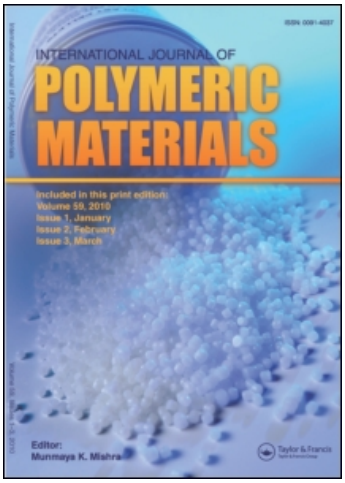

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INFLUENCE OF DISPERSANTS ON THE PARTICLE SIZE AND SIZE DISTRIBUTION OF PHYSICAL BLOWING MICROCAPSULES

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INFLUENCE OF DISPERSANTS ON THE PARTICLE SIZE AND SIZE DISTRIBUTION OF PHYSICAL BLOWING MICROCAPSULES

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In this paper, several powdered dispersants and water-soluble polymer dispersants were used in preparing physical blowing microcapsules. The particle size, size distribution and shape of the microcapsules were observed by optical microscope and electron microscope respectively, and analyzed with digital picture analysis system. The results showed that either powdered or water-soluble polymeric dispersants had obvious effects on the particle size and size distribution of the physical blowing microcapsules.

Keywords: physical blowing microcapsule, powdered dispersant, water-soluble polymeric dispersant

INTRODUCTION

Physical blowing microcapsules, because of their expandable property, have been used in three-dimensional pigment printing and their applications have been extending widely into other special fields in recent years. Foamed rubber articles are, for example, used as press cushions; foamed paper can be used as thermal isolation material, foamed coating; foamed flocking fabric can be used as both thermal and sound isolating materials. As a kind of physical blowing microcapsules, they have to meet certain requirements: fineness and evenness; large rate percentage of the volume expansion and should be easily controlled; the expanded form and shape should be stable enough at the blowing temperature

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so as to keep the foamed appearance. Usually, a special suspension polymerization or, namely, the limited coalescence polymerization is used in preparing physical blowing microcapsules. In order to get products with suitable average particle size and size distribution, parameters that may influence the quality of the products must be adjusted and controlled. Both powdered and water-soluble polymeric dispersants are needed. The influences of such dispersants on the particle size and size distribution of the microcapsules were investigated in detail.

PREPARATION OF THE PHYSICAL BLOWING MICROCAPSULE [1]

The process of preparing physical blowing microcapsules was a special suspension polymerization, i.e. the so-called limited coalescence polymerization in which polymer molecules formed in droplets and transferred from the suspended solution system onto the interface of the oil and aqueous phases, forming a shell. The whole course of preparation could be described as follows:

Forming a Stable Suspension System

The aqueous phase, formed with distilled water, both powdered and water-soluble polymeric dispersants, common salt and other additives, and the oil phase, formed with vinyl monomers, hydrocarbons (blowing agents) and an initiator, were mixed by a high-speed mixer. The oil phase was then dispersed into fine droplets with an average diameter of about 10 μm. The powdered dispersant absorbed onto the surface of the fine oil droplets, the water-soluble polymeric dispersant formed a stable protecting layer by absorbing onto the interface of the oil and aqueous phases, decreased their interfacial tension, and at the same time the polymeric dispersant contributed to a higher viscosity of the aqueous phase. This ensured the stability of the system.

Polymerization in the Droplet

At an elevated temperature, the initiator decomposed into active free radicals (active center), and the active free radicals initiated the polymerization of the monomers. The polymer molecules formed and transferred immediately from the oil phase onto the interfacial phase because of their lyophobic character.

Forming the Capsule Shell

As the polymerization went on, the transfer of the polymer molecules continued, forming a thin layer of shell enclosing the oil phase within it.

And finally, when all the monomers were converted into polymers, the shell reached the maximum thickness. In this way a microcapsule with a shell thick enough, in which the organic solvent (blowing agent) was tightly enclosed, was obtained.

EXPERIMENTAL

Reagents Used

Vinyl monomers: vinylidene chloride(AR), acrylonitrile(AR), methyl methacrylate(AR); initiator: azobisisobutyronitrile(AR); blowing agent: pentane(AR); water-soluble polymeric dispersants: polyvinyl alcohol (PVA 1788, available from Shanghai Petroleum Chemicals Co., Ltd), polycondensates of adipic acid and diethanolamine (with different acid values, prepared in the lab.) and polyvinyl-pyrrolidone (PVP, different K values, available from Zhejiang New Materials Co., Ltd); powdered dispersants: colloidal silica(available from Shanghai Petroleum Chemicals Co., Ltd), and magnesium hydrate (AR).

