (<120 °C), medium temperature (between 120 and 180 °C) and high temperature (higher than 180 °C) [20–22]. To date, there are few reports about high temperature TEMs [3, 12]. Kawaguchi and coworkers [1, 23] successfully prepare TEMs with excellent heat resistance by using AN, MAN and MAA as monomers. The maximum expandable temperature of TEMs can reach 195 °C. On this basis, the effect of crosslinking agent on TEMs is explored, and the relationship between monomer structure and thermal expansion effect is explored by comparing the addition of different third monomers. Hu *et al*.[24] synthesize the TEMs with a poly(acrylonitrile-methyl methacrylate-*n*-butyl acrylate) (poly(AN-MMA-BA)) as the shell material and p-toluenesulfonyl hydrazide (TSH) as core material by suspension polymerization. The results show that the monomer composition is an important factor to determine the expansion performance and stability of the TEMs. The microspheres prepared by them have good expansion property and heat stability at 150 °C [24]. Jonsson *et al*. [4] synthesize TEMs with poly(AN-MAN) copolymer as shell. By adjusting the type and content of

foaming agent and crosslinking agent, the maximum expansion temperature of the microspheres can reach 224 °C [4].

TEMs have a history of more than 30 years, but according to the current research results, the heat resistance of many TEMs is insufficient [25, 26]. In other words, the initial expansion temperature and maximum expansion temperature of many TEMs are not high enough. In recent years, the demand for TEMs for lightweight treatment of polyvinyl chloride and other plastics has increased year by year. For such applications, microspheres are generally required to have high expansion ratio and excellent heat resistance at the same time. Therefore, in order to meet this social demand, the development of high temperature TEMs is essential. Moreover, due to the complex preparation process (composed of dozens of raw materials), long production cycle (reaction time is generally 18–25 h), uneven particle size distribution (different sizes of microspheres in the same batch) [27–29], the international market is basically occupied by a few companies such as AkzoNobel and Matsumoto Yushi Seiyaku Co., Ltd.

In this paper, thermally expandable microspheres with excellent high temperature expansion property were prepared by Pickering suspension polymerization. The present study examined microspheres with a poly(acrylonitrile-*co*-methacrylic acid) (poly(AN-*co*-MAA)) as the shell, *N*,*N*-dimethylacrylamide (DMAA) as the third monomer (to control the polymerization rate), to determine the relationship between the expansion property and the following three parameters: initiator concentration, crosslinker concentration, and types of modified monomer.

2. Experimental procedure
2.1. Materials
Deionized water was purchased from Sichuan YouPu ultrapure Technology Co., Ltd. Silicon dioxide (20 nm diameter, hydrophilic) was provided by Jiangsu TianXing New Materials Co., Ltd. (China). Polyvinyl pyrrolidone (PVP K17, average molecular weight = 8000 g/mol) was offered by Shanghai Xushuo Biotechnology Co., Ltd. (China). Hydrochloric acid (HCl) was purchased from Nanjing Chemical Reagent Co., Ltd. (China). Acrylonitrile (AN) was made in Sinopec QiLu Petrochemical Company (China). Methacrylic acid (MAA), methyl acrylate (MA), *N*,*N*-dimethylacrylamide (DMAA), sodium chloride (NaCl), ethanol were bought from Sinopharm Chemical

Reagent Co., Ltd. (China). Sodium nitrite (NaNO$_2$), *n*-butyl acrylate (BA), ethyl acrylate (EA), 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, PVP K17, sodium chloride, sodium nitrite ethanol and deionized water (mass ratio 7/45/0.03/0.06/150) were added to a 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 boiling three-necked flask placed in an ice-water bath for reserve.

2.2.2. Preparation of oil phase
AN, MAA, DMAA and BA (mass ratio 15/4.6/2.3/1.15) were added to a glass beaker to obtain a monomer mixture. AIBN (0.55 wt% based on the monomer), EGDMA (0.39 wt% based on the monomer) and *n*-pentane (25.8 wt% of the oil phase) were dissolved into the monomer mixture and mixed with a magnetic stirrer.

2.2.3. Suspension polymerization
The oil phase mixture was slowly injected into a three-necked flask containing prepared aqueous phase at 800 rpm 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 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. Thermally expansion microspheres were dried in a blast drying oven at 50 °C for 24 h.

2.3. Measurements
The micromorphology and particle size of microspheres were observed 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 a nitrogen atmosphere with applying a load of 0.06 N to the probe. The onset expansion temperature (T_{start}), maximum expansion temperature (T_{max}) and maximum expansion displacement (D_{max}) of the microsphere were monitored by the displacement of the probe. The expansion process of microspheres was obtained 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). Thermogravimetric analysis (TGA, PerkinElmer, 8000) was conducted to investigate the content of blowing agent and thermal stability of microspheres and heated from 50 to 500 °C at the rate of 3 °C/min under nitrogen atmosphere.

