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Preparation, characterization and foaming performance of thermally expandable microspheres

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Abstract
Thermal expansion microcapsules (TEMs) are widely used in various fields due to their unique structures. In recent years, TEMs have attracted much attention and have broad market application prospects. In this study, thermally expandable microcapsules with a core–shell structure were prepared by suspension polymerization using acrylonitrile (AN), methyl methacrylate (MMA), and methyl acrylate (MA) as monomers and low-boiling alkane as the core material. Through particle size analysis, morphology test, thermal analysis and other methods, the effects of core material types, single core material and mixed core material, dispersion system on the microcapsule structure, particle size distribution, and expansion properties were compared. Moreover, the core material with a content of 35% can make the expansion ratio of the microcapsules up to 4 times. The expansion performance of the microcapsules with a mixture of isopentane and isooctane (ratio 1:1) as the core material was increased by 27% compared with that of a single core material. In addition, comparing with colloidal SO₂/PVP dispersant, the expansion ratio of the microcapsules with magnesium hydroxide as the dispersant was increased by 20%. Finally, the optimized method for preparing thermally expandable microcapsules was obtained.

1. Introduction
Microcapsule is a small container with a core–shell structure formed by wrapping a solid, liquid or gas in a natural or synthetic polymer material [1–3]. As a kind of microcapsule, the thermally expandable microspheres (TEMs) has been reported in the 1970s. Since then, the thermally expandable microspheres have developed rapidly [4–8]. The shell of TEMs is thermoplastic polymer and the inner core material is a low-boiling alkane [9–11]. When the microcapsule is heated to a certain temperature, the core material generates internal pressure through vaporization. When the temperature reaches the glass transition temperature of the microsphere shell, the shell starts to be softened and expanded. When the thermoplasticity of the polymer shell matches the pressure generated by the core material, the microcapsules will exhibit the excellent expansion performance. Under the action of internal pressure, shell expansion increases the volume and decreases the density of microspheres. Generally speaking, when the microspheres are heated and expanded, the particle size increases to several times as much as the original size, and the volume increases to tens or even hundreds times of the original size. At the same time, the expanded microspheres do not shrink after cooling [12, 13]. Due to its special expansion characteristics, thermal expansion microcapsule can make the product have surface modification, low density, heat insulation, sound insulation and other effects. (a) Surface modification: ceiling, wallpaper and artificial leather, etc. The microcapsules attached to the surface of the object can make the object have a matt surface appearance, 3D effect, non-slip performance and soft touch. (b) Low density: the microspheres can expand to extremely low densities, resulting in weight loss by adding a small amount of the expanded microspheres to the cargo compartment. This can reduce freight costs and installation costs, as well as the risk of item damage. (c)
Isolation: adding thermal expansion microcapsules to the matrix can improve the heat and sound insulation effects of the matrix itself. Thermal insulation is mainly achieved by reducing heat transfer. Since gas is an excellent insulator, the use of microspheres to form voids in the substrate can improve the insulation performance of the substrate. In addition, TEMs have the characteristics of low pollution, so TEMs meet the requirements of environmental protection. It has been widely used in many fields, such as printing ink \[14\], specialty adhesive \[15\], new composite materials \[16\] and so on.

At present, the most commonly used method to prepare physical expansion microcapsules is suspension polymerization \[17–20\]. However, few people have studied how to improve the microcapsules properties in terms of the type of foaming agent, particle size and dispersant. In this study, the performance of the microcapsules was significantly improved by using magnesium hydroxide as a dispersant. Specifically, the expansion ratio of the microcapsules can be increased by selecting the type and content of the blowing agent.

2. Experiment

2.1. Experimental materials

Unless otherwise noted, the reagents were obtained from commercial suppliers and were used without further purification. Acrylonitrile (AN), AR, Tianjin Fuchen chemical reagent factory; methyl methacrylate (MMA), octane, isoctane, azodiisobutyronitrile (AIBN), MgCl₂ · 6H₂O, AR, Tianjin institute of fine chemicals; methyl acrylate (MA), CP, Xilong chemical co., Ltd; n-hexane, cyclohexane, methyl cyclohexane, sodium hydroxide, sodium chloride, hydrochloric acid, AR, Beijing chemical factory; isopentane, 99+%, Mr Sharon chemical co., Ltd; dimethyl 1,4-butanediol acrylate (BDDMA), AR, Aladdin reagent co., Ltd; Sodium dodecyl sulfate, CP, Tianjin institute of fine chemicals.

