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Size adjustment of spherical temperature-sensitive hydrogel beads by liquid–liquid dispersion using a Kenics static mixer

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ABSTRACT

Temperature-sensitive hydrogel beads were prepared by Kenics static mixer technology. The temperature-sensitive monomer N,N-diethylacrylamide and photo-crosslinkable pre-polymer ENT were used as model hydrogel materials. Drop dispersion of high viscosity polymer material in low viscosity hexadecane was made using the static mixer. Drops of a solution of the mixed materials were rapidly photo-crosslinked by UV irradiation after mixing in the static mixer, and spherical hydrogel beads with narrow, normal size distribution were thus prepared. The Kenics static mixer is a useful device for the preparation of spherical beads of temperature-sensitive hydrogels. The Sauter Mean Diameter of the hydrogel beads swollen in deionized water at 293 K was measured. The experimentally determined dimensionless swollen hydrogel bead diameter was well correlated with the Weber number, degree of swelling and viscosity ratio. The effects of gelation and ENT addition on the bead size were evaluated from the degree of swelling. The correlation equation can be used for size adjustment of temperature-sensitive spherical hydrogel beads.

1. Introduction

Temperature-sensitive hydrogels such as polyN-isopropylacrylamide (NIPA) and polyN,N-diethylacrylamide (DEAA) have been widely used for many applications because of their large, reversible changes in volume and characteristics in response to small changes of temperature. The applications include recycle adsorbents [1–5], dehydrating agents [6], flow control actuators [7] and biomedical materials [8,9]. Adsorption of metal ions by hydrogels has attracted increasing attention over the past several years [3,4,10].

In applications of hydrogels, the important gel characteristic is swelling and shrinking, and the rate of volume change, in particular, is much affected by the dimensions and shape of a hydrogel [11,12]. To control the dimensions of hydrogels, several strategies for hydrogel preparation have been used, including the falling-drop method [1], emulsion polymerization [13,14], synthesis of porous gel [15–17], and microfluidic methods [18,19]. Hydrogels prepared by these methods have limited size, typically several millimeters or less than several micrometers in length. For example, although the microfluidic methods [18,19] are the effective means for synthesis of nearly monodispersed microgels, usable hydrogel size is limited to the range of less than 100 μm. In general, adsorbents such as activated carbon and ion-exchange resin are spherical with mean diameter in the range of tens to hundreds of micrometers. A preparation method is needed to easily control a wide range of hydrogel bead sizes without changing the properties and form of the beads.

As a strategy to control hydrogel bead size and size distribution, we propose photo-crosslinked hydrogel bead formation via static mixers. Static mixers are motionless mixing devices composed of mixing elements in a straight, empty tube. Two immiscible fluids are introduced into the static mixer, and mixed through flow by three kinds of mixing mechanisms, namely flow-reversal, division of flow and radial mixing. As a result, one fluid is dispersed in the other fluid, and narrow drop size distribution is obtained. In addition, static mixers generally have continuous operation capability, small size, flexibility in installation in processes and low power requirements, compared with batch mixers [20]. When applied to pre-gel solution/insoluble continuous liquid phase systems, these mixing mechanisms will achieve narrow size dispersion of the hydrogel-forming solution in the continuous liquid phase. If the drops of dispersed material are rapidly converted to hydrogel by heating or irradiation, hydrogel beads can be prepared with narrow size distribution, so that an effective hydrogel bead formation process can be realized. Although the hydrogel beads size has a narrow dispersion, the hydrogel formation using static mixer can cover a wider range of hydrogel bead size. Due to the tube-type geometry of the reactor, it is easy to design a continuous process

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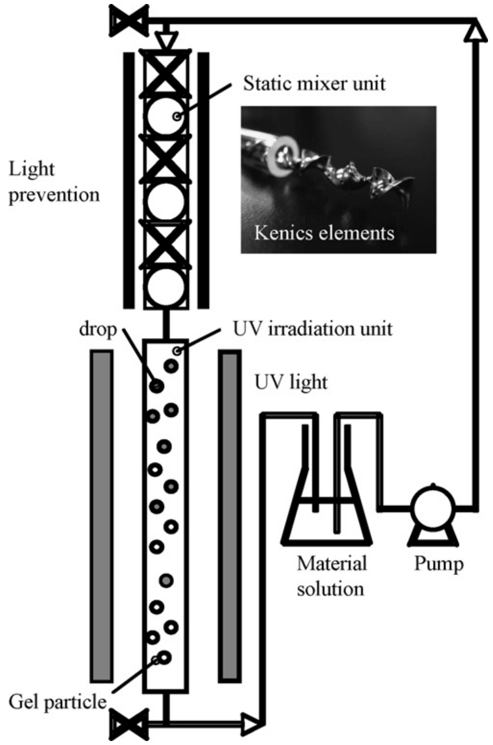

Fig. 1. Schematic drawing of hydrogel bead formation apparatus.

for hydrogel bead formation. In addition, it has been shown that the static mixer gives better micromixing efficiency than a continuous flow stirred tank reactor at the same power consumption rate [21].