Laboratory Apparatus

High-speed shearing emulsifiers, modelBME100L; autoclave, model-GCF-2, refrigerator, model DYH-15; vacuum filter.

Preparing the Physical Blowing Microcapsule [2]

According to the formula, pentane, vinylidene chloride, acrylonitrile, methyl-methacrylate, etc. were mixed homogeneously and the azobisisobutyronitrile was dissolved in to form the oil phase, while the powdered dispersant, water-soluble polymeric dispersant, common salt and $NaNO_2$ were dissolved in distilled water and the mixture was acidified to form the aqueous phase. Then both the oil and aqueous phases were emulsified with a high-speed mixer at a speed of about 2,500 r.p.m. for 5 minutes under cooling. The emulsified system was transferred into an autoclave, then the autoclave was sealed and pressurized with N_2 gas until an initial pressure of 0.2–0.5 MPa was reached. The system was heated slowly to a temperature of about 60°C, and this temperature was kept for over 20 hours to finish the micro-encapsulation. Finally, the system was cooled, the pressure was released, the mixture was drawn out, the product was separated and obtained by filtering, washing twice with tap water, and dehydrating.

Measurements of the Average Particle Size and Size Distribution of Physical Blowing Microcapsules

These were conducted with XSP-BM microscope and Panasonic photographic finder with digital picture analysis system.

Observation of the Morphological Structure of Physical Blowing Microcapsule

The morphological structure was observed by JSM-5600LV (Japan) electron microscope.

RESULTS AND DISCUSSION

Effect of Powdered Dispersants on the Particle Size and Size Distribution of Physical Blowing Microcapsules

Effect of Different Powdered Dispersants on the Particle Size and Size Distribution of the Microcapsules

In the suspension polymerization, the tiny solid particles of the powdered dispersant absorbed on the surface of oil droplet, forming a mechanical barrier to prevent the droplet from merging with others [3]. Figure 1 shows that the size distribution of microcapsules prepared with the colloidal silica as the powdered dispersant was narrower than that with magnesium hydrate. The particle size concentrated at about 10 μm. Table 1 shows that the average diameter of microcapsules

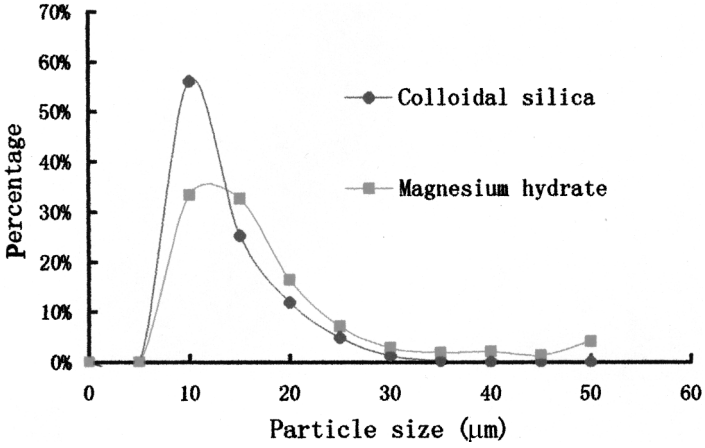

FIGURE 1 Effect of powdered dispersants on size distribution of the microcapsules.

TABLE 1 The Relationship Between the Powdered Dispersant and Average Particle Size of the Physical Blowing Microcapsules

Powdered dispersant	Average diameter of microcapsules (μm)
Colloidal silica	10.8
Magnesium hydrate	19.7

prepared with colloidal silica as the powdered dispersant was smaller than that prepared with magnesium hydrate. Both Table 1 and Figure 1 makes obvious that the dispersion performance of the colloidal silica in preparing physical blowing microcapsules was superior to that of magnesium hydrate. This might be related to their own particle sizes, since the particle size of colloidal silica was far, far smaller than that of the magnesium hydrate.

Effect of the Quantity of Colloidal Silica on the Particle Size and Size Distribution of the Microcapsules

Figure 2 shows the effect of the quantity of the colloidal silica on the particle size and size distribution of the microcapsules. As the amount of colloidal silica increased from 5% to 10% by weight of the monomers, the particle size distribution of the microcapsules became very narrow, and concentrated at about 10 μm. The microcapsules coalesced into clusters without colloidal silica as one of the dispersants.