3. Results and discussion
3.1. Effect of initiator content on expansion property
The proportion of monomer, cross-linking agent and blowing agent remains unchanged, and the content of initiator (as a percentage of oil phase monomer) is changed individually to explore the effect of the content of initiator (AIBN) on the expansion properties of microspheres.

Figure 1 shows the SEM pictures of TEMs with different initiator contents. Lin [30] reported that the initiator concentrations have a significant effect on the characteristics of the polymeric microspheres. If the initiator concentrations are low, the polymerization rate is low over time [30]. Using a low initiator concentration, the unstably formed microspheres were destroyed, as shown in Figure 1a. The prepared microspheres with 0.35% initiator were slightly unstable as having some broken particles from Figure 1b. On the other hand, the microspheres prepared with a sufficient initiator amount showed a stable steric morphology without crashing, as shown Figure 1c, 1d. When the initiator content reaches 0.65% or more, some microspheres are broken again (Figure 1e, 1f).
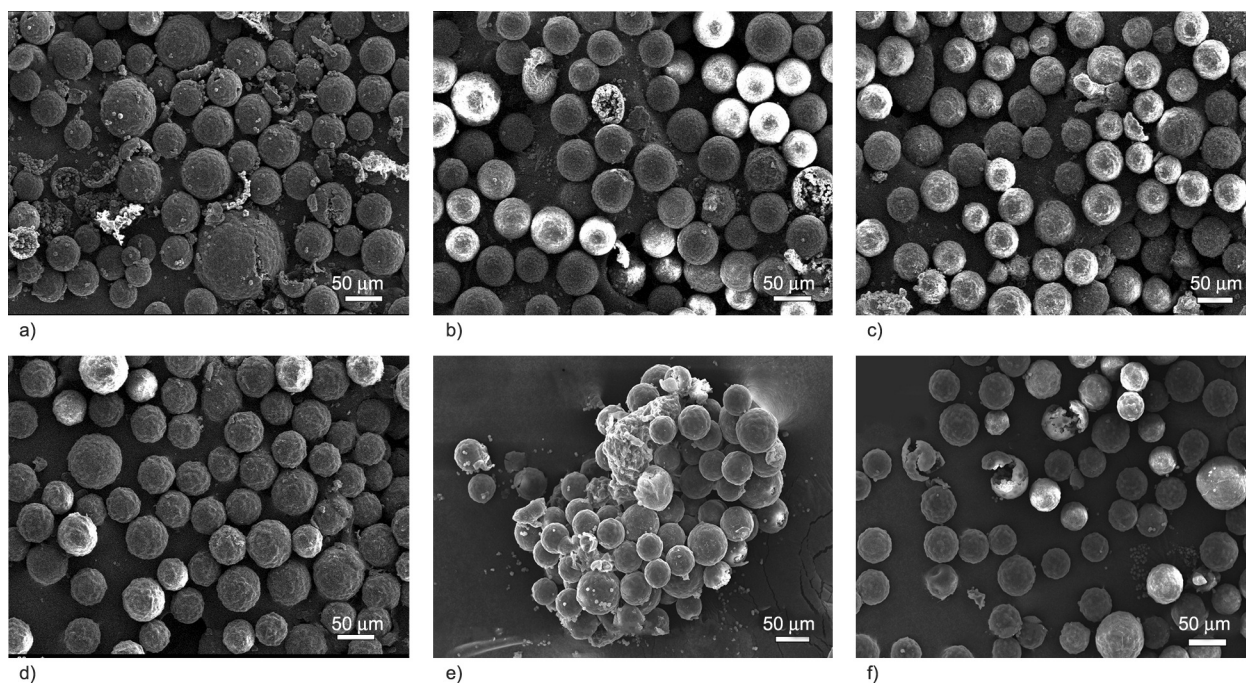
Figure 1. SEM pictures of TEMs with different initiator contents: (a) 0.25% (b) 0.35% (c) 0.45% (d) 0.55% (e) 0.65% (f) 0.75%.

The main reason is that the polymerization rate becomes faster due to the excessive content of initiator. In the process of polymerization, the long chain segment of polymer is formed rapidly, resulting in the precipitation of polymer from small droplets miscible with foaming agent [10]. Some polymers do not have time to form shells at the water-oil interface. Under the action of centrifugal force and surface tension, some polymers are deposited in oil droplets and polymerized into several plastic particles to form multi-core structure. Therefore, the shell formed at the water-oil interface is thin and easy to break in the polymerization process. As shown in Table 1, with the gradual increase of initiator concentration, the size of unexpanded microspheres gradually decreases. This is mainly due to the higher the initiator content, the higher the monomer conversion, which leads to the thickening of the polymer shell of the

microspheres. In the process of suspension polymerization, each suspension droplet contains a certain amount of reactant, so the higher the initiator content, the thicker the shell, and the smaller the size of the microspheres.

The TMA curves of TEMs are shown in Figure 2. When using 0.35% initiator, the onset expansion temperature of the microspheres was 156.5 °C. The onset expansion temperature was mainly determined by the T_g of the microsphere shell and the boiling point of the blowing agent. When the temperature gradually reached 222.9 °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 3 shows the polarizing microscope images of before and after expansion. Originally, the expansion properties of microspheres increased

Table 1. The effect of different content of AIBN on the expansion properties of TEMs.