Despite these advantages, little study of the hydrogel formation process has been conducted with static mixers. Hass [22] has demonstrated gelation of trichloroethylene drops to accurately measure drop size in the organic liquid 2-ethyl-1-hexanol, in a Kenics static mixer. A correlation equation was derived as a function of Weber number, Reynolds number and the ratio of fluid viscosities. Belyaeva et al. [23,24] have proposed material dispersion and an in situ reaction method with an SMX static mixer for thermal gelation. They discussed the mean size of thermal gel beads of carrageenan. The shape and size distribution of gel beads, however, were not clear, though they are an important factor in the use of hydrogels for chemical industries.

The aim of the present study was to be able to easily adjust the shape and size of hydrogel beads as desired. The formation processes of photo-crosslinked hydrogel beads in a static mixer were investigated experimentally with a laboratory-scale experimental apparatus, focusing on the hydrogel bead size and distribution. A Kenics-type static mixer, which is the most widely used type [20], was utilized in this study. The mixing elements of the mixer are shown in Fig. 1. The cross-sectional area of the mixer is divided into two approximately semi-circular passages by means of a number of helical thin partitions. Each of the mixing elements is twisted through 180° and is right- or left-hand rotation. Elements of alternate rotation are joined sequentially so that perpendicularity is maintained between the rearward and forward edges of adjacent elements. To increase the mechanical strength of hydrogel beads, photo-crosslinkable pre-polymer (ENT3400 or ENT1000) was added to the gel material [1,2]. Radical polymerization with UV irradiation was carried out to retain the size distribution of the hydrogel material drops in the fluid.

2. Experimental

2.1. Materials

The temperature-sensitive monomer N,N-diethylacrylamide (DEAA, kindly supplied by Kojin Co., Ltd., Japan) and additives (photo-crosslinkable pre-polymer ENT3400 and ENT1000, 40 wt% aqueous solution, kindly provided by Kansai Paint Co., Ltd., Japan) to enhance the strength of DEAA hydrogel, were used as hydrogel materials. The ENTs are polyethylene glycol-based pre-polymer and are hydrophilic [2]. Difference between ENT3400 and ENT1000 is the chain length of the polyethylene glycol (degree of polymerization $n = 70$ for ENT3400, $n = 23$ for ENT1000). The photoinitiator was 2-hydroxy-2-methyl-propiophenone (Aldrich Chemical Co., Ltd., UK). Hexadecane from Wako Chemical Co., Ltd., Japan, was used as the continuous phase: DEAA and ENTs were found in preliminary experiments to have low solubility in hexadecane. All reagents were used without further purification.

2.2. Preparation of hydrogel material solution

Pre-gel solution (dispersed phase) was prepared by mixing DEAA and ENT at room temperature. The molar ratio of ENT to DEAA was 0.005 for all preparations of DEAA–ENT gel beads. The DEAA–ENT solution was stirred at 400 rpm for 20 min. After adding 0.3 mmol of the photoinitiator, the solution was further stirred for 5 min in the dark, then hexadecane (the continuous phase) was gently added to the pre-gel solution. The typical volume fraction of pre-gel solution phase in hexadecane was about 0.09 because it has been shown that the mean drop size is hardly affected by volume fraction of the dispersed phase <0.3 [25].

2.3. Formation of liquid–liquid dispersion and hydrogel beads

Hydrogel beads were prepared from a liquid–liquid dispersion. A drop dispersion of high viscosity pre-gel solution in low viscosity hexadecane was briefly prepared by passage through the Kenics static mixer. Fig. 1 shows a schematic drawing of the gelation apparatus. The static mixer unit was installed vertically, and drops of pre-gel solution were formed by agitation in the mixer unit in the absence of light. The mixing elements of the mixer were made from SUS316 stainless steel (Noritake Co., Ltd., Japan), and the housing tube was a Pyrex glass tube with inner diameter, D_m, 5.0 mm and length 100 mm. Twelve mixing elements were inserted in the mixer unit. Pre-gel solution was fed with hexadecane to the static mixer unit by a peristaltic pump (Masterflex, Cole-Parmer Instrument Company, USA). The total volume flow rate, determined by collecting the effluent from the outlet side tube, was varied from 0.15 to 0.46 $\mathrm{dm^3\,min^{-1}}$. To form homogeneous hydrogel drop dispersion, the fluid that was passed through the static mixer was recycled in the apparatus. The dispersed drops were immediately irradiated with six UV lamps (wavelength 365 nm, power 1.2–3.0 $\mathrm{mW\,cm^{-2}}$) at the UV irradiation unit that was made of a Pyrex glass tube with inner diameter 6.0 mm and length 300 mm. After passing through the UV irradiation unit, the fluid was returned to the material solution flask to gelate sufficiently pre-gel drops. The mixing–irradiation cycle was repeated for 2.5–10 min, which was defined as the operation time. The resultant hydrogel beads were recovered by decantation of the continuous phase after the hydrogel preparation operation was stopped.