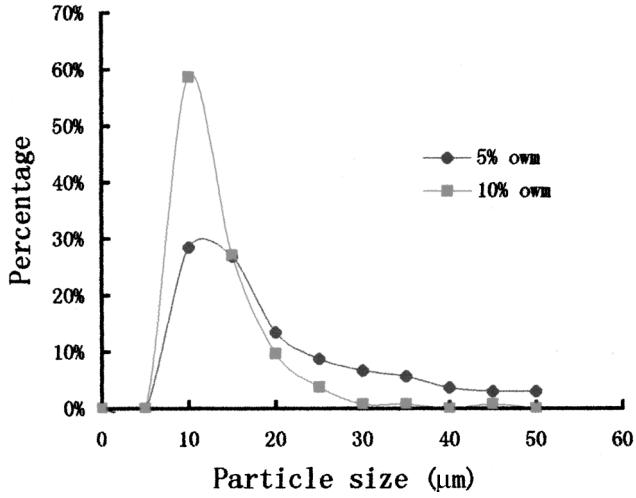

FIGURE 2 Effect of the quantity of the colloidal silica on size distribution of the microcapsules.

Effect of the Water-Soluble Polymeric Dispersants on the Particle Size and Size Distribution of the Microcapsules

Beside the powdered dispersants, the water-soluble polymeric dispersants were also needed in preparing the physical blowing microcapsules. The mechanism was that the water-soluble polymeric dispersant molecules absorbed on the surface of the droplet and formed a protecting layer of colloid, depressing the interfacial tension of the system. Concomitantly, the dissolved polymer increased the viscosity of the aqueous phase [3]. The water-soluble polymeric dispersant acted as a mechanical barrier, as an interfacial agent that reduced the interfacial tension, and as a protective colloid simultaneously. In this paper, the PVA, PVP and the polycondensates were investigated as dispersants in preparing physical blowing microcapsules.

Effect of Different Types of PVP on the Particle Size and Size Distribution of the Microcapsules

Table 2 and Figure 3 show the effect of the K value of PVP on the particle size and size distribution of the microcapsules. The particle size distribution of microcapsules prepared with PVP K-17 appeared the narrowest and the average particle diameter was the smallest in the range of the PVPs used. The particle size distributions of microcapsules prepared with the other K values of PVP were similar to each other and obviously wide, the average particle sizes being larger than that with PVP K-17. This indicated that as a dispersant in preparing microcapsules, the K-17 type of PVP was the best one from the 5 types of PVP used. Since the K value denotes the molecular weight of PVP, the larger K value implies a higher molecular weight. Thus when the K value was too small (e.g. K-12), the solubility of PVP would be too large, both adsorption at the interface, i.e. the interfacial activity and contribution to the viscosity of the aqueous phase would be too low. On the other hand, if the K value is too big, the solubility would be too small to provide enough stabilizing effects to the system.

TABLE 2 The Relationship Between the K Value of PVP and Average Particle Size of the Physical Blowing Microcapsules

K value of PVP	Average diameter of microcapsules (μm)
K12	15.6
K-17	10.8
K20	13.7
K25	14.5
K30	16.4

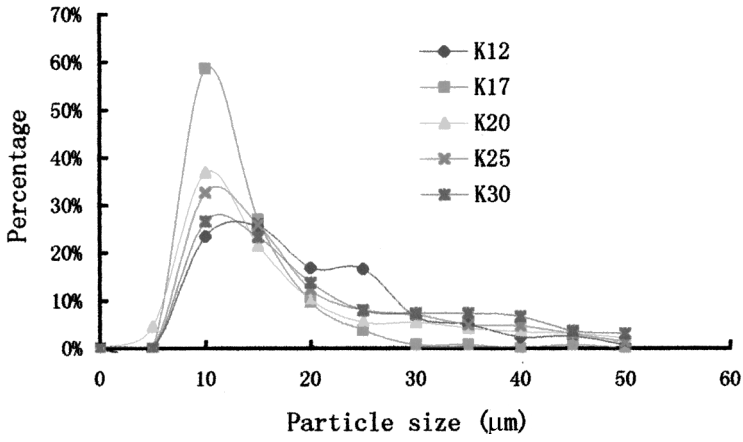

FIGURE 3 Effect of different K values of PVP on size distribution of the microcapsules.