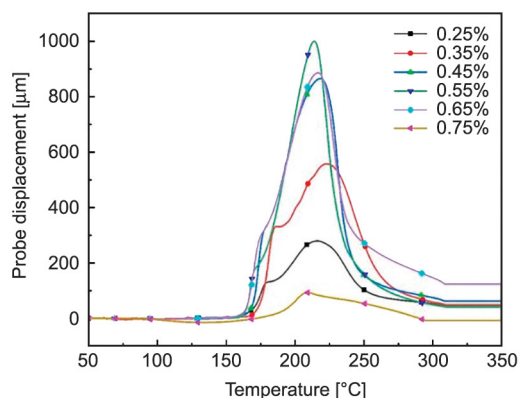| M_{AIBN} [%]	Particle size, d_0 [μm]	T_{start} [°C]	T_{max} [°C]	D_{max} [μm]	Max. expanded particle size, d_m [μm]	Expansion ratio, d_m/d_0 [–]
0.25	54.7	145.4	217.0	279.8	99.6	1.82
0.35	53.4	156.5	222.9	557.4	117.4	2.20
0.45	52.3	166.9	219.3	864.7	134.8	2.58
0.55	51.9	159.5	213.9	1000.1	159.0	3.06
0.65	49.2	156.8	216.1	805.7	127.8	2.60
0.75	48.3	171.7	209.1	92.8	83.2	1.72

Figure 2. TMA curves of TEMs with different initiator contents (AIBN).

with the increase of initiator content. The ratio of diameter of expanded microspheres (d_m) to diameter of unexpanded microspheres (d_0) (d_m/d_0) was used to characterize the expansion ratio of microspheres. When the content of initiator was 0.55%, the expansion performance of microspheres was the best, and the maximum expansion ratio was 3.06 times (Table 1). However, with the increase of initiator content, the expansion properties of microspheres gradually weakened. This is mainly because the monomer reaction rate is too fast, resulting in uneven shell thickness of microspheres.

Figure 4 shows the TGA curves of TEMs with different initiator content. All microspheres showed a two-step decomposition. The first stage occurred due to the eruption and evaporation of the blowing agents in the microspheres, and the second stage was followed decomposition of the polymeric shell of the microspheres. When the encapsulated microspheres were heated above the boiling point region of the blowing agents, the microspheres began to expand and burst because the polymeric shell could not endure the pressure of the hydrocarbon [31]. Therefore, the expendable microspheres weight begins to decrease abruptly at above the boiling point of the hydrocarbon. The evaporation loss of the microsphere blowing agent was used as the encapsulation quantity of the blowing agent. The decrease in the first step in Figure 4 (enlarged portion) is the encapsulation content of the blowing agent. The thermograms in Figure 4 show that the microspheres contain a large amount of blowing agent, ranging from 5 to 15%, under different conditions. In particular, when using 0.55% initiator, the hydrocarbon begins to decompose at 159.5 °C and the encapsulated content of *n*-pentane in microspheres was 14.62%.

3.2. The effect of crosslinker content on the expansion property

Under the condition that the ratio of monomer, initiator and blowing agent is ensured, the content of crosslinking agent (EGDMA) (percentage of oil phase monomer) is separately changed to explore the influence of crosslinking agent content on the expansion performance of microspheres.

Crosslinking agents are used to enhance the strength of synthesized polymeric shell to have the improved performance in thermal expansion of the capsules [32]. Figure 5 shows that the microspheres are formed successfully by using EGDMA crosslinking agent. From Figure 5, as the amount of crosslinker is increased, the degree of distortion of the microspheres becomes greater having more wrinkles on the shell. These distorted wrinkles enhance the expansion performance. When the blowing agent vaporizes, the internal pressure within the microspheres suddenly increases and collapsed section starts to expand first and the wrinkles support the shell upon the further expansion. The results show that the higher the degree of cross-linking, the better the expansibility of the microspheres. It is noted that the increasing cross-linking agent also improved the first decomposition temperature (T_{start}) as an index of expansion properties as shown in Table 2. This is mainly due to each molecule of crosslinking agent EGDMA contains two unsaturated carbon-carbon double bonds, and the chain segment is long. In the process of free radical polymerization, the unsaturated double bonds at both ends of EGDMA molecule undergo addition reaction to connect their independent linear polymer segments to form a three-dimensional network structure [33]. Therefore, with the increase of crosslinking agent content, the T_g of polymer shell increases, and the high temperature resistance of microspheres is improved [32].