2.4. Hydrogel bead size distribution analysis

Photographs of the DEAA–ENT gel beads swollen in deionized water at 293 K were taken, and the digitalized images analyzed with a PC employing the image analysis program Image J-1.39u, developed by the U.S. National Institutes of Health. The hydrogel bead sizes and their distribution were analyzed with a sample containing at least 500 randomly selected beads. It was confirmed in preliminary tests that for a sample of at least 400 beads, the number of beads in the sample had an insignificant effect on the mean size and their distribution. Sauter Mean Diameter, *SMD*, defined by Eq. (1), was used to characterize the size of the hydrogel beads:

$$SMD = \frac{\sum N_i D_i^3}{\sum N_i D_i^2} \qquad (1)$$

where N_i is the number of hydrogel beads in the range of i and D_i is the middle diameter of the size range i. The standard error of all data was within 3.4% of *SMD*.

2.5. Swelling and shrinking analysis

The volume of packed hydrogel beads was measured in deionized water in a thermostatted graduated glass cylinder. First, the glass cylinder packed with hydrogel beads was kept at 277 K and the volume of the beads was measured at equilibrium swelling. The equilibrium volume of the beads was then recorded with gradually increasing temperature up to 343 K. The apparent degree of swelling, S_{app}, based on the bulk volume of the hydrogel beads in water, and normalized by the volume of absorbable water, was calculated from the equation:

$$S_{app} = \frac{V_T - V_{343}}{V_{277} - V_{343}} \qquad (2)$$

where V_T, V_{277} and V_{343} are the equilibrium volume of hydrogel beads at a certain temperature, 277 K and 343 K, respectively.

The degree of swelling was determined by measuring the length of each side and calculating the volume of rectangular sheets of DEAA–ENT hydrogel. DEAA–ENT solution was poured into a hydrogel sheet preparation cell with dimensions 20.3 mm × 39.3 mm × 1.25 mm. The initial volume of solution was defined as the cell volume. After gelation, the length of each side of

