Preparation and Characterization of Surfactant-Free Stimuli-Sensitive Microgel Dispersions

James M. Griffin,[1] Ian Robb,[2] Alexander Bismarck[1]

[1]*Department of Chemical Engineering, Polymer & Composite Engineering (PaCE) Group, Imperial College London, South Kensington Campus, London, SW7 2AZ, United Kingdom*
[2]*Halliburton Energy Services, Halliburton Technology Centre, Duncan, Oklahoma*

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ABSTRACT: A surfactant-free method to produce responsive polymer microgels is introduced. As an example, poly(methacrylic acid) hydrogels with varying crosslinking density have been synthesized in bulk and then chopped using a high shear mechanical cutter to form microgel particles dispersed in water. The mechanical cutting technique enables the concentration and particle size distribution of the microgel suspensions to be easily controlled, therefore making the rheology of the suspensions tuneable. The particle size distribution of the dispersions, characterized using light scattering, was dependent on the speed and duration of mechanical cutting. The particle size distribution also depended on the degree of crosslinking of the hydrogel. The higher the crosslinking density, the lower the average mean diameter of the resulting microgel particles. The lower the crosslinking density of the hydrogel, the larger the difference between the maximum and minimum particle size. The time to complete swelling of the particles upon change in pH was measured to be up to 45 s, depending on the particle size. The rheology of the resulting suspensions as a function of pH was investigated. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1912–1919, 2007

Key words: microgels; methacrylic acid; stimuli-sensitive polymers; suspensions; rheology

INTRODUCTION

An area of increasing interest in the pharmaceutical and chemical industries is the synthesis, characterization, and application of responsive colloidal systems.[1,2] Extensive research into stimuli-sensitive polymers has been carried out.[3–19] The two main areas of research are *N*-isopropylacrylamide (NIPAM) based polymers[20–27] or copolymers,[28–30] which undergo a temperature induced volume phase transition at approximately 32°C, and polyelectrolyte systems,[8,31–35] which are sensitive to external stimuli such as pH and ionic strength. The synthesis of such microgels is often achieved by emulsion and inverse emulsion polymerization.[17,36–43] Particles synthesized via emulsion polymerization generally range from 10 nm to several micrometers. Emulsion polymerization involves the use of surface active agents that can have a significant cost and yield particles with limited particle size distributions. Crosslinked polymer particles in size range between 10 nm and several micrometers are often referred to as ''microgels.'' The first time the term ''microgel'' was used was in 1949 by Baker.[44] However, the first report of the synthesis of such particles was in 1935 by Staudinger and Husemann,[45] but the particles were not referred to as microgels. Staudinger and Husemann synthesized polystyrene microgels rather than hydrogel microgels. The term ''hydrogel'' is often used to describe a superabsorbent gel network that adsorbs large amounts of water.

Responsive polymer microgel particles can exist at or between two states: swollen or collapsed. The transition between these states can be used as a ''switch'' to change the rheological properties of dispersions.[1] Stimuli-sensitive dispersions have a wide range of applications especially in the case of nanohydrogels or microhydrogels that possess a volume phase transition temperature. If the volume phase transition temperature is similar to that of human body temperature they can be used for drug delivery systems.[46–50] Iwai et al.[51] developed a series of novel microgel thermometers covering the range of 18–47°C. This was achieved by fluorescent labeling of polyNIPAM based microgels and linear polymers. Various monomers were incorporated into the NIPAM to change the volume phase transition temperature and enable the fluorescence to be detected at different temperatures. The stimuli response, i.e., the swelling behavior of polyelectrolytes and polyelectrolyte hydrogels, including acrylic acid based systems, has been extensively studied and several review articles have been published.[28,52,53] Microgels[54] have also been used to stabilize oil-in-water emulsions. However, there is also considerable interest in stimuli responsive polymers for oil field applications or for drilling muds.[55] It is obvious that these applications require large quanti-

Correspondence to: A. Bismarck (a.bismarck@imperial.ac.uk).

ties of stimuli responsive microgels with particle sizes in the range of 10 μm upwards, which represents a challenge for commonly used synthesis routes for microgels.