Figure 6 indicates the TGA thermograms of the microspheres synthesized with different amounts of EGDMA crosslinking agent where two-step decompositions are witnessed. The first stage of weight loss originates from the vaporization of hydrocarbon blowing agents and the second stage is attributed to the thermal decomposition of the polymeric shell. Increase in crosslinking concentrations leads to increase of the first stage decomposition temperatures. In fact, the decomposition temperatures of microspheres change from 140 to 180 °C when the amount of crosslinking agent increases from 0.22 to 0.48%,
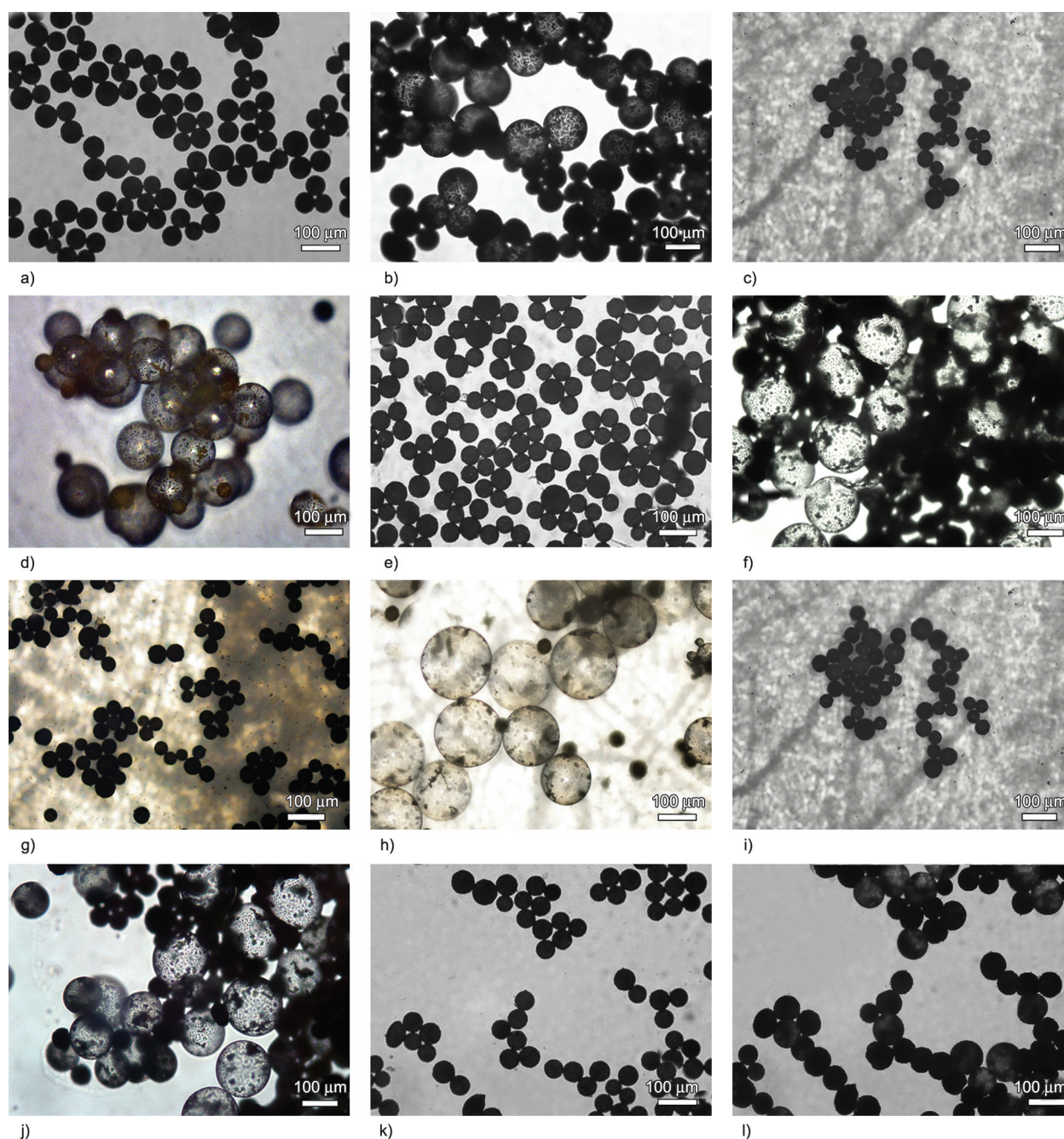
Figure 3. Polarizing microscopy of TEMs with different contents of initiator before and after foaming: (a, c, e, g, i, k) picture of microspheres before foaming, (b, d, f, h, j, l) picture of microspheres after foaming. (a, b) 0.25%, (c, d) 0.35%, (e, f) 0.45%, (g, h) 0.55%, (i, j) 0.65%, (k, l) 0.75%.

respectively. Rheem reported that the weight loss at the first decomposition temperature reached about 5%, and at that temperature the microspheres started to burst [10]. However, in this study, the weight loss at first decomposition temperature, which started from the removal of unreacted monomers and residual water in the microspheres, was confirmed to be about 4.4%. The second stage decomposition temperatures range from 190 to 220 °C, where there is no significant difference despite of increasing amount of crosslinking agent.

