

Preparation and Characterization of Poly(methyl methacrylate) Beads

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ABSTRACT: For fluid-dynamic experiments involving concentrated suspensions and complex geometries, particles which are neutrally buoyant and which have the same refractive index as both the suspending fluid and the bounding container are needed. Poly(methyl methacrylate) (PMMA) particles can meet these requirements simultaneously. Therefore monodisperse beads with the refractive index and density of pure PMMA were needed. For comparison with particle migration theory, it is also important that bead size and sphericity be accurately controlled. In our fluid mechanics experiments, 500- μm diameter was required, a size where suspension polymerization is suitable.

This article describes the controlled formation of PMMA beads in substantial quantities with desired size and a narrow particle size distribution. Reaction scale-up using a 2-L Büchi reactor allowed batch yields of 200 g of PMMA beads with desired shape and size. However, microcavities reduced bead density and optical clarity. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1814–1822, 2008

Key words: suspension polymerization; poly(methyl methacrylate); particle size distribution; microstructure; thermal properties

INTRODUCTION

Suspensions are studied in fluid mechanics for many applications including polymer processing, industrial waste processing, and biological systems. Blood, a concentrated suspension of red cells, is a prominent example among biological fluids. Suspension fluid mechanics experiments require particles which must satisfy several requirements, including uniform shape and size, density, refractive index, and low cost. In gradually developing complex experiments, it is desirable to commence with the simplest of suspensions: those containing only one size of particle, a rigid sphere. If the small forces which propel particle migration are to be investigated, it is also vital that buoyancy forces be minimized, by using particles which neither rise nor sink. The study, with optical measurement methods, of particle–particle interactions in concentrated suspensions is particularly challenging, but can be achieved using particles which have the same mean refractive index as the suspending fluid.¹ For experiments involving complex geometries, it is also convenient to have the fluid match the refractive index of the bounding container. All these technical requirements can be simultaneously met with particles of poly(methyl methacrylate) (PMMA) (refractive index 1.49, density 1.19 g/cm³), but commercial products are too expensive to be practical in experiments involving substantial quantities. Cheaper sources typically prove unacceptable, the particles having wide size distribution and density discrepancies and lacking uniform shape. Ideally, the beads were required to be monodisperse in diameter, density, and refractive index. The local experiment for which the product was intended required beads of 500- μm diameter initially, with the possibility of later demand for monodisperse beads 100–1000 μm in size.

Suspension polymerization is commonly used in the production of spherical particles with diameters in the range 100–5000 μm ,² and is employed, for example, in the commercial production of expandable polystyrene and certain grades of PVC.³ A significant difficulty associated with suspension polymerization is the breadth of the particle size distribution (PSD). An example of a commercially produced product is shown in Figure 1. There is a wide range of bead sizes in the sample, with larger particles $\sim 75\text{-}\mu\text{m}$ in diameter and very small particles less than 5 μm . Hashim and Brooks⁴ and Dowding and Vincent⁵ have investigated the control of the PSD in acrylic-water systems and the factors contributing to it. Agitation speed, stabilizer concentration, agitator and reactor geometry, interfacial tension, and the dispersed and continuous phase viscosity all have an effect on the particle size distribution.⁶

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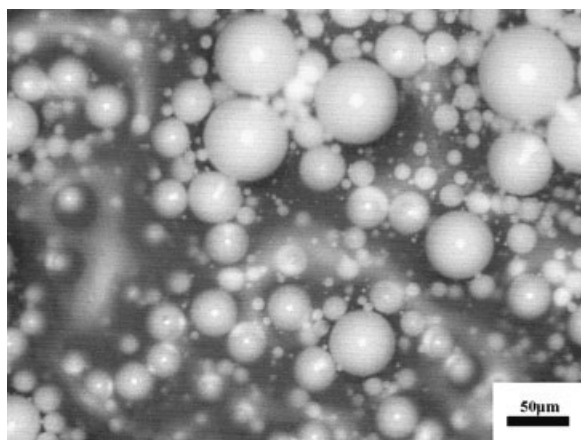


Figure 1 Commercially sourced polymer beads.

Suspension polymerization involves a dispersed phase containing predominantly the monomer and a continuous phase supporting the dispersed phase. These two phases are brought into widespread contact via agitation. Commonly the dispersed phase is known as the “oil phase” and the continuous phase is known as the “aqueous phase”, as the monomer is usually hydrophobic and the suspending agent commonly water (“oil-in-water system”). Inverse suspensions are also known, where the suspending agent is oil-based (“water-in-oil systems”).⁷

The formation of uniform monomer droplets as precursors to beads of narrow PSD has been recently studied by Kotoulas and Kiparissides,⁸ who describe two mechanisms for both coalescence and droplet break-up. Droplet coalescence occurs by either immediate coalescence or continuous-phase-inhibited coalescence and droplet break-up occurs by “through break-up” or erosive break-up (Fig. 2).

