A New Technique for Foaming Submicron Size Poly(methyl methacrylate) Particles

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ABSTRACT: About 0.7–2 μm diameter poly (methyl methacrylate) (PMMA) foamed particles were prepared via thermally induced phase separation (TIPS) from a PMMA/ethanol mixture and vacuum dried. It was found that ethanol, known to be a poor solvent to PMMA, could dissolve PMMA when the temperature was over 60°C. The solubility of PMMA (M_w = 15,000 and M_w = 120,000) in ethanol was measured and was found to increase as the temperature increased. PMMA particles on the scale of submicron and single micron diameter could be precipitated from the PMMA/ethanol solution by temperature quenching. Then, since the precipitated particles contained a certain amount of ethanol, the precipitated particles could be foamed using the ethanol as a foaming agent in a vacuum drying process. Vacuum drying at temperatures slightly below the glass transition temperature of the polymer could make the particles foam. The effects of foaming temperature and the molecular weight of the polymer on the size of foamed particles were investigated. The experimental results showed that the vapor pressure and the molecular weight of the polymer are key factors determining the expandability of the micro particles. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2825–2830, 2007

Key words: foam; poly(methyl methacylate); thermally induced phase separation; polymeric particles

INTRODUCTION

Polymeric particles are used for many purposes such as the stationary phase in chromatography, adsorbents, catalyst supports, drug delivery vehicles, and polymeric foams. Thermally expandable microspheres are one class of polymeric particles that are used for polymeric foam production as blowing agents or as lightweight fillers. For example, these particles are used in printing inks to provide the production surface textures, and they are also used to achieve weight-reduction of various matrices and improve the physical properties of the resulting products.[1,2] Dow Chemical originally invented the concept of a thermally expandable particle which encapsulates a low boiling point hydrocarbon within a thermoplastic polymer. These particles have been improved, and several kinds of particles have been produced. The expandable polystyrene beads (EPS) are known as one of the most widely used expandable polymeric particles. They are prepared by suspension polymerization of atactic polystyrene containing pentane as a blowing agent. Because of environmental concerns, Crevercoeru et al. modified the EPS process and prepared water expandable polystyrene particles by incorporating water in the early stage of polymerization, stabilizing the particle with the addition of a suitable surfactant, and using water as a blowing agent.[3–5] Kawaguchi et al. used acrylonitrile, methacrylonitrile, and vinyl acetate to create a shell for a thermoplastic expandable microsphere.[6,7] In most of the previously reported processes, polymeric particles are prepared by suspension polymerization where a monomer phase is suspended in a water phase containing a stabilizing agent, and polymerization is conducted in the monomer droplets. Furthermore, most of the prepared expandable particles are 5–50 μm-sized particles before expansion, and no expandable particles in the submicron and single micron size range have been reported.

Thermally induced phase separation (TIPS) is one of the techniques that can produce smaller polymeric particles. In the TIPS process, polymer is dissolved in solvents at high temperature. Upon the removal of thermal energy by cooling, a phase separation is induced, i.e., nucleation. Schaaf et al. prepared polymeric particles from the crystallization of semi-dilute solutions of polyethylene and poor solvents in a TIPS process[8] where the particle size was in the range of 1–10 μm diameter. Hou and Lloyd reported the preparation of fairly uniform nylon polymer particles using a TIPS process,[9] and they produced 5–13 μm sized particles. Polyethylene particles were prepared using phase separation between solvent (decane) and non-solvent mixture (tetraglyme),[10] and submicron sized polypropylene particles were made by Matsuyama et al. from a mixture of polypropylene and diphenyl

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ether (DPE).[11] Nano/micro size PMMA particles were prepared by cooling PMMA and 1-propanol mixtures,[12] and it was shown that the particle size was in the range of 0.1–10 μm. The particles produced by TIPS are normally smaller than those produced by suspension polymerization. However, there have been no reports on submicron and single micron size expandable polymeric particles prepared via a TIPS process.