In Figure 7, the TMA thermograms show the expansion properties of microspheres with different concentrations of crosslinking agents. While the microspheres are heated, the polymeric shells should endure the pressure of vaporized hydrocarbon. The gasified hydrocarbon molecules interpenetrate the shell due to the inherent gas permeability of the polymer. Therefore, the control over the degree of crosslinking and the careful choice of monomer are always important for the TEMs to have a good gas barrier property [3, 4]. If the amount of crosslinking agent is low, the
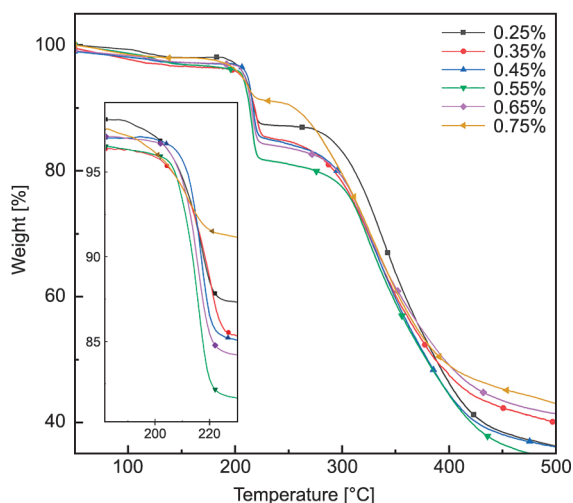
Figure 4. TGA curves of TEMs with different content of initiator (AIBN).

ability to maintain good expansion performance is insufficient to overcome the pressure of gasified hydrocarbon. On the other hand, the too high amount of crosslinking agent is also not desired for expansion performance since exorbitant crosslinking may suppress the expansion of TEMs. Thus, the optimum amount of crosslinking agent is required to have good expansion performance. In Figure 7, the expansion properties of microspheres were dramatically improved using 0.39% EGDMA, which presented the maximum displacement about 1000.1 µm (Table 2). Excessive content of crosslinking agent will result in high crosslinking density and rigidity of polymer in microsphere shell, and obvious decrease of elasticity of microsphere shell. When the amount of crosslinking agent was 0.43%, the expansion property of the microspheres decreased significantly, and the expansion ratio was only 1.33 times. When the amount of crosslinking agent was 0.48%, the shell of the microsphere was too brittle and the TEMs hardly expand [3].
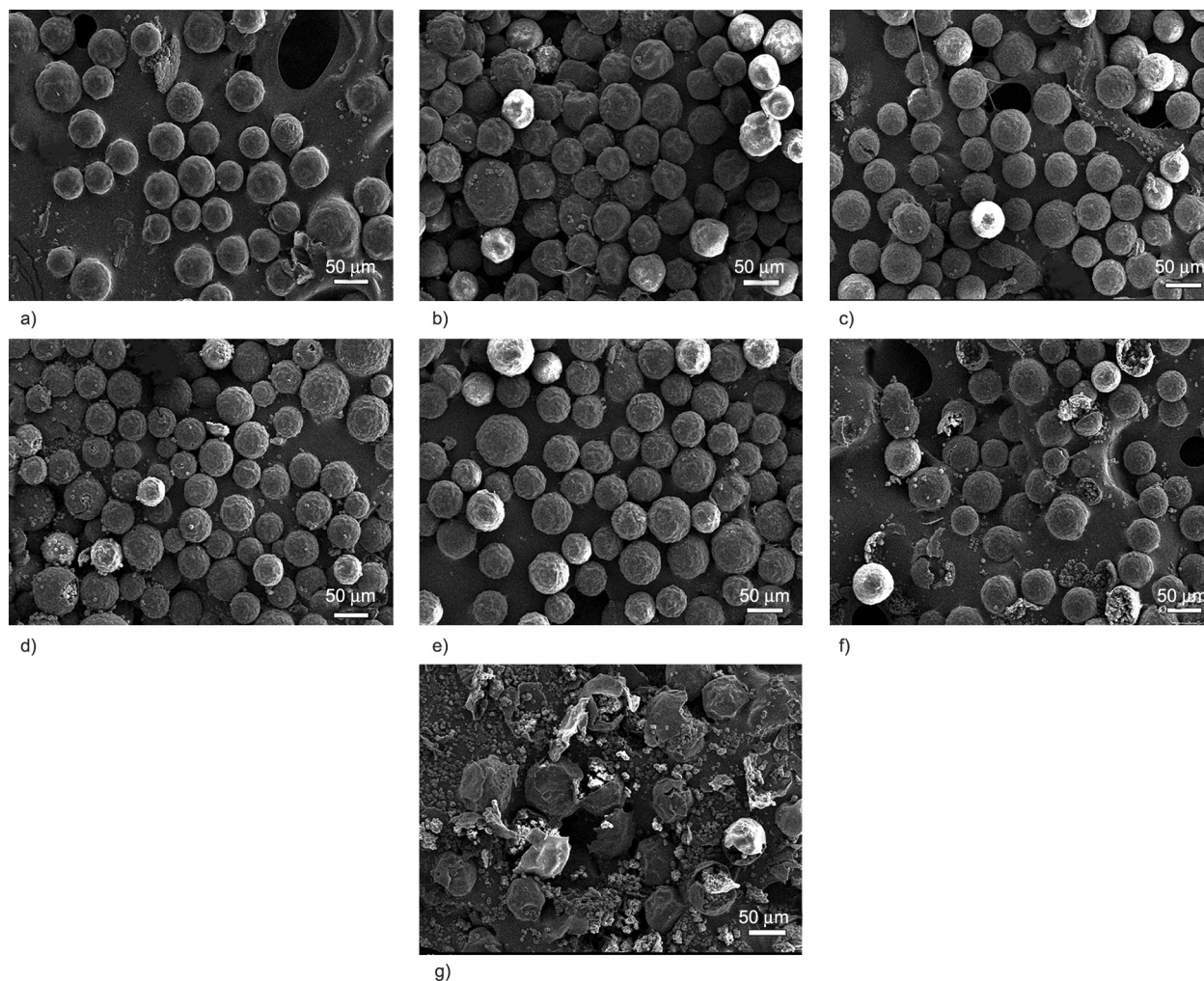