The size of the polymer droplets depends on the balance between coalescence and break-up, with a higher rate of coalescence leading to an increased droplet size, and a higher rate of break-up reducing the droplet size. These mechanisms are then used to generate population balances to predict the mean particle diameter generated by a particular system.

Once the dispersion is formed, some type of stabilizer (also known as a dispersant or a Pickering emulsifier) must be added to the reaction to form a protective colloid and provide an interface between the continuous and the dispersed phase. The concentration and the type of stabilizer used significantly affects the PSD. An increased stabilizer concentration will lead to a reduction in the PSD. Typical stabilizers may be natural polymers, synthetic polymers, or fine-particle inorganic powders,⁹ although the latter often require the addition of surfactants to assist wettability.¹⁰

Poly(vinyl alcohol) (PVA) is the most commonly used stabilizer in the acrylic–water system and has

been widely reported.^{4,11} The main issue associated with PVA is that it grafts onto the surface of the polymer bead and so is difficult to remove. Because of its widespread use, much information has been generated about the most effective type. Mendizabal et al.¹² described the effect of molecular weight and degree of hydrolysis on stabilization efficiency, and reported that PVA with a high molecular weight (in excess of 70,000 g/mol) and ~ 88% hydrolysis was best. High-molecular weight PVA allows the formation of a thicker protective film and improves resistance to droplet coalescence. Although PVA is extensively used for suspension polymerization stabilization, a limitation is surface grafting which can make beads more hydrophilic and so harder to dry, and also increase optical haze through a bead.

Stabilizers which do not graft onto the surface of the polymer bead have also been investigated. Polyelectrolyte stabilizers including sodium polymethacrylate (Na-PMA) have been used successfully as a stabilizing agent by Georgiadou and Brooks.¹³ Inorganic stabilizers can be removed by acid post-treatments.

Batch size scale-up has been reported to be particularly difficult when dealing with suspension polymerization. Hamielec and Tobiata¹⁰ consider that the main challenge is maintaining the dimensionless groups (Reynolds, Froude, and Weber numbers) to allow constancy of flow conditions. In fact, keeping all these dimensionless groups constant is impossible without altering the composition of the system, and so scale-up cannot be achieved without adjustment of reactant concentrations.

In this work, we describe the conditions that lead to the formation of spherical PMMA beads of controlled particle size. Mean diameter can be tailored

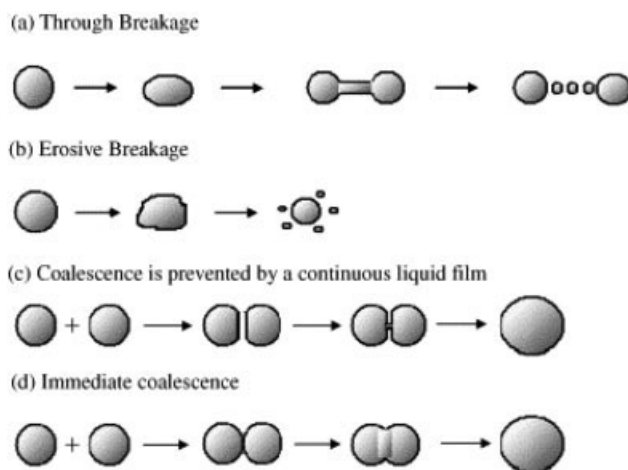


Figure 2 Coalescence and breakage mechanisms as proposed by Kotoulas and Kiparissides.⁸ Reprinted with permission from Kotoulas, C.; Kiparissides, C. *Chem Eng Sci*, 2006, 61, 332, Copyright 2006, Elsevier.

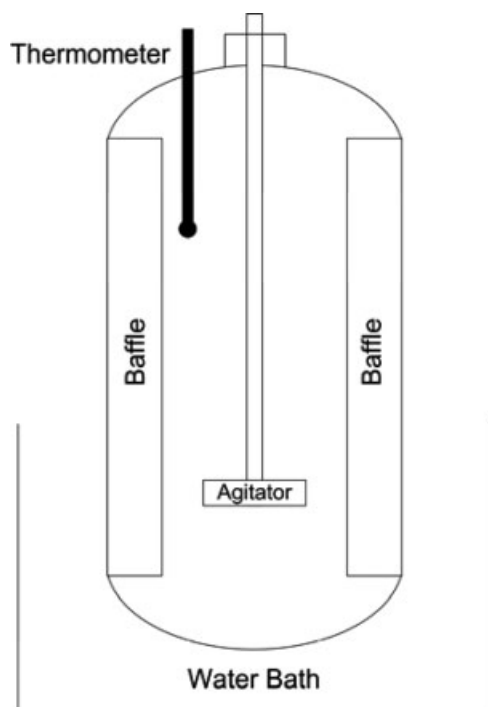


Figure 3 Schematic of bench-top apparatus.

from 200 to 600 μm , with PSD standard deviations typically between 60 and 360 μm . Bead characteristics were examined using particle size analysis, microscopy (both optical and electron) and thermal analysis, and the density of the beads was measured. Microcavities leading to a reduction in particle density were observed. The source of these inclusions was investigated with a number of possible reasons identified.