2.2. Preparation of thermally expandable microspheres

To prepare oil phase: the monomer acrylonitrile (14 g), methyl methacrylate (4 g), methacrylate (2 g), initiator azodiisobutyronitrile (0.43 g), crosslinking agent dimethyl 1,4-butanediol acrylate (0.04 g) and blowing agent (8.77 g) were added into a flask and mixed with magnetic stirring.

To prepare aqueous phase: adding NaOH (2.5 g) and distilled water (45 g) into the flask, mix thoroughly to form a NaOH solution. MgCl₂ · 6H₂O (6 g) and distilled water (45 g) were added into another flask and mixed fully. When both were dissolved completely, the NaOH solution and some of sodium dodecyl sulfate were added into a three-necked flask with mechanical agitation for some time. After that, MgCl₂ · 6H₂O solution was added at a certain speed with a funnel and stirred with higher speed to form the relatively stable magnesium hydroxide particles dispersion. Then, the dispersing aids sodium chloride, sodium nitrite and absolute ethanol were added to the flask and stirred well to obtain an aqueous phase. Finally, the water phase and oil phase were mixed and emulsified with a homogenizer, which made the oil phase become dispersed in the water phase.

The uniform suspension was transferred into three-necked flask with a water bath at 65 °C and reacted for 15 h–20 h under mechanical agitation at 150–400 rpm. Next, the products were cooled to room temperature to obtain the pre-microcapsules.
2.3. Post-processing
The suspending agent was removed from the microsphere particles by acidifying the pH of the solution to 3–4 with diluted hydrochloric acid under stirring. The residual products were washed repeatedly with water and filtered, and then the microcapsules were finally dried. A 106-grain powder sieve was used to remove agglomerates and larger particles in the dispersion to obtain the final physically expanded microspheres. Figure 1 is the synthesis process of thermal expansion microcapsule.

2.4. Analysis test
The TG curve was measured by NETZSCH TG 209C, and the curve was used to analyze the initial weight loss temperature and completely volatile temperature of the blowing agent. The DSC curve was measured by the DSC 214 of NETZSCH. Using the DSC curve to analyze the glass transition temperature of the polymer shell and phase transition temperature of the blowing agent. Infrared spectrum (IR) was measured by the American Nicolet 6700 senior Fourier transform infrared spectrometer. Using KBr tabletting method to measure infrared spectra of the product microcapsules. The thermal expansion curve of the microcapsules was measured by a thermal dilatometer (DIL, Germany NETZSCH Technology Company, DIL402PC). Weigh 0.005 g sample in a special alumina crucible. The sample should be evenly spread on the bottom of the crucible and the height should not exceed 1/5 of the height of the crucible. After that, use tweezers to put the alumina cover into the crucible, and lightly press the alumina cover with the alumina holder until the sample is in close contact with the crucible. Use tweezers to move the crucible with the sample horizontally to the original position of the furnace cavity, and observe whether the relative position of the sensor and the bracket is abnormal. After there is no abnormality, start testing the sample. The sample was heated from 30 °C to 300 °C at a heating rate of 5 °C min⁻¹. This curve was used to accurately analyze the initial foaming temperature (Tstart), maximum expansion temperature (Tmax) and expansion rate (dL/dθ) of the microspheres. The volume average particle diameter MV (μm) and particle size distribution of the microspheres were measured by a laser particle size analyzer. The particle size dispersion (D90-D10)/D50 was calculated. It showed that the smaller the particle size distribution, the narrower the discrete degree. The morphologies of samples were studied by Japanes HITACHI company SU8020 scanning electron microscope.

3. Results and discussion

3.1. Microcapsules contain a blowing agent
As shown in the infrared spectrum of figure 2, the peak shape at 3545.4 cm⁻¹ was wide and rounded, so this peak was a hydroxyl group. This indicated that the polymer formed an intermolecular association through the hydroxyl groups of the carboxylic acid. The peak at 2955.3 cm⁻¹ was the stretching vibration of CH₂–CH₂ in n-hexane. Therefore, the microcapsule successfully wrapped the core material. The peak at 2244.7 cm⁻¹ was clearly the characteristic absorption peak of –C≡N. The absorption peak at 1732.7 cm⁻¹ was strong and sharp, which was the –C=O group. From the above analysis, it could be seen that the microsphere shell contained a carboxyl group, a methyl group, an ester group and a cyano group. These groups were consistent with the
characteristic functional groups of acrylonitrile, methyl methacrylate and methyl acrylate monomers. This confirmed that the shell of the microcapsule was composed of three monomers.

Therefore, it could be confirmed by the infrared spectroscopy that the microcapsules successfully coated the foaming agent. Meanwhile, this method could successfully prepare thermal expansion microcapsule.