Figure 5. SEM pictures of TEMs with different content of EGDMA. (a) 0.22%, (b) 0.26%, (c) 0.30%, (d) 0.35%, (e) 0.39%, (f) 0.43%, (g) 0.48%.

Table 2. The effect of different EGDMA content on the properties of TEMs.

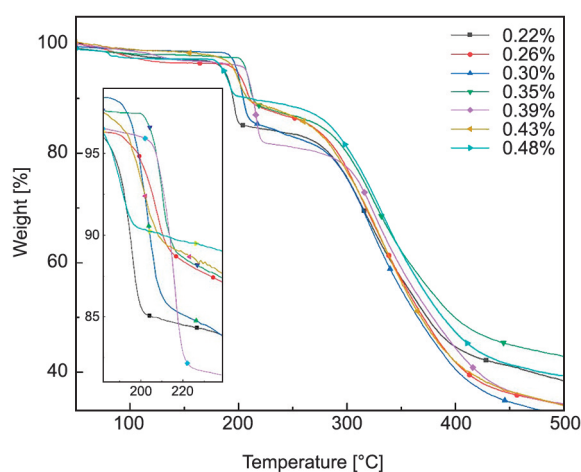| M_{EGDMA} [%]	Particle size, d_0 [μm]	T_{start} [°C]	T_{max} [°C]	D_{max} [μm]	Max. expanded particle size, d_m [μm]	Expansion ratio, d_m/d_0 [–]
0.22	54.6	140.4	192.2	332.4	103.4	1.89
0.26	51.7	142.1	202.1	547.3	116.7	2.26
0.30	52.7	148.3	206.5	598.8	120.8	2.30
0.35	52.9	151.8	212.1	845.6	130.9	2.47
0.39	51.9	159.5	213.9	1000.1	159.0	3.06
0.43	53.0	160.9	216.8	80.5	70.6	1.33
0.48	52.3	179.3	219.6	18.56	52.8	1.01

Figure 6. TGA and curves of TEMs with different content of EGDMA.
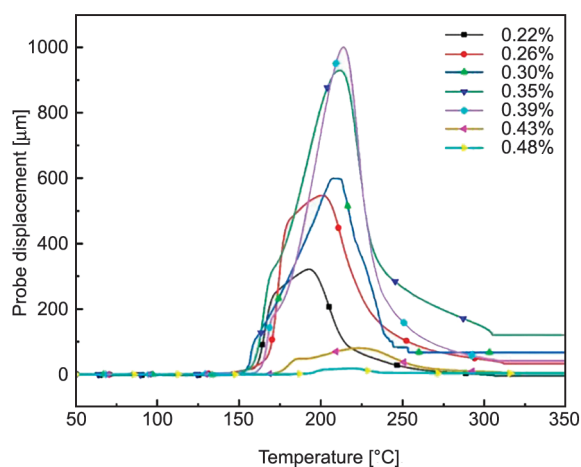

Figure 7. TMA curves of TEMs with different crosslinking agent contents.

3.3. Effect of modified monomer type on expansion property

The expansion properties of TEMs largely depends on the glass transition temperature of the microsphere shell polymer. The addition of different types of modified monomers can adjust the properties of the microsphere shell, thereby significantly affecting the expansion properties of the microspheres [34]. This study fixed the proportion of the remaining monomers, using methyl acrylate (MA), ethyl acrylate (EA), and *n*-butyl acrylate (BA) to explore the effects of different modified monomers on the properties of TEMs.

The particle size range of microspheres with different modified monomers is concentrated in 50–52 μm (Table 3). From Figure 8, the surface of microspheres with modified monomer MA is smoother. This indicates that the addition of MA can better copolymerize with other major monomers. As can be seen from Table 3, Table 4 and Figure 9, with the increase of the glass transition temperature of the homopolymer of the modified monomer, both the onset and maximum expansion temperatures of the prepared microspheres increased. When the modified monomer was MA, the onset expansion temperature of the microspheres was 163.2 °C, the maximum expansion temperature was 223.5 °C.