We report the preparation and properties of μm to mm sized surfactant-free hydrogel particles by a straightforward mechanical cutting method. The particle size distribution of poly(methacrylic acid) based microgel particles was controlled by the duration and cutting rate of the mechanical cutter. This enables the rheology of the dispersions to be controlled. The swelling behavior was determined by measuring the particle sizes of the microgels by dynamic light scattering, and the rheological properties were determined using a controlled stress/strain rheometer.

EXPERIMENTAL

A series of poly(methacrylic acid) hydrogels crosslinked with *N*,*N*-methylenebisacrylamide (MBA) was synthesized via free radical solution polymerization in deionized water (Elga system S with UV, High Wycombe, UK) using potassium persulphate as an initiator. The reaction was carried out in 25-mm-diameter scintillation vials at 70°C at pH 4–5 for 2 h. The amount of MBA incorporated into the gels was varied to yield hydrogels with different crosslinking densities. MAA (99.9%) was purified by column chromatography through activated aluminum oxide as the stationary phase to remove the hydroquinone inhibitor. All other chemicals were 99% or higher purity and supplied by Sigma-Aldrich (Gillingham, UK) and used as received.

The crosslinking density of the hydrogels was varied by increasing the amount of MBA from 1 to 15 wt % with respect to the amount of MAA. The amount of initiator used for all polymerization reactions was fixed to 1.25 mol % of MAA. Table I summarizes the composition of the synthesized hydrogels.

Preparation of microgel particles

Synthesized hydrogel blocks of about 15 g were first cut into approximately 0.5 cm^3 cubes to enable better handling. The cubes were then placed in a glass beaker containing (DI) water (200 mL) and then broken down into smaller pieces using a high shear mechanical cutter (Kinematica Polytron P1600E homogenizer, Littau-Lucerne, Switzerland) at speeds of 10,000–30,000 rpm. The particle size distribution was monitored over a cutting period of 4 h to determine

TABLE I
Composition Data of Synthesized MAA Hydrogels

Composition (g)\sample	1	2	3	4
Water	120	120	120	120
MAA	20	20	20	20
MBA	3	2	0.8	0.2

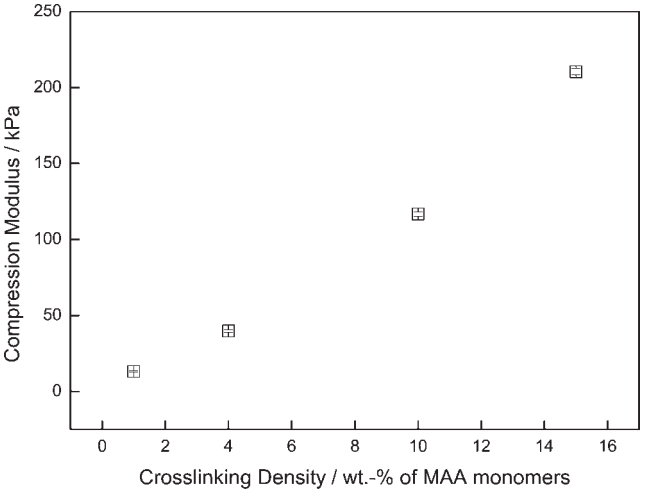

Figure 1 Compression modulus of unswollen MAA hydrogels.