EXPERIMENTAL

Materials

The monomer methyl methacrylate (MMA) was purchased from Sigma-Aldrich (St. Louis, MO) in 98% pure form. The inhibitor monoethyl hydroquinone (MEHQ) was removed using basic alumina. The stabilizer PVA, 87–89% hydrolyzed with stated molecular weight range 146,000–186,000, the initiator 1,1'-azobis(cyclohexanecarbonitrile), and the crosslinker ethylene glycol dimethacrylate (EGDMA) were also purchased from Sigma-Aldrich.

Procedure

Suspension polymerization experiments were conducted in a 1-L glass reactor with a diameter of 100 mm. Two 20-mm wide stainless steel baffles were inserted into the reactor. A flat, single-bladed agitator and IKA (Staufen, Germany) overhead stirrer were used to form the dispersion. Figure 3 is a schematic of the apparatus used. Larger-scale reactions

were conducted in a 2-L Büchi (Flaivil, Switzerland) reactor (autoclave) with a diameter of 90 mm as shown in Figure 4, with a baffle inserted in the center.

Control of the polymer size distribution requires that either the stirrer speed or the stabilizer concentration be altered. The monomer fraction and the initiator concentration remained essentially constant (0.1 vol % and 1.6 g/L, respectively). The initial reaction conditions were as used by Jahanzard et al.⁶ Conditions were then altered to achieve a mean particle size of 500 μm . The order of reactant addition remained constant throughout.

Three separate series of reactions were conducted at a temperature of 80°C. In Series A, the stabilizer concentration was varied while maintaining the agitator at a low rotation speed (300 rpm) to maximize mean particle size. The stabilizer concentration was altered to center the PSD at about 500 μm , and so maximize the yield of suitable particles. In Series B, the effects on the polymerization reaction of adding a crosslinking agent (EGDMA) were investigated. The added EGDMA varied from 1 to 3 mL, while maintaining constant agitator speed and stabilizer concentration. The third series of reactions (C) investigated scale-up using the Büchi reactor, with the conditions that were found ideal for the 1-L reactor being used initially.

The rotation rate of the stirrer was set by a position on a dial, corresponding to an actual rate measured with a tachometer responding to a reflective strip attached to the stirrer shaft. The agitator tip speed is then the product of the circumference of the stirrer and the rotation rate in revolutions per second. Freshly boiled deionized water was then added



Figure 4 Büchi reactor and Julabo (Seelbach, Germany) water bath.

and the temperature maintained at 80°C. The inhibitor-free monomer was then added, followed by initiator and stabilizer. The stirrer was then activated and samples removed at hourly intervals to assess monomer conversion, based on bead hardness and the presence of residual monomer.

POLYMER CHARACTERIZATION

Size distribution

A particle size analyzer (Coulter LS 230; Fullerton, CA) employing a laser diffraction method was used to measure PSD. A suspension containing the polymer beads was generated in the fluid module, and a trace of surfactant was added to assist wetting of the polymer beads. Data from this were used to generate curves showing the proportion of particles falling in a particular size range. From these, the mean, median, standard deviation, and polydispersities were computed.

Density analysis

A 200 g solution of magnesium sulfate was prepared by adding 125.2 g of distilled water to 74.8 g of magnesium sulfate heptahydrate, with the density of the resulting solution being 1.20 g/cm³. A series of sample tubes was then created with liquid densities spaced from 1.19 to 1.15 g/cm³, by diluting the original solution with distilled water. Equal quantities of polymer beads were then added to each of these solutions and the resulting mixtures photographed.

Light microscopy

Beads were set in a resin based on 2-hydroxyethyl methacrylate, and the surfaces were polished using a fine diamond abrasive to access the internal bead structure. The resin blocks were then viewed with an Olympus (Center Valley, PA) Vanox microscope with camera attachment.

Bead microstructure

The microstructure of the polymer beads was investigated using a scanning electron microscope (FEI Quanta 200; Hillsboro, OR). Polymer beads were split open using a scalpel and loaded onto a stage. The samples were then coated with gold. Images of the exposed surface were recorded digitally.