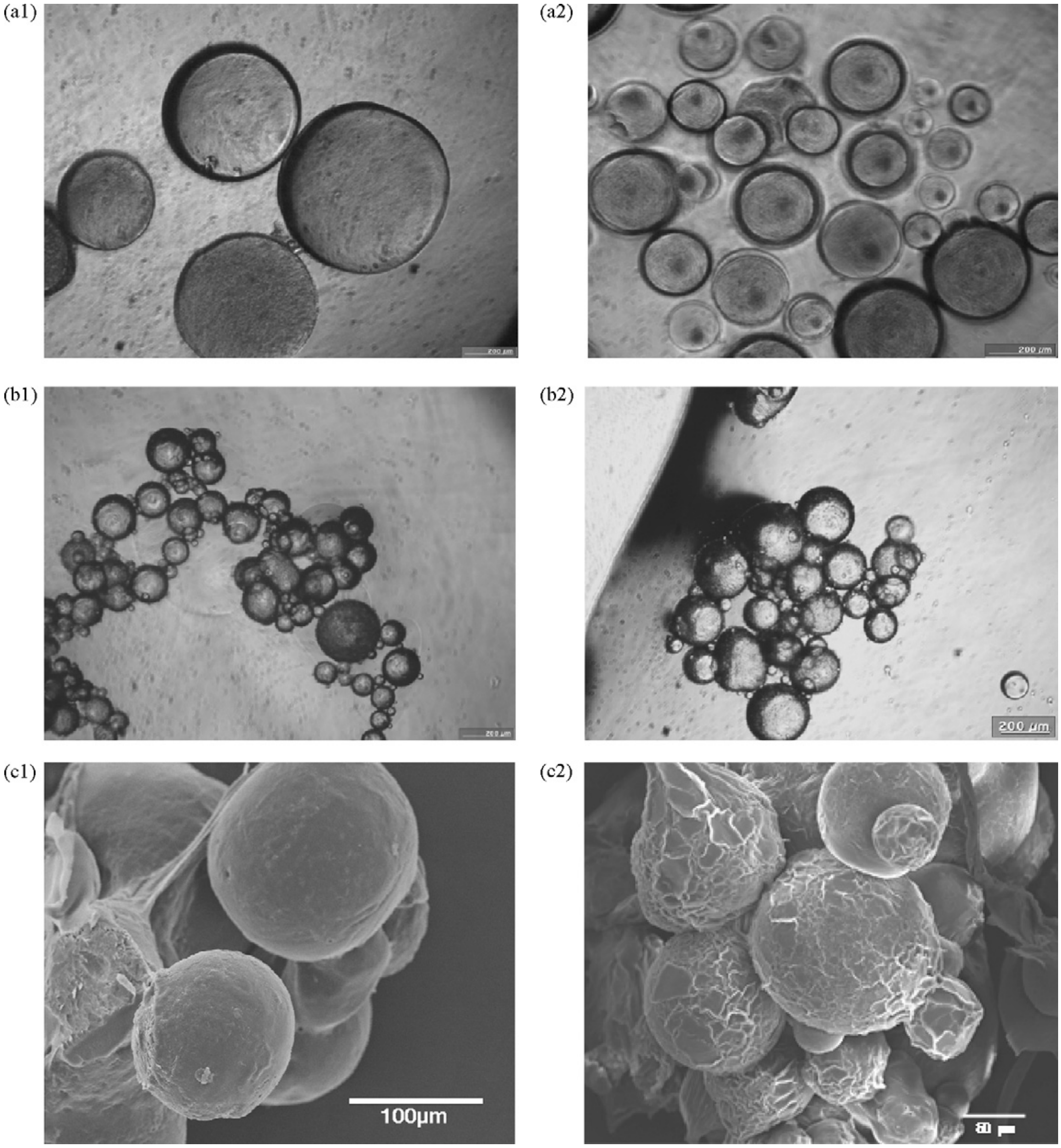

Fig. 2. Microscopic observation results of prepared hydrogel beads. (a) DEAA–ENT3400 system and (b) DEAA–ENT1000 system. Preparation conditions: total flow rate (a-1) 0.15 $dm^3\,min^{-1}$, (a-2, b) 0.34 $dm^3\,min^{-1}$; irradiation strength (b-1) 2.2 $mW\,cm^{-2}$, (a, b-2) 2.6 $mW\,cm^{-2}$; operation time 2.5 min. (c-1) and (c-2) SEM results for (a-1) and (a-2), respectively.

the rectangular sheet was measured. The equilibrium length of the hydrogel sheet was also measured in deionized water. The ratio of the average lengths was taken as the degree of swelling.

3. Results and discussion

3.1. Typical hydrogel bead characteristics and size distribution

The hydrogel material (DEAA–ENT3400 or DEAA–ENT1000) solution dispersed easily in hexadecane on passing through the static mixer unit. In the subsequent UV irradiation unit, the DEAA–ENT drops that had been formed were converted to hydrogel beads. The drop sizes at the mixer exit were representative of mixer performance [26]. If the DEAA–ENT solution drops dispersed by the static mixer retained their form and size during the gelation reaction, the prepared hydrogel drops were spherical and their volume fraction size distribution was narrow with a normal distribution, as a result of the performance of the Kenics static mixer [27,28].

Fig. 2 shows the typical appearance of hydrogel beads after swelling in deionized water at 293 K. SEM images of the prepared hydrogels dried (the size is smaller than the swollen hydrogels because of the shrinking) were also shown in Fig. 2. Many of the swollen hydrogel beads prepared at fixed operation time were spherical, discrete single beads with diameter 0.2–0.5 mm that was independent of other experimental conditions. This result indicates that the dispersed DEAA–ENT solution drops in hexadecane were photo-crosslinked with retention of the spherical drop form. A small number of other larger sized beads formed by agglomeration of single beads were observed. The formation of larger beads would have resulted from recycling of hydrogel beads in the pre-gel solution, and drop collision and coalescence before photo-crosslinking of drops occurred in the UV irradiation unit. These larger beads affected the bead size distribution. Fig. 3 shows the thermosensitivity of the prepared hydrogel beads at different temperatures. The apparent degree of swelling decreased with increase in temperature, and the volume change of the hydrogel was complete at about the lower critical solution temperature of DEAA (305 K) [29]. Even at increased temperature, the deswelled hydrogel beads retained a spherical form. The hydrogels possessed to a large extent the thermosensitive properties of DEAA. The thermosensitivity of all of the hydrogels was very similar, which indicates that the composition of hydrogel beads prepared in various conditions was almost the same. For size adjustment of hydrogel beads, it was necessary to select the required temperature.

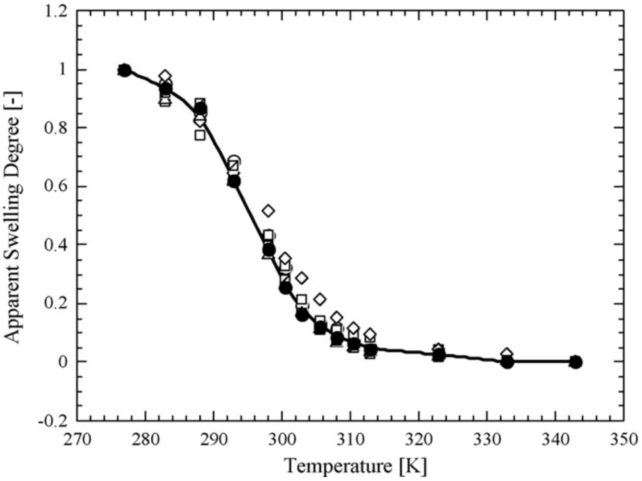

Fig. 3. Normalized equilibrium swelling ratio of DEAA–ENT3400 hydrogel in the temperature range 343–277 K.