In this study, since polymeric particles prepared by a TIPS process show submicron size particles and also contain solvent upon precipitation, both submicron size and single micron size expandable polymeric particles were prepared. Single micron or submicron sized PMMA particles were precipitated by a TIPS process from polymer/ethanol solutions. Then, using the ethanol in PMMA particles as a foaming agent, the particles were foamed by a pressure difference and vacuum pressure. The effects of the foaming temperature and vacuum pressure on particle size and morphology were investigated.

EXPERIMENTAL

Materials

Two different molecular weights of poly (methyl methacrylate), (PMMA 15k and PMMA 120k) were purchased from Aldrich Chemical Co. Their weight average molecular weights (M_w) and polydispersity indexes (PI) were measured using a gel permeation chromatography (Shimadzu RID-10A, eluent: chloroform, column: Shim-pack GPC-802C and 804C, calibration curve: polystyrene standards). The M_w and PI were 14,600 and 1.53 for PMMA 15k and those were 123,000 and 1.96 for PMMA 120k, respectively. They were powder-like materials and were used without further purification. The glass transition temperatures (T_g) of the PMMA materials were measured using a differential scanning calorimeter (Pyris 1, Perkin-Elmer Japan) at 10°C/min in a nitrogen purged atmosphere. Ethanol (99.9% in purity, Wako Pure Chemical, Japan) was used as received.

Solubility of PMMA in ethanol

To conduct the temperature quenched TIPS process, the solubility of PMMA in ethanol was essential to know. The solubility of PMMA in ethanol was measured from the weight loss of the PMMA sample after immersing the polymer in ethanol. The disk-shaped thin film samples were prepared from PMMA by a compression-molding machine (Big press., Imoto, Japan). The sample was dried at room temperature in a vacuum chamber for more than one day, and weight w_i was measured. Then, the sample was immersed for 5 h into w_e gram ethanol in a cylindrical glass cell with a plug sealing screw cap at a specified temperature under well-mixing conditions. After immersion of the sample in ethanol, the solid sample was retrieved and dried at room temperature in the vacuum chamber. The completely dried PMMA sample was weighed by an electric balance (AT261 Delta Range, Mettler Toledo, Germany) to obtain the weight w_f. The weight of the sample decreased because some amount of the polymer dissolved into ethanol. From the weight measurements, the solubility of PMMA in ethanol was calculated by eq. (1)

$$S = \frac{w_i - w_f}{w_e} \qquad (1)$$

where S is solubility of the polymer in ethanol [g-polymer/g-ethanol], w_i is the initial weight of the sample, w_f is the weight of the sample after soaking, and w_e is weight of ethanol.

Preparation of PMMA particles

PMMA particles were prepared by a TIPS process with ethanol in a 150 mL glass cell. The cell was sealed with a screw cap and immersed in an oil bath where the temperature was controlled within ±0.1°C around a given setpoint. 5 g of ethanol and 0.05 g of powder-PMMA were put into the cell and heated up to the setpoint. By stirring the solution with a magnetic stirrer at 100 rpm for 30 min, a homogeneous and transparent solution was obtained. Then, the solution was quickly cooled down to a lower temperature, 25°C. When it was cooled down, the mixture showed a slightly opaque color characteristic of colloids. The colloidal suspension was filtered by vacuum filtration with a membrane filter of 0.1 μm pore size.

Foaming PMMA particles by vacuum drying

The ethanol remained in the precipitated PMMA particles because the particles were prepared by phase separation using the TIPS process. The ethanol in PMMA could be used as a physical blowing agent to foam the particles. The filtered PMMA particles were put into a pre-heated vacuum dry oven immediately after filtration. The temperature of the vacuum oven was controlled within a precision of ±1°C around a set-point in the range of 25–110°C. After putting the particles into the vacuum oven, the pressure in the oven was reduced down to 0.1 kPa within 5 min, and the vacuum pressure condition was kept for 10 min at the specified temperature. The vapor pressure of ethanol is a function of temperature. When the particles were heated, the vapor pressure was established inside the particles by the ethanol, while the particles were soft. The vacuuming operation at a certain

temperature created a pressure difference between the inside and the outside of the particles. The pressure difference made the particles foam. In this stage, heating alone could not make the particles foam, since under atmospheric pressure, a higher temperature would be needed to establish a sufficient pressure difference to expand the particles, but this higher temperature would reduce the viscoelasticity of polymer too much and would often lead to particle agglomeration and melting.