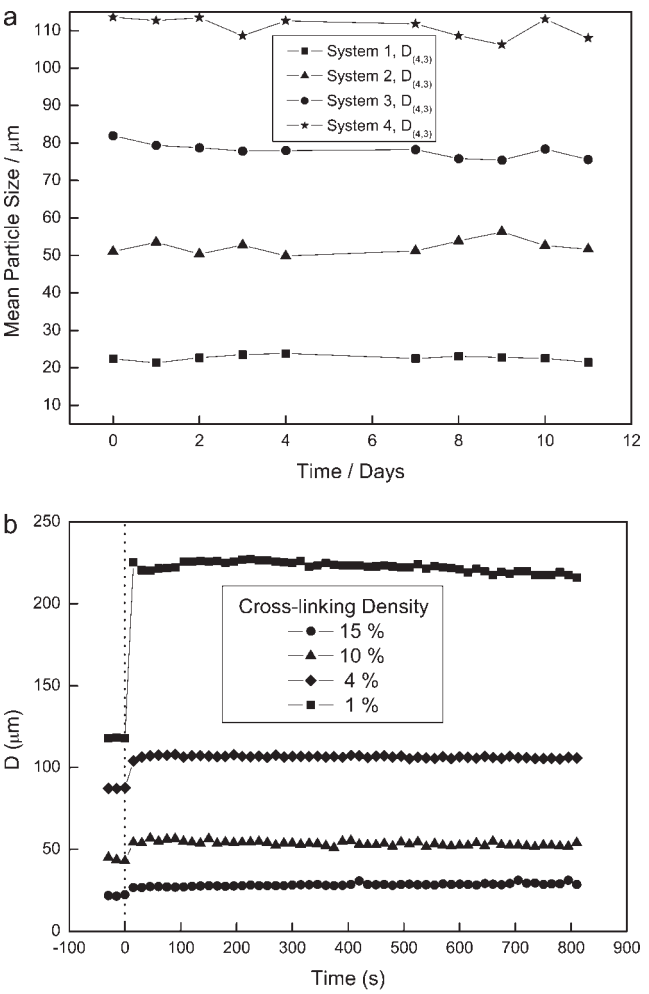

Figure 2 (a) Swelling of system 1–4 microgels over a period of 11 days. (b) Swelling of system 1–4 microgels upon addition of $NaOH_{(a.q.)}$ at time = 0 s.

the effect of both time and rotation speed of the mechanical cutter on the average particle size. The resulting microgel particles were suspended in DI water. The duration of cutting was varied to investigate the effect of cutting time on the particle size distribution.

Characterization of the resulting microgel particles

The microgel particles were characterized with respect to their particle size distribution using laser diffraction (Malvern Mastersizer 2000, Malvern Instruments, Malvern, UK). The volume weighted mean ($D_{[4,3]}$) also called De Brouckere Mean diameter was determined. The particles did not have a uniform size or shape (see optical micrograph Fig. 3). $HCl_{(a.q.)}$ or $NaOH_{(a.q.)}$ was added to the suspensions to change the pH.

Determination of the compression modulus of bulk hydrogels

The compression modulus of each of the bulk hydrogel blocks was determined via simple compression tests (Lloyds EZ 50, Fareham, UK). All measurements were carried out using cylindrical hydrogels with a diameter of 2.5 cm and a height of 4.0 cm with a 1 kN load cell at a loading rate of 1 mm/min. A stress/strain curve was then plotted and the gradient of the initial linear region was used to determine the compression modulus of the hydrogel.

Compression modulus of bulk hydrogels

The results of compression testing show that as the amount of crosslinker, and hence the degree of crosslinking of the resulting hydrogels, increased, the compression modulus of the hydrogel blocks increased (Fig. 1). The observed trend is relatively linear between 1 and 15 wt % crosslinking density. However, the linear trend may not continue at very low or very high crosslinking density.

Preparation and characterization of cut bulk hydrogels: Microgels

When a block of hydrogel is placed in deionized water it is seen to swell over a period of a few days until equilibrium is established. It was therefore important to measure the particle size distribution of freshly prepared microgels when they are at their equilibrium swelling position rather than immediately after cutting. The particle size of microgels from systems **1–4** of Table I was followed for several days to determine the time needed for the microgels to become fully swollen [Fig. 2(a)]. The volume weighted mean diameter of the microgels is represented by D. The particle size of the microgels remained constant over a period of 12 days [Fig. 2(a)]. All particle size measurements were taken 1 h after mechanical cutting. Therefore, it can be assumed that the microgel particles reach their swelling equilibrium during the mechanical cutting procedure. Upon changing the pH of the suspension