### 3.2. Effect of particle size on the performance of microcapsules

As shown in figure 3 and table 1, the particle size distribution of the microcapsules was tested. D50 is the median diameter of the microspheres, which is 56.01 μm. The volume average particle diameter of the microspheres was 66.70 μm. By calculating the dispersion PDI particle size \(=(D90-D10)/D50=1.21\), indicating that the microsphere size distribution range was narrow. Therefore, the particle size distribution of the microcapsules prepared by this method was uniform and the particle size was moderate.

#### Table 1. Particle size characteristics parameters of microspheres.

| Particle diameter/D | D10  | D20  | D30  | D40  | D50  | D60  | D70  | D80  | D90  | D95  |
|---------------------|------|------|------|------|------|------|------|------|------|------|
| Eigenvalues/μm      | 34.10| 42.13| 47.14| 51.55| 56.01| 60.96| 67.29| 77.03| 102.31| 151.30|

Note: Microcapsules with a loading rate of about 35% of n-hexane as a blowing agent.
The prepared samples were passed through standard sieves of 106 \( \mu \)m, 63 \( \mu \)m, 45 \( \mu \)m and 20 \( \mu \)m in sequence, thus four kinds of samples with different particle sizes were obtained. The particle size distribution and morphology of the samples were shown in figures 4 and 5, respectively. By calculating the particle size dispersion, the particle size dispersion of the above four samples was 0.99, 0.65, 0.62, 0.63. Therefore, the dispersion degree less than 1 indicated that the microspheres had a narrow particle size distribution after layered sieving. This method further proved that the prepared microcapsules had uniform particle size distribution and moderate particle size.

Using acrylonitrile, methyl methacrylate and methyl acrylate monomer as the shell and n-hexane as the core material, the thickness change of thermal expansion microcapsule shell before and after heating expansion was approximately calculated.

Volume of microcapsules before expansion:

\[ V_{S,1} = V_{M,1} - V_{C,1} \]

Volume of microcapsules after expansion:

\[ V_{S,2} = V_{M,2} - V_{C,2} \]

where \( V_{S,1} \) and \( V_{S,2} \) are the shell volume before and after the expansion of the microcapsule; \( V_{M,1} \) and \( V_{M,2} \) are the volume before and after the expansion of the microcapsule; \( V_{C,1} \) and \( V_{C,2} \) are the volume of the core material before and after the expansion of the microcapsule. The density change before and after the expansion of the microcapsule shell was ignored, and the microcapsule was regarded as a standard sphere. According to existing data, the average particle size of the microcapsules before expansion was 28.25 \( \mu \)m, the average particle size after expansion was 184.75 \( \mu \)m, and the loading rate was 17.5%. After calculation, the shell thickness of the microcapsules before expansion was 9.81 \( \mu \)m, and the shell thickness after expansion was 0.16 \( \mu \)m.

The thermal expansion properties of the above microsphere samples were tested and the thermal expansion curve was shown in figure 6. The results showed that there were significant differences in the expansion rates of

![Figure 5. SEM images of microspheres (before and after expansion) after sieving; (a), (e) less than 20 \( \mu \)m, (b), (f) 20–45 \( \mu \)m, (c), (g) 45–63 \( \mu \)m, (d), (h) 63–106 \( \mu \)m.](image)

![Figure 6. Thermal expansion curve of microspheres in a sample with relatively separated particle size.](image)
microspheres of different sizes. Samples smaller than 20 μm have the lowest expansion ratio and a higher initial expansion temperature. As the particle size increased, the initial expansion temperature and the maximum expansion temperature of the microspheres showed a downward trend. Furthermore, because of the same batch of microcapsules, microcapsules of different particle sizes had almost the same shell thickness. The larger the size of the microcapsules, the greater the foaming agent content of the microcapsules. Therefore, the larger size of the microcapsules results in a higher expansion rate. In contrast, smaller sized microcapsules contained a small amount of core material, so they can not resist to the internal pressure of the microcapsules, resulting in poor foaming effects.

Therefore, it was necessary to screen the particle diameter of the microcapsules after preparing the thermal expansion microcapsules. However, too large microcapsules cannot be selected, which was not conducive to the practical application of microcapsules. Therefore, it was suitable to select microcapsules with a particle size of 45–85 μm.