Effect of Different Acid Values of Polycondensates on the Particle Size and Size Distribution of the Microcapsules

Polycondensates with different acid values were used as dispersants in preparing physical blowing microcapsules. The results are shown in Figure 4 and Table 3. It can be seen from Figure 4 and Table 3 that acid values of polycondensates noticeably affected the particle

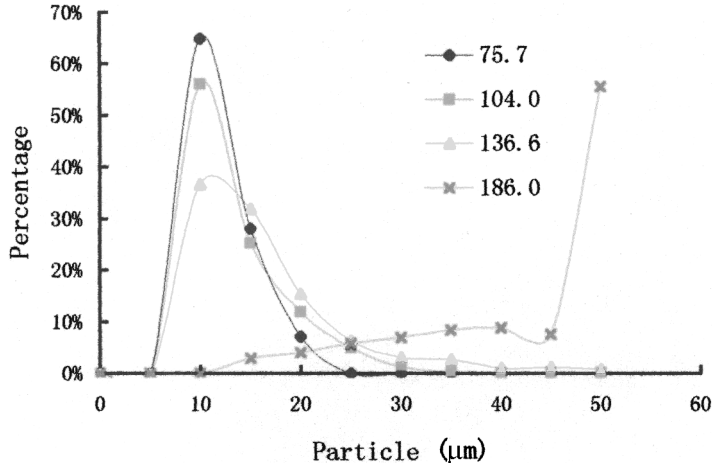

FIGURE 4 Effect of different acid values (mgKOH/g) of polycondensates on the size distribution of microcapsules.

TABLE 3 The Relationship Between the Acid Value of the Polycondensate and the Average Particle Size of Microcapsules

Acid value of polycondensate (mgKOH/g)	Average diameter of the microcapsules (μm)
75.7	9.6
104.0	10.9
136.6	18.5
186.0	46.1

size and size distribution of the physical blowing microcapsules. The particle size distributions of the microcapsules prepared with polycondensates (acid values from 75.7 and 104.0) were narrow, and concentrated round 10 μm, and the difference of the average particle sizes was small. But the particle size distributions of the microcapsules prepared with polycondensates (acid values from 136.6 and 186.0) were very wide; the average diameters of the microcapsules prepared with such polycondensates as dispersants were evidently large. And that prepared with the polycondensate with an acid value of 186.0 mgKOH/g was as large as 46.0 μm. This could be explained as follows: the larger acid valued implied lower $\overline{DP}$ of the polycondensates. And a polycondensate with too small $\overline{DP}$ provided little viscosity to the aqueous phase and too weak adsorption onto the fine droplets, and thus too weak interfacial active effect (poor dispersing effect). On the other hand, the polycondensate system would be led to gelation if the acid value became too small. Thus the range of acid values of polycondensates suitable for dispersants in preparing physical blowing microcapsule should be 75.7 to 104.0 mgKOH/g.

Effect Comparison of PVP (K-17), PVA (1788) and Polycondensate (Acid Value: 75.7 mgKOH/g) on the Particle Size and Size Distribution of the Microcapsules

Figure 5 shows a comparison of the effects of the selected polycondensate (acid value 75.7 mgKOH/g) and PVP (K-17). They all possessed good dispersion performance in preparing physical blowing microcapsules, and the performance of the polycondensate with an acid value of 75.7 mgKOH/g seemed a little better than that of PVP (K-17).

Finally, PVA was also investigated in preparing the physical blowing microcapsules, but the products were aggregates of clusters.

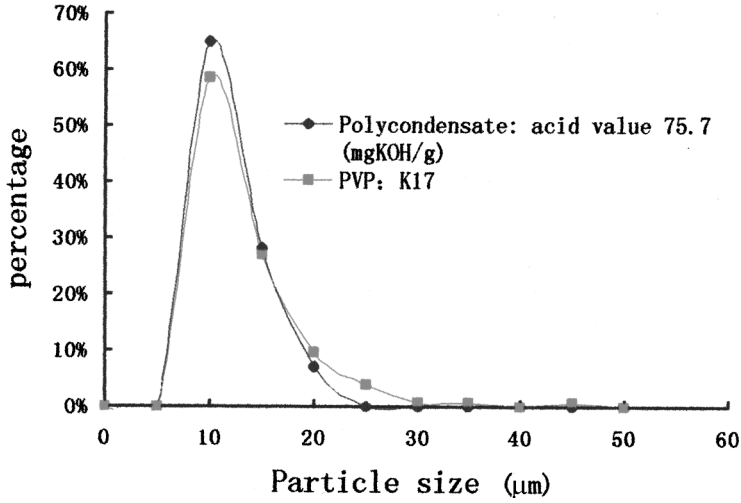

FIGURE 5 Effect of PVP (K-17) and a polycondensate with an acid value of 75.7 mgKOH/g on size distribution of microcapsules.