Thermal properties

A differential scanning calorimeter (TA Instruments DSC 2010; New Castle, DE) was used to determine the glass transition temperatures of the polymer

beads. The temperature was ramped up to 160°C at 10°C/min, allowing the glass transition temperature to be determined. Samples weighing ~ 7.5 mg in open A1 pans were heated in a nitrogen atmosphere.

A thermogravimetric analyzer (TA Instruments TGA 2950) was used to estimate the amount of residual monomer and water present in the polymer beads, as this would ultimately indicate the extent of polymerization. A heat-and-hold method was used, where the temperature was ramped at 20°C/min up to 120°C (slightly above the boiling point of the monomer) and then maintained. The weight loss is the sum of residual monomer and water. The weight losses recorded therefore give an over-estimate of any residual monomer; the boiling points of the MMA monomer and water are very close (98 and 100°C). To approximate this over-estimate, a control sample was prepared where particles were placed in a vacuum oven at 60°C to remove volatile components. The sample was then placed in a water bath at 80°C for 3 h (matching the reaction conditions), and then the samples were allowed to dry before thermogravimetric analysis.

RESULTS

In total, 38 trials were conducted, with eight trials in the larger Büchi reactor and 30 in the 1-L reactor; ~ 3.5 kg of powder product was produced. The effects of stabilizer concentration, agitation velocity, crosslinker concentration, and reaction scale-up were investigated. The product batches manufactured had mean sizes ranging from 150 to 600 µm. Typical polydispersities ranged from 1.5 to 3.

Reactor fouling occurred when the reaction mixture was stirred at less than 250 rpm. At higher stirrer speeds, dispersions were effectively formed. Geometrical factors such as the size and shape of the reactor and of the agitator tip affected the value of

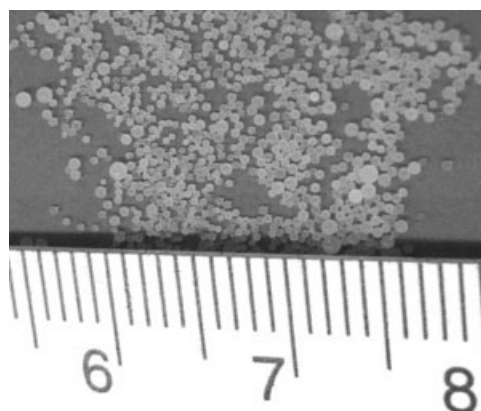


Figure 5 Polymer product formed using suspension polymerization, speed 300 rpm, stabilizer concentration 0.065 g/L.

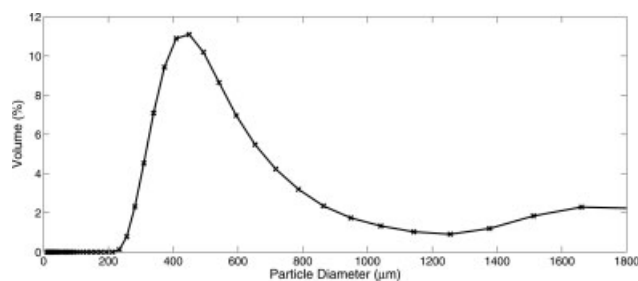


Figure 6 Size distribution centered near 500 μm from Series A (speed 280 rpm, stabilizer concentration 0.063 g/L).

this threshold. For example, a twin-blade stirrer led to catastrophic fouling.

Particles were initially rather polydisperse ($\sigma > 100 \mu\text{m}$), as indicated in Figures 5 and 6. Increased stabilizer concentration reduced polydispersity, but also reduced the mean particle diameter. Obtaining large particles of low dispersity required both a low stabilizer concentration and a low stirring rate.

The data provided in Table I are typical. The reaction conditions and the stirring rate used for the three different series of reactions are given, together with the median of the particle size distribution. The median particle sizes presented in Table I show a distinct trend for Series A, of particle size decreasing with increased stabilizer concentration. Crosslinker had little effect on the median particle size (B of Table I). Series C of Table I relates to the 2-L Büchi reactor. To achieve median particle sizes similar to those observed for the 1-L reactor when similar stabilizer concentrations were used, the stirring rate had to be increased.

The variables shown in Table I led to a protocol for selecting stirrer angular speed and stabilizer concentration suitable for a particular particle size. A recipe was identified for a PSD centered at the required particle diameter of 500 μm , as shown in Figure 6 (Sample 7, Series A in Table I). Greater concentrations of stabilizer led to a decrease in the mean particle diameter, but also led to a decrease in the breadth of the PSD.