Particle size measurements

The foamed particles were dried in the vacuum chamber at room temperature and coated with a thin Pd-Au film for FE-SEM measurement. The particle size was measured from micrographs taken by a field emission scanning electron microscope (FE-SEM) (JSM-6340FS, JOEL). The particle diameter was determined by averaging the diameter of about 300 particles observed in the FE-SEM micrographs, and the coefficient of variation (CV) of the sample diameter was also calculated from the data to evaluate variability. The number average diameter and CV were calculated by eqs. (2) and (3), respectively

$$d_{\text{avg}} = \frac{\sum_{i=1}^{N} d_i}{N}, \quad (2)$$

$$\text{CV[\%]} = \frac{0.5 \times \left(\frac{\sum_{i=1}^{N} (d_i - d_{\text{avg}})^2}{N-1} \right)}{d_{\text{avg}}} \times 100, \quad (3)$$

where, d_{avg} is the average diameter of particle (μm), N is the total number of particles to be measured, and d_i is the diameter of the ith particle (μm). CV stands for the coefficient of variation.

RESULTS AND DISCUSSION

Glass transition temperature of PMMA

The measured glass transition temperatures, T_g, of both PMMA grades are listed in Table I. The T_g of PMMA 15k was 88°C, which was lower than that of PMMA 120k.

TABLE I
Glass Transition Temperature of PMMA Samples

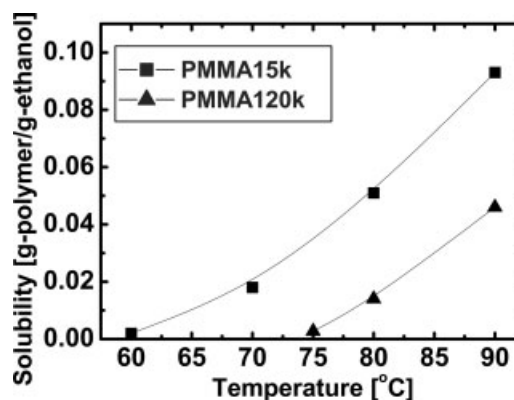|	PMMA 15k	PMMA 120k
T_g (°C)	88	108

Figure 1 Solubility of PMMA in ethanol at different solution temperatures.

Solubility of PMMA in ethanol

The solubility measurement was conducted by varying solution temperature from 60–90°C. The resulting solubility data are given in Figure 1. In Figure 1, squares represent the solubility of PMMA 15k and triangles represent that of PMMA 120k. The solubility of PMMA 15k in ethanol increases at temperatures over 60°C, and the solubility of PMMA 120k increases at temperatures over 75°C. Ethanol is known to be a poor solvent to PMMA, but it can dissolve PMMA as the solution temperature increases. The solubility data clearly showed that the TIPS method could be performed to precipitate PMMA particles from the PMMA/ethanol mixture.

PMMA particles prepared by TIPS

PMMA 15k particles were prepared by the TIPS process at various initial PMMA concentrations in ethanol. Figure 2 shows an SEM micrograph of PMMA
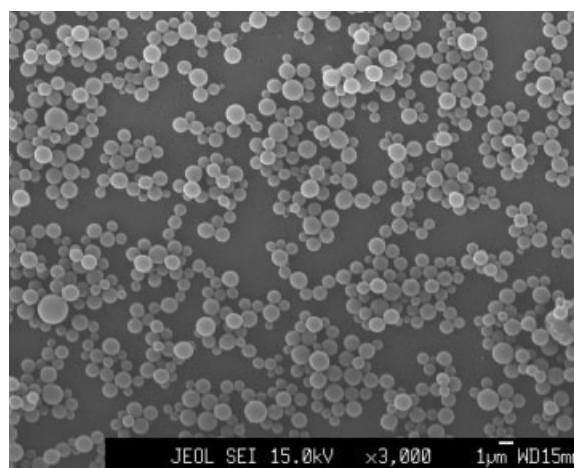