Surface Morphological Structure of the Physical Blowing Microcapsules Prepared by Different Water-Soluble Polymeric Dispersants

The electron microscope photos of the physical blowing microcapsules prepared with polycondensates of 75.7 acid value and PVP K-17 as dispersants are shown in Figures 6,7,8 and 9.

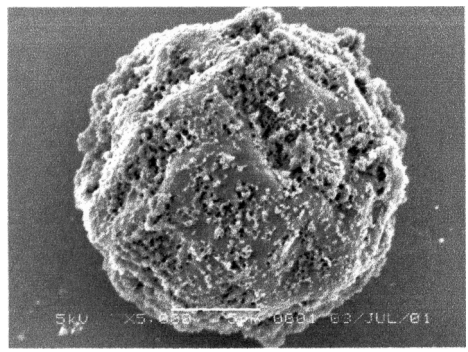

FIGURE 6 An SEM photo of high−temperature (150°C) blowing microcapsules prepared with PVPK-17 as a dispersant.

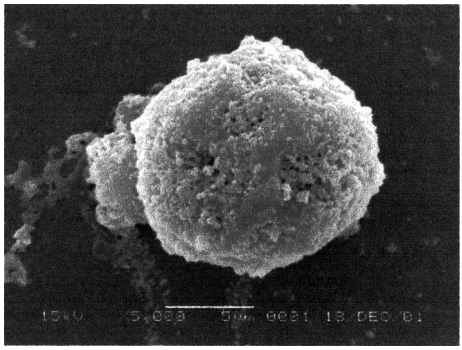

FIGURE 7 An SEM photo of high–temperature (150°C) blowing microcapsules prepared with acid value 75.7 polycondensate as a dispersant.

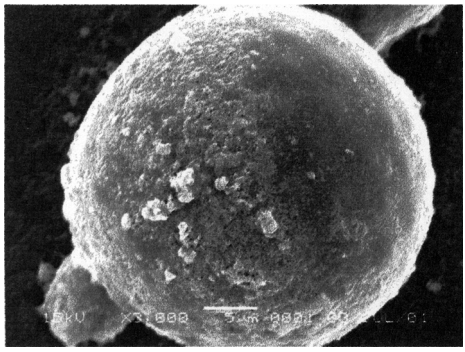

FIGURE 8 An SEM photo of low–temperature (90°C) blowing microcapsules prepared with PVP K-17 as a dispersant.

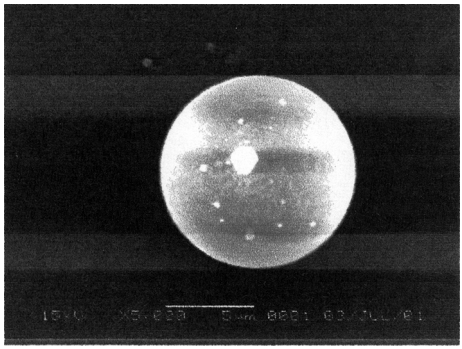

FIGURE 9 An SEM photo of a low–temperature (90°C) blowing microcapsules prepared with acid value 75.7 polycondensate as a dispersant.

It is obvious from Figures 6, 7, 8 and 9 that the physical blowing microcapsules prepared with water-soluble polymer dispersants, no matter what they were, PVP (K-17) or polycondensate (acid value of 75.7), all of the microcapsules possessed single-cored spherical shape. But the large difference is between the high-temperature and low-temperature blowing types of the microcapsules: the surface of the high-temperature blowing capsule is evidently rougher than that of the low-temperature blowing capsule. This is probably because of the different flexibility of the polymer chains; the polymer chain of the high-temperature blowing capsule is relatively rigid compared to that of the low-temperature one.

CONCLUSIONS

(1) As necessary powdered dispersants for preparing physical blowing microcapsules, colloidal silica is much better than magnesium hydrate.
(2) Both PVP K-17 and the polycondensate with an acid value of 75.7 mgKOH/g could be used as the necessary water-soluble polymeric dispersants in preparing a physical blowing microcapsule.
(3) The K-values of PVP possessed a significant effect on the particle size and size distribution of physical blowing microcapsules.
(4) The acid value of the polycondensate affects the particle size and size distribution of physical blowing microcapsules significantly.
(5) The physical blowing microcapsules prepared with both polycondensates of 75.7 acid value and PVP K-17 as dispersants show a single-cored spherical shape.

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