The two PSDs shown in Figure 7 illustrate that a target PSD can be replicated using different recipes,

as Sample 27 had EGDMA crosslinker present and this crosslinker had essentially no effect on the PSD. A particle size distribution relating to the experiments conducted in the large Büchi reactor is shown in Figure 8.

Density

The density of the polymer beads was measured based on the density-gradient techniques commonly used in industries (ASTM D 1505-03).¹⁴ Polymer beads were added to test tubes containing solutions of varying densities, from 1.15 to 1.19 g/cm^3 ; see Figure 9. PMMA particles crosslinked with EGDMA were found to be denser (1.17–1.18 g/cm^3) than non-crosslinked PMMA particles (1.16–1.17 g/cm^3). Note that the expected or target density was that of bulk PMMA: 1.19 g/cm^3 .

Light microscopy

Images of single polymer beads embedded in resin reveal numerous internal pores (Fig. 10), which lead to light scattering caused by RI mismatch. Ultimately this would cause unwanted laser reflection in our blood-analog fluid-dynamic studies. A possible cause is polymerization hotspots, which can lead to volatilization of monomer and hence the formation of bubbles of gas. The polymerization temperature (80°C) was relatively close to the boiling point of the monomer (98°C), and it may be that localized gas formation occurred.

Electron microscopy

A number of different beads were investigated using SEM. Spherical voids (pores) and voids with nanobead inclusions were found. To emphasize the different scales of bead, void, and inclusion, from now on we refer to the voids as microcavities. Predominantly empty microcavities surrounded by large amounts of homogenous polymer are shown in Figure 11. Volatilized monomer is likely to have been present originally in these cavities, although air and water are other plausible contents. These contents would have been lost during sample processing for

TABLE I
Reaction Conditions and Median Particle Diameters of a Selection of Product

	Series A				Series B			Series C		
Sample number	7	10	20	023	25	26	27	035	036	038
Stabilizer concentration (g/L)	0.03	0.05	0.06	0.07	0.06	0.06	0.06	0.064	0.060	0.048
Speed (rpm)	280	288	300	300	300	300	300	300	500	500
Cross-linker amount (mL)	—	—	—	—	1	2	3	—	—	—
Median particle size (μm)	510	395	220	180	220	220	200	150	210	>1,500

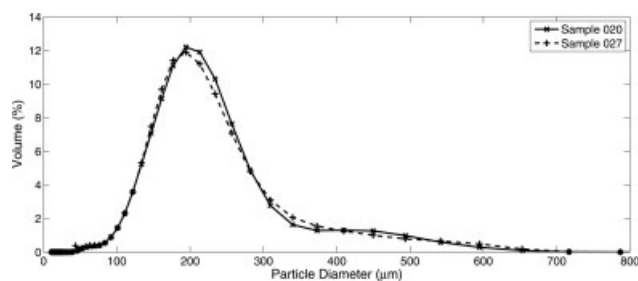


Figure 7 Samples from Series A and B (speed 300 rpm, stabilizer concentration 0.09 g/L). Sample 027 had 3 mL of crosslinker added.

microscopy. Microcavities with nanobead clusters were much less common than empty ones. Figures 11 and 12 each show one such microcavity with nanobead inclusions, and an enlargement of one is shown in Figure 13. These nanobeads may have originated in minute foreign particles, together with absorbed or entrapped monomer which has subsequently polymerized. For example, traces of stabilizer may act as nucleation sites for the formation of nanobeads.

Thermal properties

The empty pores found in these beads would originally have contained gases associated with the suspension medium (water) or residual monomer (MMA). We refer to both of these as volatiles and, as they have similar boiling points, it is necessary to determine by thermal analysis which one predominates.

Atactic PMMA normally has a glass transition temperature (T_g) in the range¹⁵ 105–107°C. The glass transition temperature of a sample of polymer product was also found to be 107°C, as shown in Figure 14. Residual monomer would allow chains to mobilize at a lower temperature (plasticize) and reduce the glass transition of the polymer. The measured

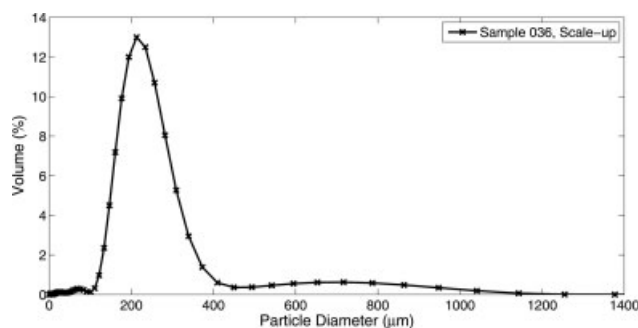


Figure 8 Sample from Series C (speed 300 rpm, stabilizer concentration 0.09 g/L).