Figure 10 shows the polarizing microscope images of before and after foaming of TEMs with different modified monomers. When adding the modified monomers of BA, TEMs showed the highest expansion

Table 3. Effect of different modified monomers on the properties of TEMs.

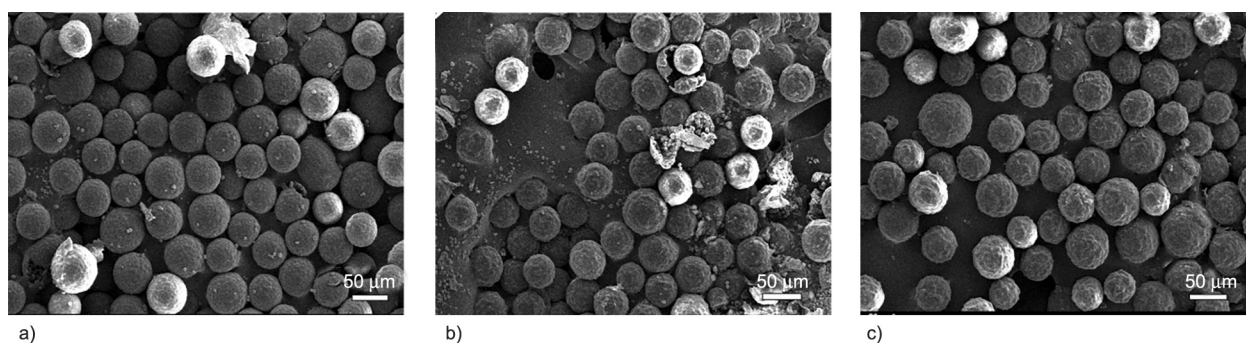| Types of modified monomers	Water solubility of modified monomer [g/l]	Particle size, d_0 [μm]	T_{start} [°C]	T_{max} [°C]	D_{max} [μm]	Max. expanded particle size, d_m [μm]	Expansion ratio d_m/d_0 [–]
MA	60.0	50.1	163.2	223.5	546.7	110.7	2.21
EA	150.0	49.8	160.3	215.6	224.0	93.1	1.87
BA	1.4	51.9	159.5	213.9	1000.1	159.0	3.06

Figure 8. SEM pictures of different modified monomer TEMs, (a) MA, (b) EA, (c) BA.

Table 4. Properties of homopolymer with modified monomers.

Modified monomer homopolymer	T_g [°C]	Elastic elongation of homopolymer [%]
PMA	9	750
PEA	−24	1800
PBA	−55	2000

Figure 9. TMA curves of TEMs with different modified monomers.

ratio, this is mainly due to the poly(butyl acrylate) (PBA) elongation is 2000% (Table 4), which makes microspheres shell softer. The elongation of polyethylene acrylate (PEA) can reach 1800%, but most of the microspheres shrink immediately after foaming (Figure 10). It can be seen from Table 4 that the water solubility of EA monomer is large, which can reach 150 g/l (20 °C water temperature). This may be due to t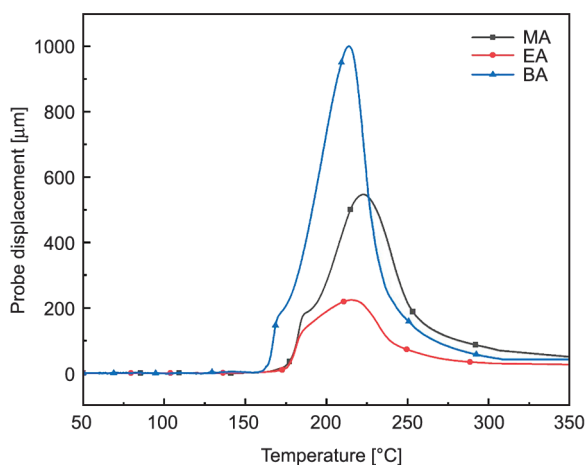he higher water solubility of the modified monomer, the easier the formation of water soluble homopolymer, resulting in unstable microsphere shell. Therefore,
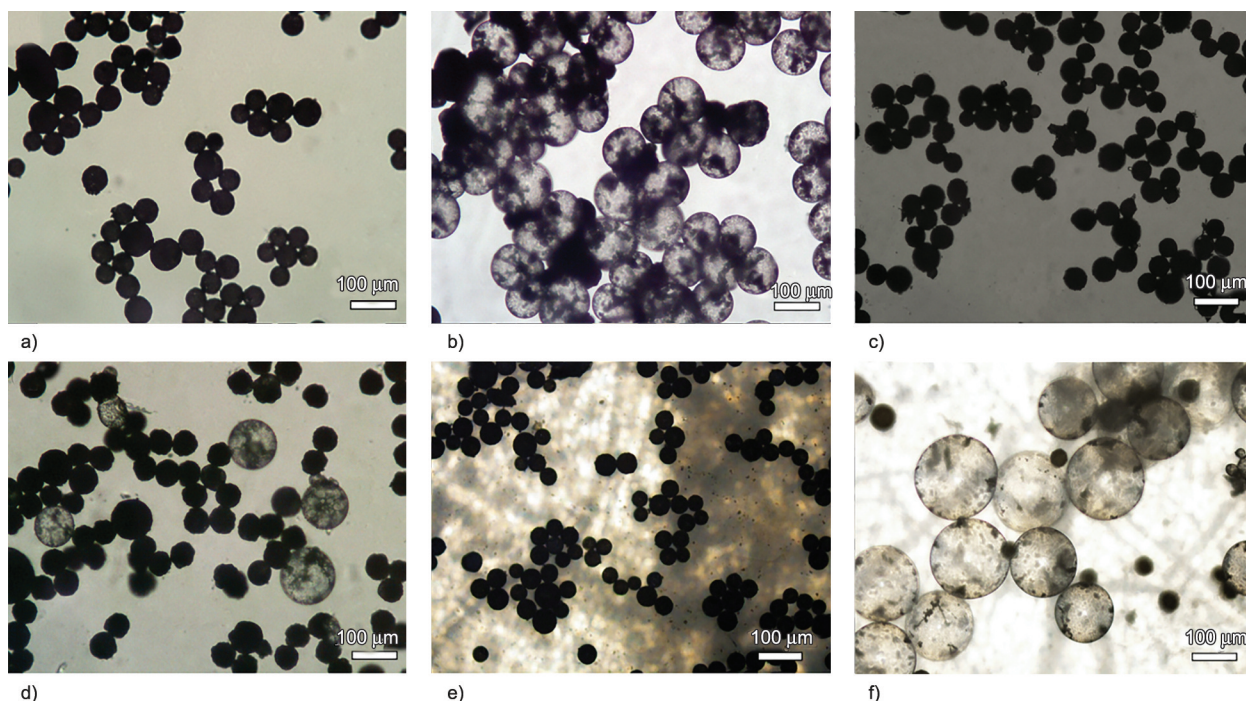