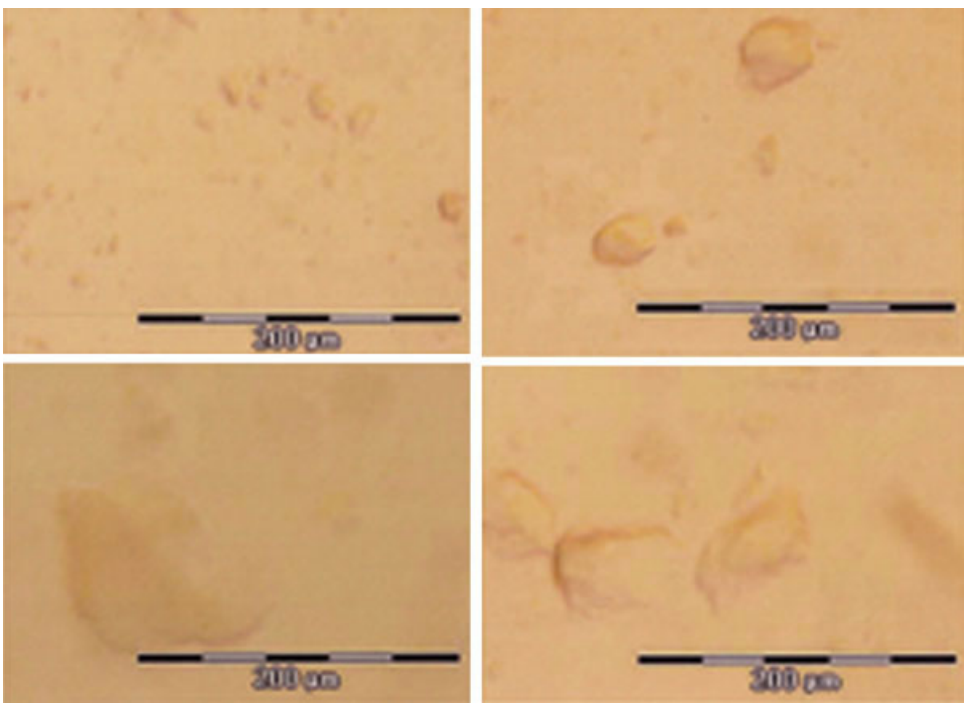

Figure 3 Clockwise from top left, micrographs of sample 1–4. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

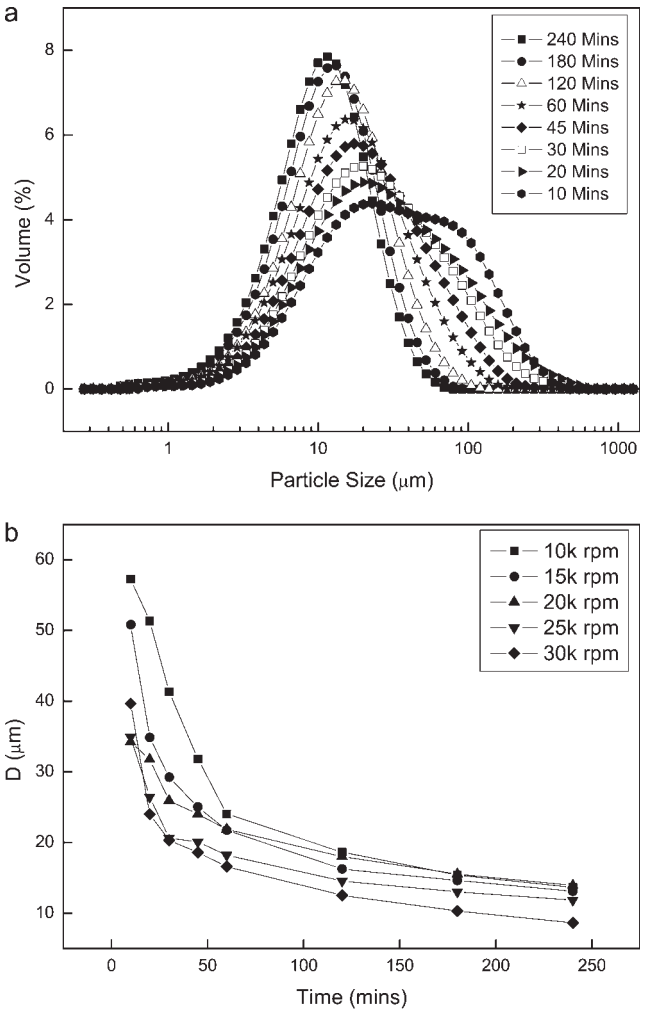

Figure 4 (a) Particle size distribution of hydrogel **1** over a 4-h period at 10 krpm. (b) Comparison of the average particle size ($D_{[4,3]}$) at different cutter speeds over a 4-h period for system 1.

the microgel particles reached equilibrium in less than a minute, as shown in Figure 2(b).