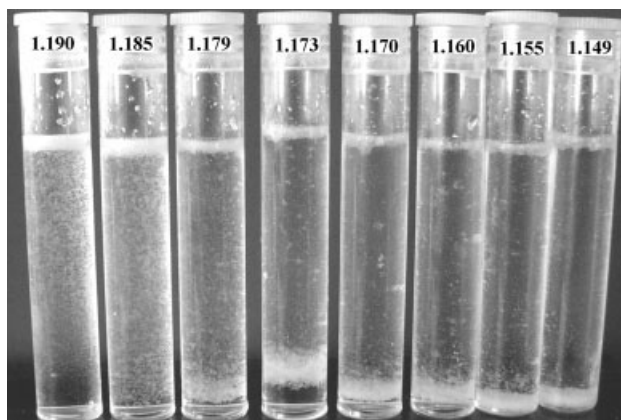


Figure 9 Crosslinked PMMA beads in solutions of varying density. Density (g/cm^3) is indicated at the top.

value for T_g is close to that of pure PMMA, indicating that there was little or no residual monomer in the sample, which would significantly reduce T_g . Further testing of the polymer samples was conducted using thermogravimetric analysis. The text-book boiling point of the monomer is 98°C; therefore the beads were heated to 120°C to remove both water and monomer, and the mass loss of the sample was recorded. To determine the water content, a small sample was removed and subsequently immersed in water at 80°C for 3 h to simulate the suspension history. The thermogravimetric analysis of this sample is labeled “water control” in Figure 15. Comparison of the two traces leads to the water content being estimated at 2.5% and the residual monomer content to be less than 0.5%. A similar weight loss was observed for samples with crosslinker added (Series B); assuming that the water content is similar, the residual monomer/crosslinker content was also $\sim 0.5\%$. In summary, water is

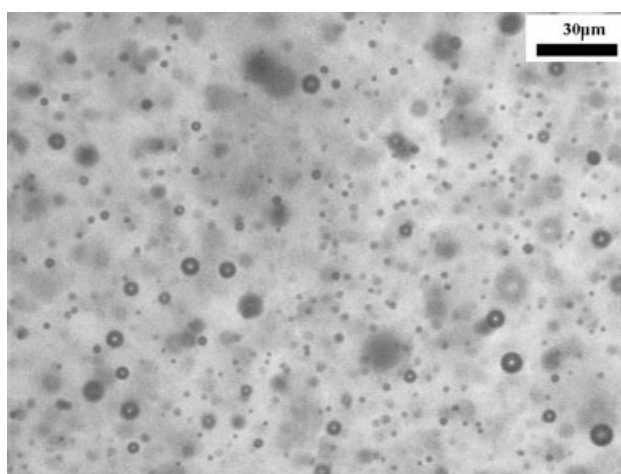


Figure 10 Part of a single bead set in resin, imaged by light microscopy.

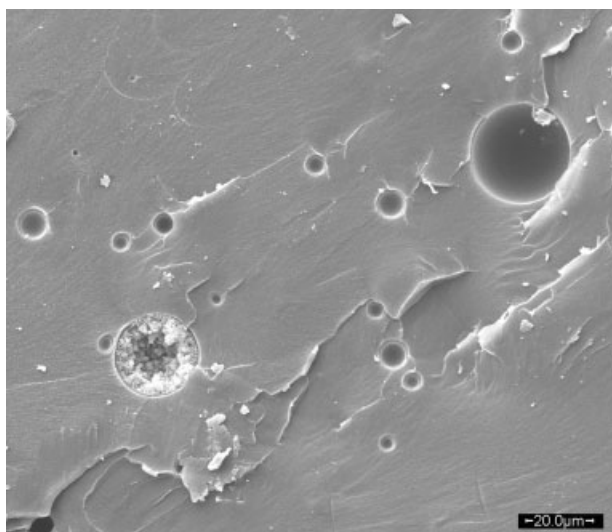


Figure 11 SEM image of voids with and without nano-bead contents.

believed to have been the predominant volatile in the beads, and is inferred to have, as water vapor, caused the microcavities to form.