Typical distributions of bead volume at 293 K are summarized in Fig. 4. The size distribution of the hydrogel beads prepared, including the secondary beads, showed a bimodal-like distribution with peak maxima at 0.40 mm for DEAA–ENT3400 (Fig. 4a) and 0.21 mm for DEAA–ENT1000 (Fig. 4c), due to the formation of secondary beads. When the number of secondary beads was omitted, the bead volume fraction distribution curves were approximately normal distributions (Fig. 4b and d). The maximum frequency diameters in the distributions were almost the same for single beads only and for all beads including secondary beads. Fig. 5 shows the effect of the operation time on the Sauter Mean Diameter of the swollen hydrogel beads in deionized water, SMD_w. Although SMD_w for the single beads was almost invariant with operation time, SMD_w for the total population of hydrogel beads slightly increased with increased operation time. These results imply that the secondary beads were produced from the single beads and pre-gel solution in the gelation process because of the cycling operation. Thus, the secondary beads can be ignored for consideration of the liquid–liquid dispersion process. The volume fraction size distribution curves of single hydrogel

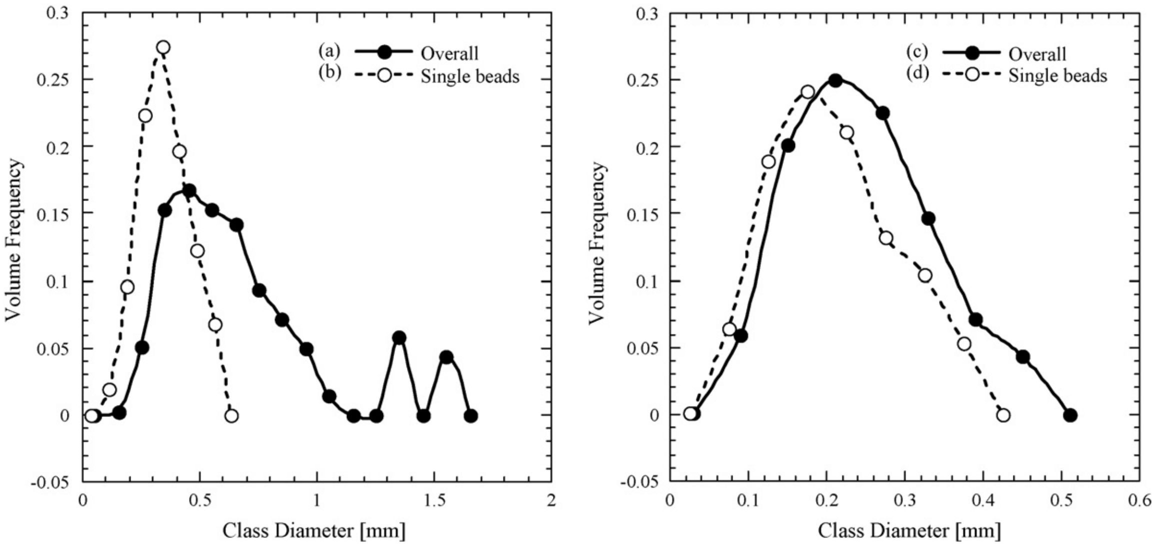

Fig. 4. Typical size distribution of prepared hydrogel beads with overall or single beads. (a) and (b) DEAA–ENT3400 system; (c) and (d) DEAA–ENT1000 system. Preparation conditions: irradiation strength, 2.6 mW cm^{-2}; total flow rate, 0.34 dm^3 min^{-1}; operation time, 2.5 min.

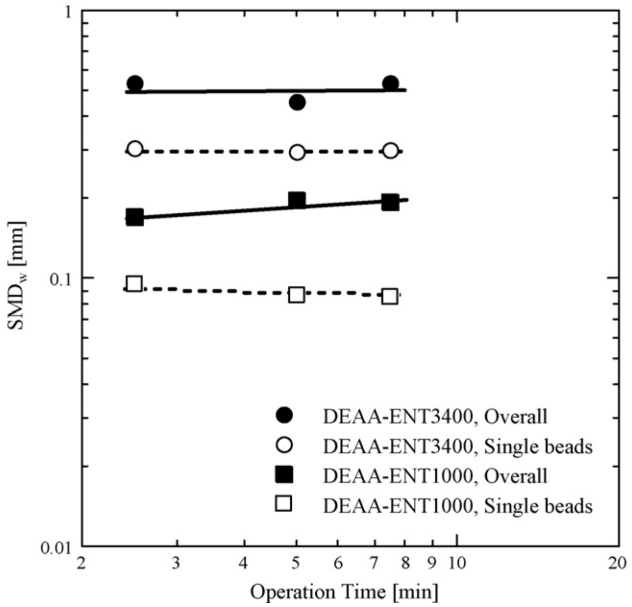

Fig. 5. Effect of operation time on hydrogel bead size. Preparation conditions: irradiation strength, 2.6 mW cm^{-2}; total flow rate, 0.34 dm^3 min^{-1}.

beads indicate that photo-crosslinking of DEAA and ENT occurred with retention of the drop size distribution. Hence the size and distribution of single beads is used in the subsequent discussion.

3.2. *Effects of operation conditions on single bead size distribution*

The operation parameters were the total volume flow rate and UV intensity in the hydrogel formation apparatus. The total volume flow rate was the operation parameter for the drop dispersion process, and the UV intensity was responsible for the gelation process. For calculation of mean bead size, the secondary hydrogel beads were not counted (for the reasons discussed above).