3.3. Effects of blowing agents on the performance of microcapsules

As shown in figure 7, the microsphere samples containing n-hexane were subjected to thermal expansion analysis and thermogravimetric analysis to obtain DIL and TG curves, respectively. The temperature at which the foaming agent began to expand was the $T_{\text{start}}$, and as could be seen from the DIL curve, the $T_{\text{start}}$ was 108.37 °C. It indicated that blowing agent has started to vaporize at this temperature. It could be seen from the TG curve that the initial weight loss temperature of the microspheres was 91.68 °C. This indicated that the blowing agent in the microspheres has totally vaporized and escaped from the voids of the microsphere shell. Therefore, it could be concluded that most n-hexane blowing agents started to vaporize at around 90 °C. The temperature at which the microcapsule shell reached the maximum expansion ratio was named the $T_{\text{max}}$. It can be drawn from the DIL curve that the $T_{\text{max}}$ was 141.79 °C. It indicated that the amount of blowing agent gasification and the amount of escaping from the shell layer at this time were balanced. At the temperature of 176.13 °C, the expansion ratio of the blowing agent began to decrease rapidly. This could prove that most of the blowing agents had been gasified. Therefore, the gasification temperature range of blowing agent was about 90 °C–170 °C.

As the heating temperature increased, the microspheres gradually expanded from the shrinking state, resulting in an increase in diameter. When the temperature of maximum expansion ratio was reached, the polymer shell became very thin. Continued elevated temperatures results in a large amount of gaseous blowing agent escaping through the walls of the microspheres, causing the pressure inside the microsphere to become smaller and smaller. Under the action of atmospheric pressure, the shell shranked and the diameter decreased. When the temperature continued to rise, the microsphere shell adhered and a decomposition reaction occured. Therefore, the expansion process of the microcapsules could be observed through thermal expansion analysis and thermogravimetric analysis.

The particle size distribution of microspheres with different blowing agent contents (15%, 20%, 25%, 30%, 35%, 40%) was studied with n-hexane as a single blowing agent. The average particle diameters were 57.60 μm, 56.23 μm, 60.72 μm, 66.70 μm, 63.11 μm and 66.23 μm, and the particle size dispersion was 0.87, 0.92, 0.88, 1.21, 1.11 and 0.99. Therefore, when the content of the blowing agent reached more than 30%, the particle size of the microcapsules did not change much.
Figure 8 showed the thermal expansion rate of microspheres with different blowing agent contents. When the content of the blowing agent was 15%, the microcapsules were difficult to foam. As the content of the foaming agent increased, sufficient pressure could be generated inside the microcapsules, and the initial expansion temperature of the microcapsules would gradually decrease. However, it could be seen from the figure that the initial expansion temperature does not change much after the core material content of the microcapsule reached 30%. The microsphere expansion rate increased with the addition of the blowing agent. However, when the content of the blowing agent was too large, the expansion ratio was rapidly lowered. This was because as the amount of nuclear material increased, the inner gasification at the same temperature increased rapidly, while the wall materials of the microspheres cannot expand further, leading to the wall material cracking and the expansion rate decreasing. The content of the blowing agent was closely related to the thermoplasticity of the microcapsule wall, and had a significant influence on the plasticity and strength of the microsphere. Therefore, in the preparation of microcapsules, the content of core material should match the thermoplastic of wall material to obtain a higher expansion rate.

As could be seen from table 2, the particle size distribution of the microspheres was similar for different types of blowing agents. The study found that when low boiling point blowing agents (isopentane and n-hexane) were used, the initial expansion temperature of the microcapsules was also relatively low. Meanwhile, since the initial foaming temperature was much lower than the glass transition temperature (Tg), the microcapsules had a relatively wide expansion temperature range. Therefore, the expansion rate of microcapsules would also increase with the slow increase of temperature. When a high boiling point blowing agent (n-octane) was used, the microcapsules had a relatively high initial expansion temperature. When the high-boiling alkane in the microcapsules was not completely vaporized, the outer polymer shell has begun to decompose. The results

| Foaming agent     | MV(μm) | PDI | Boiling point/°C | T_start/°C | T_max/°C | dL/d0 |
|-------------------|--------|-----|------------------|------------|----------|-------|
| isopentane        | 66.7   | 1.2 | 30.0             | 89.5       | 133.5    | 2.2   |
| normal hexane     | 56.2   | 0.9 | 68.7             | 116.8      | 144.8    | 2.7   |
| cyclohexane       | 60.7   | 0.9 | 80.7             | 162.9      | 176.5    | 0.1   |
| isooctane         | 55.8   | 1.3 | 99.2             | 130.4      | 144.1    | 2.2   |
| methyl cyclohexane| 70.2   | 0.9 | 100.3            | 141.5      | 187.3    | 0.3   |
| normal octane     | 67.3   | 0.8 | 125.6            | 160.0      | 198.4    | 0.2   |
showed that the expansion rate of microcapsules with high-boiling alkane as core material was lower. By investigating the types of blowing agents, it has been found that the blowing agents suitable for the three wall materials of acrylonitrile, methyl methacrylate and methyl acrylate are as follows: isopentane, n-hexane and isooctane.