Figure 2 FE-SEM micrograph of PMMA 15k particles precipitated from 0.5 wt % PMMA/ethanol mixture and dried at 25°C under atmospheric pressure. Scale bar is 1 μm.
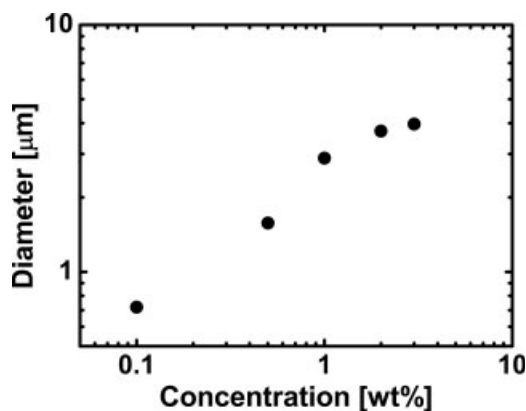
Figure 3 Effect of initial polymer concentration on the diameter of precipitated PMMA 15k particles.

particles precipitated from a mixture. The precipitated PMMA particles are spherical with a fairly uniform particle size and a smooth surface. Figure 3 shows the effect of the initial polymer concentration on the average particle size. As the concentration increases, the diameter of the precipitated particles increases. Table II shows the CV value of the particles obtained at each initial polymer concentration. Because of the lowest variability, the PMMA particles precipitated from 0.5 wt % PMMA 15k and 99.5 wt % ethanol solution were further used for the foaming experiments.

PMMA particle foaming using the vacuum drying process

To confirm whether the precipitated particles contained ethanol, simple drying experiments were conducted on precipitated particles, and the dried particle size was measured. Without vacuuming, the particles, which were precipitated from a mixture of 0.5 wt % PMMA 15k and ethanol, were dried in an oven at 25°C by varying drying time from 10 min to 24 h, and the average particle diameter was measured. Figure 4 illustrates the change in the diameter of the dried particles versus drying time. As shown in Figure 4, the diameter of the particles decreased with drying time, which indicates that the particles contain ethanol, which swells the particle initially and then gradually diffuses out from the particles.

TABLE II
Average Diameter of PMMA 15k Particles Prepared by Temperature Quenching from 80–25°C

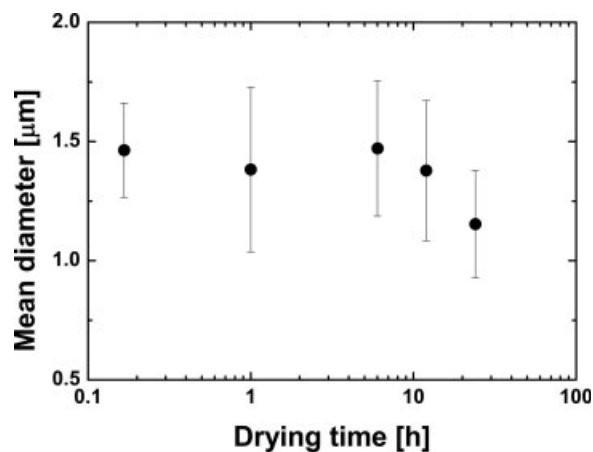|	Initial PMMA conc. in ethanol [wt %]				
	0.1	0.5	1.0	2.0	3.0
Diameter (μm)	0.72	1.51	2.89	3.72	3.97
CV (%)	16.9	14.7	15.2	16.3	17.8

Figure 4 Change in the average diameter of PMMA 15k particles against drying time. The particles were dried at 25°C immediately after precipitation.

The precipitated particle, which was prepared from 0.5 wt % PMMA/ethanol mixture, was foamed in a vacuum oven at 110°C under −0.1 kPa-gauge pressure conditions. Figure 5 illustrates an FE-SEM micrograph of foamed PMMA 15k particles. The foamed particles were spherical, and their diameter expanded to be 1.3 times as large as that of the nonfoamed particles in Figure 2.