Fig. 6 shows the change in SMD_w at 293 K with total flow velocity, u, of the pre-gel solution–hexadecane system. SMD_w of the hydrogel beads was in the range 0.13–0.70 mm, and decreased with increase in the total volume flow velocity. The variation of SMD_w is due to the dependence of the static mixer performance on the flow velocity. The slopes for the experimental data were in the range −1.1 to −1.2, thus:

$$SMD_w \propto u^{-1.1} \text{ or } u^{-1.2} \tag{3}$$

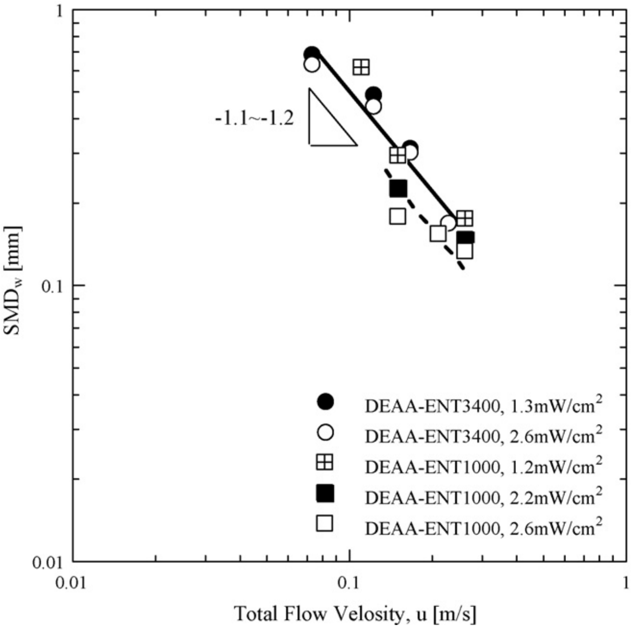

Fig. 6. Effect of total flow velocity in Kenics static mixer on SMD_w.

The UV intensity affected SMD_w slightly in the range of the UV intensities used in the experiments, as also shown in Fig. 6. SMD_w increased with decrease in the UV intensity at fixed volume flow velocity, in spite of the initial drop size being the same before gelation. The degree of swelling of the hydrogel beads in deionized water contributed to the drop size reduction. It is known that the degree of swelling of hydrogel beads can be expressed as a function of the degree of crosslinking and the thermodynamic interaction parameter of the solvent [30]. The degree of crosslinking is affected by the UV intensity and the reaction time (the operation time in this study). Consequently, the effects of the reaction conditions on the hydrogel bead size are typified by the degree of swelling.

3.3. *Relation of hydrogel bead size to pre-gel solution drop size*

In the liquid dispersion process, the most important physical property is the interfacial tension. The most popular equation for the mean size of dispersed drops for immiscible fluids expresses the mean size as a function of the Weber number.

For drop dispersions the relationship between the dimensionless drop mean diameter, SMD_l/D_m, and the Weber number, We, based on the inner diameter of the mixer is well represented by a simple form as the equation does not include the effects of viscosity and concentration:

$$\frac{SMD_l}{D_m} = \alpha \cdot We^{\beta} \tag{4}$$

$$We = \frac{D_m u^2 \rho_c}{\sigma} \tag{5}$$

where D_m is the inner diameter of the Kenics static mixer, SMD_l is the Sauter Mean Diameter of dispersed drop, ρ_c is the continuous fluid density, and σ is the interfacial tension between the immiscible fluids. For the Kenics static mixer, generally the dimensionless mean diameter is correlated with $\alpha = 0.49$ and $\beta = -0.6$ [26]. The α value is different for various mixing conditions and is empirical. The value of β for liquid–liquid dispersion, not only in a static mixer, is theoretically −0.6 according to Kolmogoroff [31] and Hinze [32], and many empirical correlations for drop size in liquid–liquid dispersions have adopted a β value about −0.6. If the pre-gel solution drops are converted to hydrogel beads with retention of their shape and size, the experimentally determined dimensionless mean diameter of hydrogel beads in water, SMD_w/D_m, is theoretically expressed as a function of the −0.6 power of We.

The experimentally determined SMD_w/D_m values are plotted as a function of We in Fig. 7. The surface tension of n-hexadecane was obtained from literature data [33] to estimate the interfacial tension of DEAA–hexadecane from the Young equation for simplicity, and the effect of addition of small amounts of ENTs on the interfacial tension was ignored. The surface tension of hexadecane against air measured by the Ring method was within 5% of literature data. The surface tension of DEAA solution against air was measured by this method. Under the experimental conditions, the slopes of the fitted lines were about −0.6, so that $SMD_w/D_m = \alpha\, We^{-0.6}$ (coefficient of determination $R^2 = 0.81$–0.94). The value of the exponent is in good agreement with that for the total flow velocity (−1.1 to −1.2) as shown in Fig. 6. The relationship indicates that the average hydrogel bead size can be predicted and reasonably well controlled by the hydrogel preparation conditions, namely the static mixer size and the total volume flow velocity of hydrogel material–hexadecane