By adjusting the composition of the blowing agent, the expansion properties of the microcapsules also changed greatly. In this study, isopentane and isooctane were used as mixed blowing agents, and different proportions of blowing agents were studied. As shown in table 3, the boiling points of isooctane and isopentane were 99.2 °C and 30 °C, respectively. The initial expansion temperature of the mixed blowing agents was

| The dosage of isopentane/mol | The dosage of isooctane/mol | T_{max}/°C | T_{max}/°C | dL/d0 |
|-----------------------------|-----------------------------|------------|------------|--------|
| 100 | 0 | 89.5 | 133.5 | 2.2 |
| 70 | 30 | 97.0 | 118.2 | 0.8 |
| 50 | 50 | 99.4 | 135.8 | 2.9 |
| 30 | 70 | 104.6 | 112.5 | 0.2 |
| 0 | 100 | 112.9 | 144.3 | 2.2 |

Figure 10. Thermal expansion ratio of microspheres prepared using different dispersants.

Figure 9. SEM of microspheres prepared using different dispersants: (a), (b) colloidal silica/PVP; (c), (d) magnesium hydroxide.
between the foaming temperatures of isopentane and isooctane. As the isopentane ratio decreased, the initial foaming temperature of the microcapsules gradually increased from 89.5 °C to 112.1 °C. It could be seen from table 3 that when the ratio of isopentane to isooctane was 1:1, the expansion ratio of the microcapsules was the largest and the T_{start} of the microcapsules was only 99.4 °C. Therefore, it could be concluded from the comparison of tables 2 and 3 that when the low-boiling and high-boiling point blowing agent were mixed, the expansion ratio of the microspheres was higher than that of the single blowing agent as core material. In order to obtain a higher expansion ratio, the mixed core materials could be used as a better blowing agent.

### 3.4. Effects of dispersants on the expansion performance

In order to obtain microcapsules with a uniform particle size and prevent agglomeration between the microcapsule particles, a dispersing agent must be added to the system during the preparation of the microcapsules. Dispersants have two functions: one was to reduce the interfacial tension between water and oil and the other was to weaken the aggregation between droplets or particles. Two dispersants were compared in this study. One was to prepare a magnesium hydroxide dispersant by a precipitation method, and the other was a colloidal SiO_2/PVP composite dispersant. The average zeta potentials of magnesium hydroxide dispersant and colloidal SiO_2/PVP composite dispersant were separately measured to be −20.3 and −19.75. The inorganic dispersed particles could adsorb on the surface of the microspheres and repel each other to stabilize the reaction system.

Figure 9 showed the SEM images respectively using colloidal SiO_2/PVP and magnesium hydroxide as dispersants. The microspheres prepared with the colloidal SiO_2/PVP composite dispersion system were spherical. However, it could be seen from the image that there were many impurity particles on the surface of the microspheres prepared by the colloidal SiO_2/PVP composite dispersant. Although the microspheres were shrinking and flattened with magnesium hydroxide as a dispersing agent, the microspheres become smooth and spherical after expansion. The microspheres prepared by the magnesium hydroxide dispersant had a smooth surface and no impurity particles. As could be seen from the thermal expansion curve of figure 10, although the types of dispersants were different, the initial expansion temperatures of the two microspheres were similar. However, the expansion rate of the microspheres prepared by magnesium hydroxide was significantly better than that of colloidal silica/PVP. Therefore, in order to obtain better performance of microcapsules, magnesium hydroxide should be selected as a dispersant.

### 4. Conclusion

In summary, this study will provide some reference for the preparation and property of thermally expansion microcapsules. It can be concluded that compared with the colloidal SiO_2/PVP composite dispersion, the thermal expansion microcapsules with higher expansion rate can be obtained with magnesium hydroxide as dispersants. In addition, the types and proportions of foaming agents also play an important role in the performance of the microcapsules. The results showed that excessively increasing the dosage of the blowing agent may adversely affect the expansion performance of microcapsules. Thus, the content of the blowing agent needed to match the thermoplasticity of the microcapsule wall material. When the blowing agent contained various types, the expansion ratio was significantly higher than that of single blowing agent. Moreover, the particle size had great influence on the expansion rate of microcapsules. Accordingly, it was necessary to screen the particle size of the microcapsules before application. Therefore, it will provide reliable guidance for the product quality improvement and industrial application by systematically studying the preparation, structure and property of thermal expansion microcapsules.

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