To see the inside of the foamed particle, the foamed particles were ground in a mortar. Figure 6 shows an FE-SEM micrograph of a ground foamed PMMA 15k particle, and it clearly shows a hollow structure. The mechanism of forming the hollow structure could be as follows. The precipitated particles contained ethanol, and when they were placed in a vacuum oven, where the temperature and pressure were controlled, a certain amount of ethanol diffused from the particle
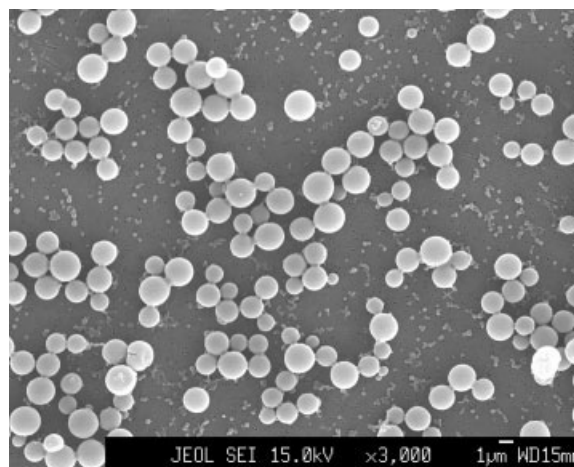

Figure 5 FE-SEM micrograph of PMMA 15k particles foamed at 110°C under 0.1 kPa vacuum. The particles were precipitated from a 0.5 wt % PMMA/ethanol mixture. Scale bar is 1 μm.
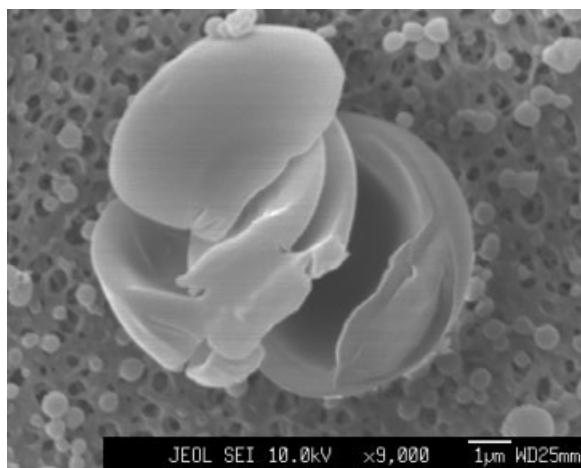
Figure 6 FE-SEM micrograph of a ground foamed particle (PMMA 15k). Scale bar is 1 μm.

surface and established a concentration profile inside the particle. Then, the pressure difference, which was created by the ethanol vapor pressure and by vacuum, induced bubble nucleation in the particles and expanded the particles. Since the ethanol had diffused from the surface of the particles, the ethanol concentration was low at the surface. Thus, the degree of solvent swelling was reduced at the surface of each particle, i.e., the surface of the particles became stiffer compared with the particle interior. Because the surface of the particles was stiff and the inside was soft, bubble nucleation occurred dominantly in the particle core, and the nucleated bubbles were easily coalesced inside the particle. This mechanism would lead to the formation of a hollow structure.

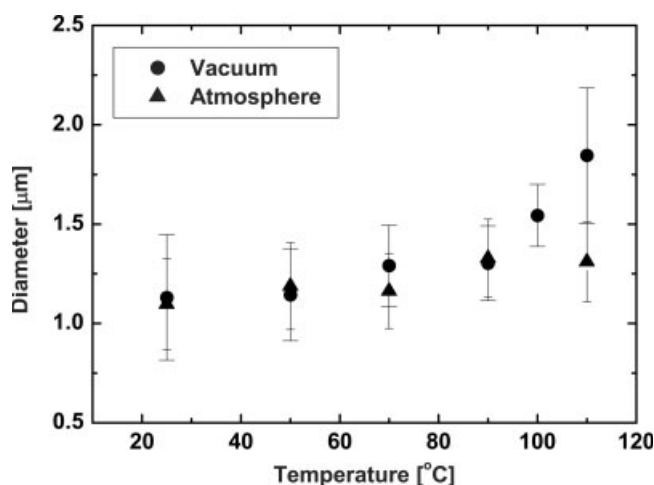The particle was foamed under vacuum for 10 min by varying the temperature in the range of 25–110°C.