DISCUSSION

For the particles to be ideal for our fluid simulation experiments, they needed to meet the specifications for size, density, and shape. Reaction conditions were identified to generate particles in a specific size range. Addition of crosslinker allowed the bead-specific gravity to be increased toward the target value, while having little effect on the size and shape of the beads. The presence of microcavities in the

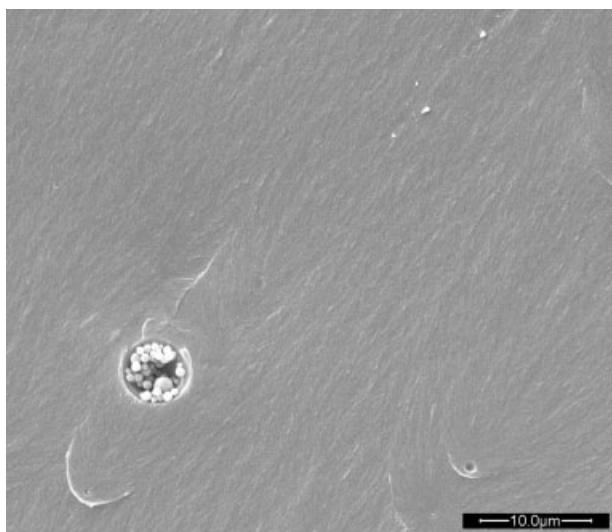


Figure 12 SEM image of a relatively large area of polymer with only a single significant inclusion.

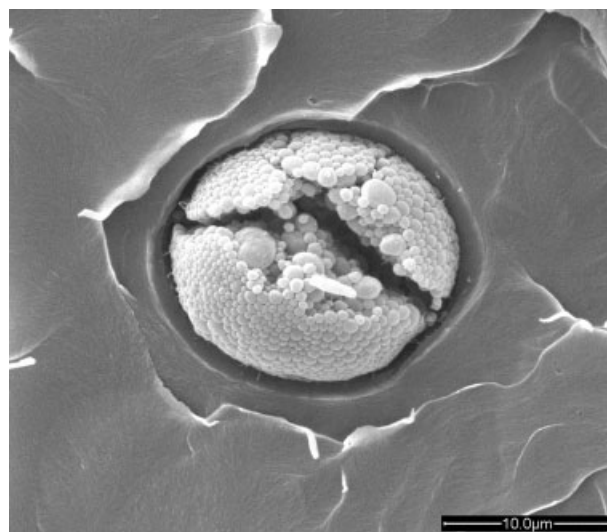


Figure 13 SEM image of a further magnified image of one of the voids and its nanobeads.

beads was of concern, but further work is currently being pursued to reduce the prevalence of these inclusions. Alternatives such as low-temperature chemical and ultraviolet initiators are being examined, and it is likely that these will reduce the number of cavities.

Detailed comparison of PSD data for product from the two reactor configurations showed subtle differences. The smaller 1-L reactor led to PSDs with a more pronounced “tail” of extra-large particles, as was shown in Figures 5 and 6. The product manufactured in the larger reactor (Fig. 8) included relatively fewer over-size particles, which may be attributed to slight differences in the reactor geometries, with large baffles being used in the small reactor and a small baffle in the large reactor. Extra-large particles may be the result of agglomeration of particles in the “sticky stage”. This occurs at the baffles, as confirmed by fouling in this section of the reactor. Sandler¹⁶ noted that acrylic systems are particularly prone to agglomeration at the “sticky stage”.

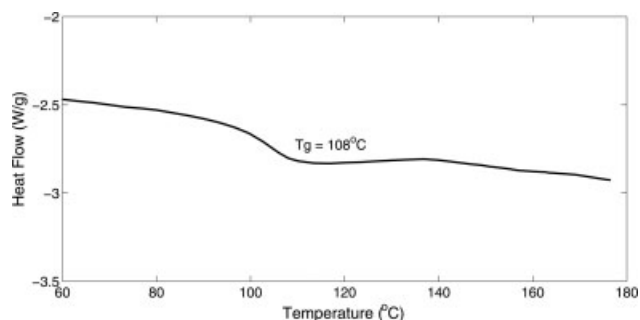


Figure 14 Differential scanning calorimetry trace indicating the glass transition temperature.

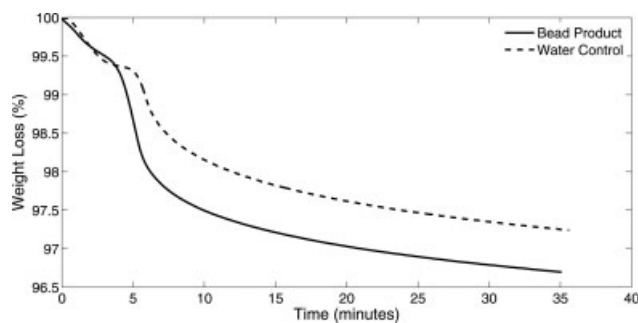


Figure 15 Thermogravimetric analysis trace indicating the total residuals and residual water in a sample.