Figure 10. Polarizing microscopy of TEMs with different modified monomers before and after foaming: (a, b) MA, (c, d) EA, (e, f) BA; (a, c, e) picture of microspheres before foaming; (b, d, f) picture of microspheres after foaming.
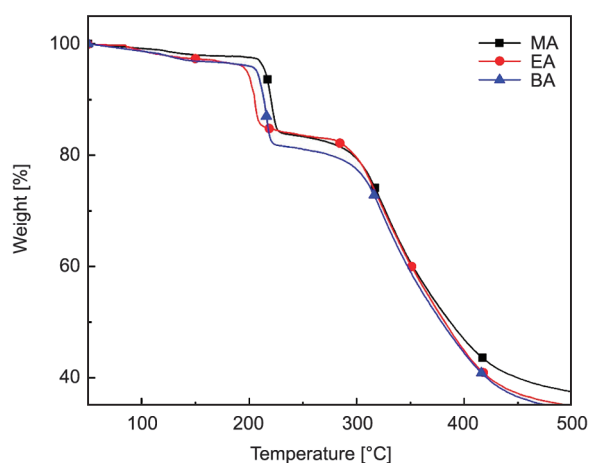
Figure 11. TGA curves of TEMs with different modified monomers.

Table 5. TG data of TEMs with different modified monomers.

Modified monomer homopolymer	Encapsulation content of foaming agent [%]
MA	14.70
EA	12.86
BA	14.62

the foaming of the prepared microspheres is unstable. When the modified monomer MA was added, the elongation of polymethacrylates (PMA) was 750%, which was much lower than that of PBA, so the expansion rate of its microspheres was lower. As can be seen from Figure 11, the shell of TEMs with modified monomer of MA has higher strength, and the encapsulation content (14.7%) of the microsphere blowing agent is higher than that of TEMs with EA (Table 5).

4. Conclusions

This study demonstrates that the high temperature expansion properties of thermally expandable microspheres depend on several concurrent parameters. With the increase of the amount of initiator, the polymer shell of microspheres becomes thicker, and the particle size of unexpanded microspheres decreases. When the initiator concentration was 0.55%, the microspheres exhibited a core-shell morphology, and the maximum expansion ratio was 3.06 times. In terms of the amount of crosslinking agent, with the increase of crosslinking agent content, the expansion properties of microspheres improved. However, excessive crosslinking agent will break some microspheres and cannot form a complete core-shell structure. Furthermore, the addition of the crosslinking

agent helps to increase the heat resistance of the microsphere shell layer. The lower the water solubility of the modified monomer, the more stable the foaming of the TEMs. The elongation of the homopolymer of the modified monomer has a great influence on the expansion properties of the microspheres. With the increase of the glass transition temperature of the homopolymer of the modified monomer, both the onset and maximum expansion temperatures of the prepared microspheres increased. When the modified monomer was MA, the initial expansion temperature of the microspheres could reach 163.2 °C, the maximum expansion temperature could reach 223.5 °C, and the encapsulation content of the blowing agent was 14.70%.

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