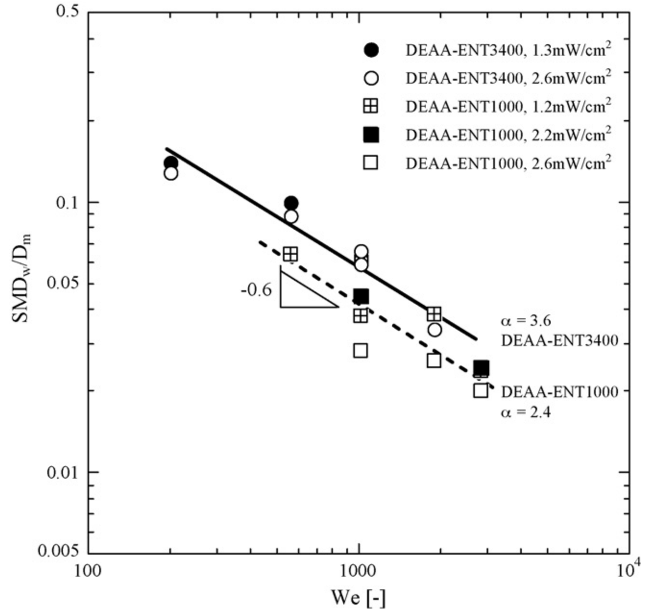

Fig. 7. Correlation of dimensionless mean diameter of hydrogel beads with Weber number.

solution, using a value for α the range 2.4–3.6 under our experimental conditions. The value of the coefficient α, however, is large, and the α value for the experimental data deviated from reported values [22,26]. In addition, the α value was different for the different additives (ENT3400 and ENT1000).

If an accurate correlation is required, three effects may need to be taken into account for correction of the α value: viscosity, Reynolds number and swelling effect. For Eq. (4), the slight dependency on viscosity and Reynolds number is negligible [27] because it was shown that the mean drop diameter was independent of dispersed phase volume fraction, ϕ, for $0.01 < \phi < 0.25$ [27]. Focusing on the swelling effect, the extremely large α value means that the hydrogel beads swelled in deionized water to a size larger than the material drop size. $SMD_w > SMD_l$ because the hydrogel beads consisted of DEAA which can strongly absorb water at temperatures below the low critical solution temperature. The experimental α value therefore must include the degree of swelling as an important factor.

3.4. *Correction of SMD by Reynolds number and degree of swelling*

Because the Reynolds number, Re, affects the mean drop size, Eq. (4) is essentially [27]:

$$\frac{SMD_l}{D_m} = \alpha_1 \cdot We^{\beta} Re^{\gamma} \tag{6}$$

In turbulent flow conditions, $\beta = -0.6$ and $\gamma = 0.1$. When the value of γ is negligible ($\gamma = 0$), this equation is equivalent to Eq. (3) [26], the correlation equation for a practicable application. In the case of drop size analysis with gel sphere formation with trichloroethylene as continuous phase and 2-ethyl-a-hexanol as dispersed phase [22], a correlation of the form of Eq. (7) was used with the wide range of Re, $Re = 184$–8090.

$$\frac{SMD_l}{D_m} = \alpha_2 \cdot We^{\beta} Re^{\gamma} \left(\frac{\mu_d}{\mu_c}\right)^{\delta} \tag{7}$$

$$Re = \frac{D_m u \rho_c}{\mu_c \varepsilon} \tag{8}$$

where ε is the void fraction of the mixer, $\alpha_2 = 1.2$, $\beta = -0.65$, $\gamma = -0.2$ and $\delta = 0.5$. Both Eqs. (6) and (7) are empirical correlations from the viewpoint of dimensional analysis. However, the experimental β value, -0.65, is empirical and inconsequential.

Eqs. (6) and (7) are based on the mean size of the pre-gel solution drops, SMD_l. These equations have to be corrected for the swollen hydrogel beads size, SMD_w. As discussed above, if the solution drops are converted to hydrogel beads then the beads swell in deionized water, for instance, Eq. (7) can be easily transformed based on SMD_w to the form

$$\frac{SMD_w}{D_m} = \alpha_3 \cdot \frac{SMD_w}{SMD_l} \cdot We^{\beta} Re^{\gamma} \left(\frac{\mu_d}{\mu_c}\right)^{\delta} \tag{9}$$

Here the ratio of SMD_w to SMD_l can be defined as the degree of swelling. Considering the processes of hydrogel bead formation (the conversion of solution to gel, the swollen hydrogel in the continuous phase (n-hexadecane), and the exchange of solvent from n-hexadecane to water), the degree of swelling, SMD_w/SMD_l, in Eq. (9) is further modified with the introduction of special mean diameters:

$$\frac{SMD_w}{SMD_l} = \frac{SMD_g}{SMD_l} \cdot \frac{SMD_h}{SMD_g} \cdot \frac{SMD_w}{SMD_h} \tag{10}$$

where SMD_g and SMD_h are the mean diameters of the hydrogel beads just after the gelation reaction and after swelling in n-hexadecane, respectively. It is then found that SMD_g/SMD_l is the degree of expansion of hydrogel to pre-gel solution, SMD_h/SMD_g is the degree of swelling of hydrogel in n-hexadecane, and SMD_w/SMD_h is the solvent effect on hydrogel bead size because it is the ratio of the degree of swelling in water to that in n-hexadecane. The value of the degree of swelling, SMD_w/SMD_l, must thus include the effects of volume change by the gelation reaction, swelling and solvent on the hydrogel bead size. The degree of swelling, therefore, can represent the effect of the processes of hydrogel bead formation on hydrogel bead size.