The long extended tail of the PSD is likely to be the result of poor distribution of the stabilizer in the dispersed phase (oil-phase), leading to a reduction in the efficiency of the stabilizer. This is a problem in stabilizer-starved systems where there is insufficient stabilizer to maintain adequately the interface between the continuous and the dispersed phases, resulting in the formation of larger particles. A remedy may be the addition of stabilizer to the monomer before charging the reactor, increasing the interaction of the stabilizer with the dispersed phase. If an excess of stabilizer is used, the problem is removed, as there is enough present for stabilizing the reaction and the order of addition does not become a problem. However, this reduces the mean particle size which is undesirable.

On the other hand, predispersing the stabilizer in the monomer phase before charging the reactor may also be undesirable. The stabilizer may become entrapped in the droplet causing increased void formation and light scattering in the final product. The stabilizer acts at the surface of the droplet and should prevent droplet coalescence while soft. Therefore, the ideal time of addition is when the droplet dispersion has initially formed in the continuous phase.

The challenges that were associated with scale-up were made apparent with the differences in the shape and means of the particle size distributions. Hamielec and Tobita¹⁰ noted the difficulty of scale-up from laboratory scale to industrial scale. Although the scale change here is modest, we found subtle differences between the two systems which needed attention. As it was very difficult to recreate conditions similar to those in the smaller reactor, the effects of different geometries became apparent. With respect to the baffles, the smaller baffle in the larger reactor led to a decrease in late-stage coalescence in the “sticky” period of the reaction. This was advantageous, as a reduction in the PSD was observed.

Changes in the baffle arrangement between the two reactors will lead to a change in the flow regimes, which was observed. The small baffle and narrow Büchi reactor configuration led to the forma-

tion of a vortex and a reduction in the “up and down” mixing associated with large well-placed baffles. The reduced mixing caused by this will ultimately lead to a poor dispersion and particle sizes and shapes that are dissimilar to those observed in the smaller reactor. As an extreme case, when swirling occurs, streamers can form. This problem is well-known industrially.

The density of the polymer beads was found to be less than the expected literature value of 1.19 g/cm^3 for pure PMMA. The lowered density of the particles was of concern as the final application required the density to be predictably that of pure PMMA. Further investigation of the microstructure of the beads has clarified the reasons for this low density.

Microscopic voids are clearly a contributor to the reduced bulk-density of the beads. Microcavities will cause laser reflection, which is to be avoided in certain fluid mechanics studies. Klodt and Gougeon¹⁷ describe with respect to expanded polystyrene where cell formation is desired, that water, stabilizer, and other reaction components can act as nucleation agents. To determine the contents of the nanobeads, energy dispersive X-ray analysis was considered. However, all reactants used in the system comprise carbon, oxygen, and hydrogen, so cannot be easily separated due to overlap of the K_{α} and K_{β} X-ray signals at low energy. We saw no evidence of heavier elements.

Removing voids completely from the beads is difficult. Crosslinker helps to reduce the incidence of voids (as shown by the higher density observed for crosslinked particles in comparison to beads that were not crosslinked). Higher-temperature drying may lead to fewer but larger voids, as the vapor pressure of the trapped residuals can lead to the rupture of internal walls between voids. This effect can occur even at relatively low temperatures (35°C), but at the low drying temperatures prevailing in our experiments ($<20^{\circ}\text{C}$) the likelihood of this scenario is reduced.

The size of the nanobeads in the microinclusions is consistent with latex particles. With the high levels of stabilizer present in the system behaving like a surfactant, the formation of micelles is possible and any initiator present will allow the formation of the observed nanobeads. Their formation is then due to a microemulsion polymerization reaction in the larger bead.

Residual monomer can be a problem for suspension polymerization, as too much residual monomer can lead to plasticization of the polymer. This is especially the case when the polymer is very soluble in its monomer, as in the present case. It has also been demonstrated¹⁸ that in vinyl ester systems the localized glass transition temperature may decrease by 25°C . Despite this, the measured T_g was at the

higher end of the quoted literature range, indicating that little plasticisation occurred. Because of the low concentration of residual monomer present in the final product, we conclude that the reactions proceeded to a high degree of completion. Residual volatile content of the polymer beads was routinely found to be below 3%, with residual water predominating and exceeding 75% of the total.

CONCLUSIONS

- The mode of the particle size distribution could be tailored to allow spherical beads of the desired size to be manufactured via suspension polymerization.
- Reducing the breadth of the particle size distribution is a challenge when dealing with suspension polymerization.
- The occurrence of microcavities in the polymer beads was observed. Their presence limits the use of the beads when optical clarity or exact density is essential.
- Addition of crosslinking agent to the reaction had little effect on the particle size distribution but increased bead density toward the target value.
- The thermal properties of the polymer beads indicated that there was little residual monomer present, consistent with a high degree of conversion.
- A limited degree of scale-up was achieved, and provided particles that were reasonably close to specification for the intended purpose.

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