To see the effect of vacuum, the particles were dried under atmospheric pressure at the same temperature. Figure 7 shows the average diameter of the foamed particles at each foaming temperature. Solid circles and triangles, respectively, represent the diameters of particles dried under −0.1 kPa vacuum gauge-pressure and those foamed under atmospheric pressure without vacuuming. Under vacuum drying conditions, the diameter increased at temperatures over 70°C, which was below the glass transition temperature of the original PMMA, 88°C. Under atmospheric conditions, the diameter of the particles was slightly increased at 80°C, but suppressed to around 1.25 μm over this temperature. This temperature corresponds to the boiling point of ethanol, which is 78°C. It can be considered that the glass transition temperature of polymer, T_g, was reduced by the dissolved ethanol, and the particles were foamed at a temperature below the original T_g due to the pressure difference between the vapor pressure of ethanol and the vacuum pressure.

Effect of molecular weight on foaming

The effect of the molecular weight of the polymer on particle foaming was investigated using PMMA 120k. The PMMA particles were prepared from 0.5 wt % PMMA 120k/ethanol solutions under the same temperature conditions in which the PMMA 15k particles were prepared. The foaming experiment was conducted under −0.1 kPa-vacuum gauge-pressure with a 10-min drying time by varying the drying temperature in the range of 25–130°C. The average diameters of the resulting particles are shown in Figure 8, with error bars indicating the max and min diameters. The diameter of the initial precipitated particles was about
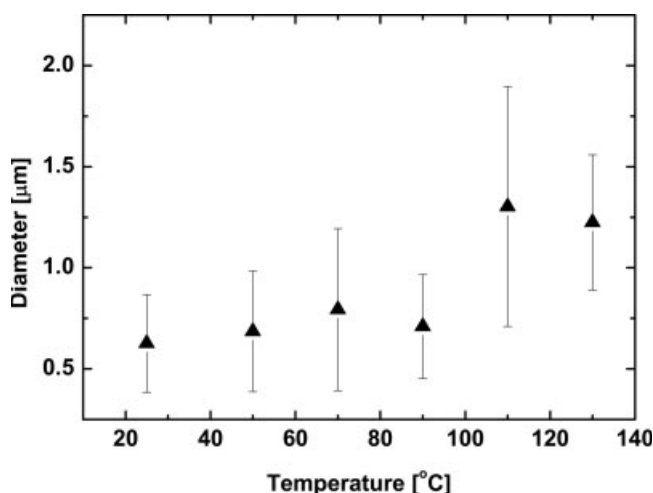

Figure 7 Average diameters of PMMA 15k particles foamed at different foaming temperatures under 0.1 kPa vacuum. Error bars indicate the maximum and minimum diameters observed on the micrograph.

Figure 8 Average diameter of foamed PMMA120k particles at different drying temperatures under 0.1 kPa vacuum. Error bars indicate the maximum and minimum diameters observed on the micrograph.

0.7 μm. The diameter actually became larger by foaming at temperatures above 100°C. The T_g of PMMA 120k is 108°C, as shown in Table I. Because of the higher T_g of PMMA 120k, the higher viscoelasticity of the PMMA matrix suppressed bubble nucleation and growth in the polymer below 100°C. The foaming temperature where the particle diameter increase of PMMA 120k occurs is at higher temperatures than those for PMMA 15k due to the difference in the T_g of neat polymers. The diameter of particles foamed at 130°C was reduced. This is due to the higher diffusivity of ethanol out from the particles.

CONCLUSION

Submicron and single micron sized PMMA expandable particles were prepared from PMMA and ethanol mixtures by the TIPS method. A new technique for preparing expandable particles was developed by the TIPS scheme with ethanol as the theta solvent. This TIPS method could be used to prepare the submicron and micron sized particles containing volatile solvent, ethanol in this study. Owing to the presence of ethanol in the particles, the particles were foamed under vacuum conditions using ethanol as a physical foaming agent. The foaming temperature is a key variable to manipulate in order to make the particle foam. The temperature should be appropriately chosen considering the glass transition temperature of the polymer and the vapor pressure of ethanol. Vacuum was needed to create a sufficient pressure difference between the inside and outside of the particles to expand the softened particles.

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