In this study we used a simplification based on Eq. (9) and determined the available α_3, β, γ and δ values for the experimental system. It is obvious that the β value is -0.6 as shown in Figs. 6 and 7. For the γ value, Eq. (3) implies that $\gamma = 0.1$ if $\beta = -0.6$ is possible. However, the experimental data were not strongly correlated with $Re^{0.1}$ ($Re = 184$–686, coefficient of determination $R^2 = 0.16$–0.31), suggesting that the γ value may be negligible in the range of the experimental conditions i.e. $\gamma = 0$. The value of δ is 0.5 according to the literature [22], because the continuous phase used in this study was organic liquid. The α_3 value was obtained experimentally. To simplify measurement of the degree of swelling, SMD_w/SMD_l, a rectangular hydrogel sheet was prepared with same materials. The sheet was swollen in deionized water at 293 K for 3 days [34] to equilibrium swelling. The ratio of the average length of each side of the DEAA–ENT hydrogel rectangular sheet in water to that in pre-gel solution was defined as the swelling degree, SMD_w/SMD_l. The degree of swelling at 293 K was 1.5–1.56 for the DEAA–ENT1000 system and 1.78 for the DEAA–ENT3400 system.

Fig. 8 shows the correction to SMD_w according to Eq. (9) with $\beta = -0.6$, $\gamma = 0$ and $\delta = 0.5$, and SMD_w/SMD_l for each material system. Introduction of the degree of swelling provided only one curve for hydrogel size correlation independent of additives and operation conditions (coefficient of determination $R^2 = 0.93$):

$$\frac{SMD_w}{D_m} = \alpha_3 \cdot \frac{SMD_w}{SMD_l} \cdot We^{-0.6} \left(\frac{\mu_d}{\mu_c}\right)^{0.5} \tag{11}$$

where $\alpha_3 = 2.6$ at 293 K, and the constant value of the α_3 was obtained. It was found that several effects in gelation process were sufficiently evaluated by the degree of swelling, SMD_w/SMD_l. Because the α_3 value is still large, the α_3 value may include other effect in dispersion process or gelation process. It is necessary for

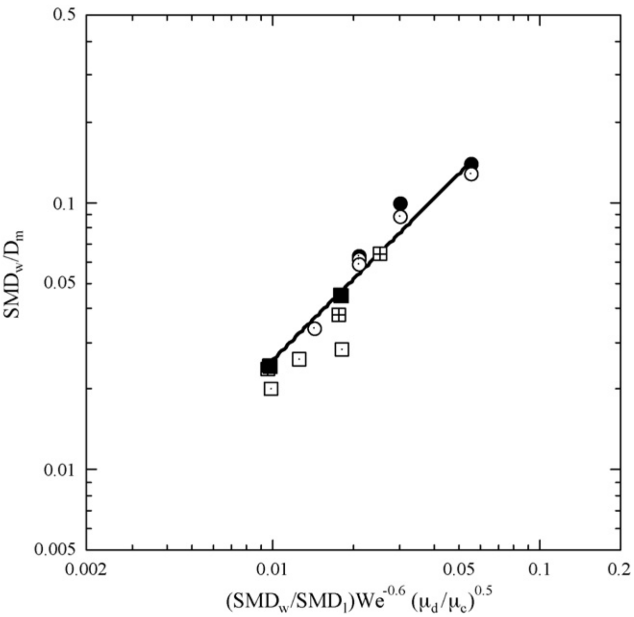

Fig. 8. Correction of dimensionless mean diameter of hydrogel beads by viscosity and degree of swelling.

the detailed discussion about the α_3 to carry out further investigation.

Finally, the temperature dependence of SMD_w is discussed. Because SMD_w depends on the swelling temperature of the hydrogel as shown in Fig. 3, the $\alpha_3(SMD_w/SMD_l)$ value will vary dramatically with the desired swelling temperature of the hydrogel. If the mean diameter of hydrogel at swelling temperature T [K] is SMD_{wT} instead of SMD_w, the swelling temperature dependence in Eq. (11) must be corrected with SMD_{wT}.

$$\frac{SMD_{wT}}{D_m} = 2.6 \cdot \frac{SMD_{wT}}{SMD_l} \cdot We^{-0.6} \left(\frac{\mu_d}{\mu_c}\right)^{0.5} \tag{12}$$

The correlation equation of spherical hydrogel bead size indicates that the average hydrogel size can be reasonably controlled on the basis of temperature, preparation conditions, and material properties of hydrogel beads.

4. Conclusions

Spherical temperature-sensitive DEAA hydrogel beads were prepared by Kenics static mixer technology. The spherical single beads had narrow and normal size distribution. The dimensionless Sauter Mean Diameter (SMD_{wT}/D_m), which is the ratio of the swollen hydrogel beads in deionized water at the swelling temperature to the inner diameter of the static mixer, was well correlated with the Weber number, the degree of swelling and the viscosity ratio. All effects of DEAA gelation, ENT additives and the swelling temperature on the bead size were simply evaluated by the degree of swelling. The hydrogel size correlation can be used for the preparation of temperature-sensitive hydrogels of desired size.

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