Figure 3 shows micrographs of hydrogel particles of system 1 to 4, respectively. Obviously, the mechanical cutting procedure is just ripping the bigger particles apart, which results in the observed random shapes of the microgel particles.

Effect of duration and rate of shear on the particle size distribution of the microgels

Figure 4(a) shows that the mean particle diameter D decreases as a function of cutting time. After 10 min of cutting the particle size distribution is bimodal but as the cutting time progresses the suspension eventually becomes monomodal. This is due to the hydrogel blocks initially being broken into smaller microgel particles in the order of 100 μm, which are further broken down into smaller microgel particles. The data in Figure 4(b) show a slight decrease in particle size with increasing shear rate.

The mode average (largest number of occurrences) of the particle size distribution of **2** [Fig. 5(a)] shifts from approximately 100 μm to 10 μm over the 4 h cutting period. The mode average particle size distribution of **2** after 10 min of mechanical cutting was approximately 100 μm, although for gel **1** the mode average is much closer to 10 μm. This indicates that the particles are initially being chopped into approximately 100 μm particles and subsequently torn in to smaller particles.

Gel **3** demonstrates the same behavior as **1** and **2** with respect to the effect of shear rate and duration of cutting on the particle size. However, the mode average particle size is larger than previous systems. Figure 6(a) shows that the particle size distribution of **3** remains bimodal throughout the whole cutting process. However, the mode average particle size

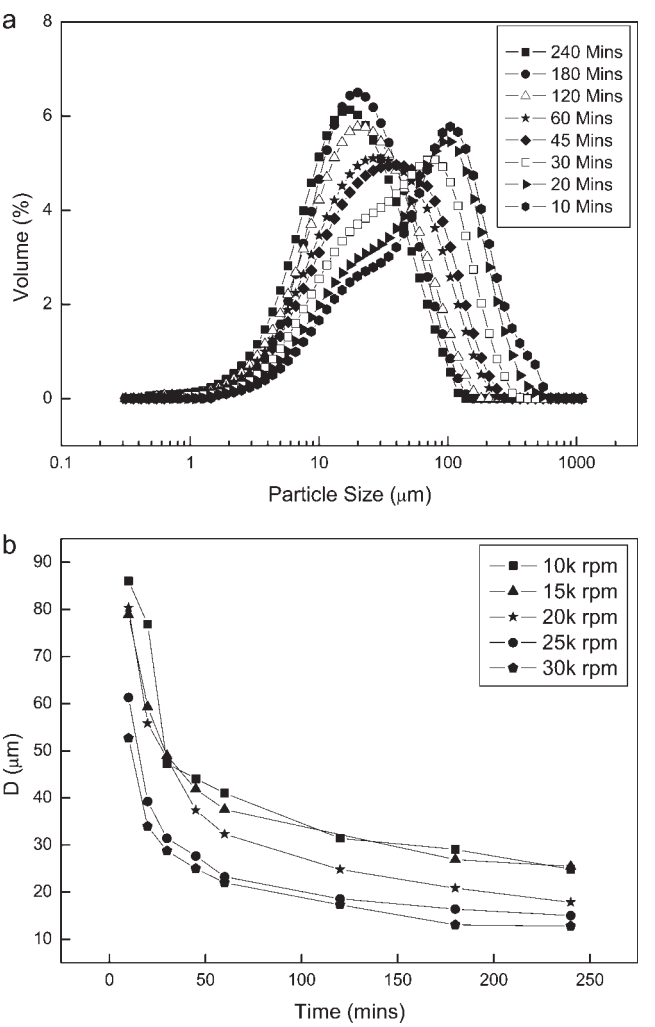

Figure 5 (a) Particle size distribution plots of hydrogel **2** over a 4-h period at a cutting speed of 10 krpm. (b) Comparison of the average particle size at different shear rates over a 4-h period for system **2**.

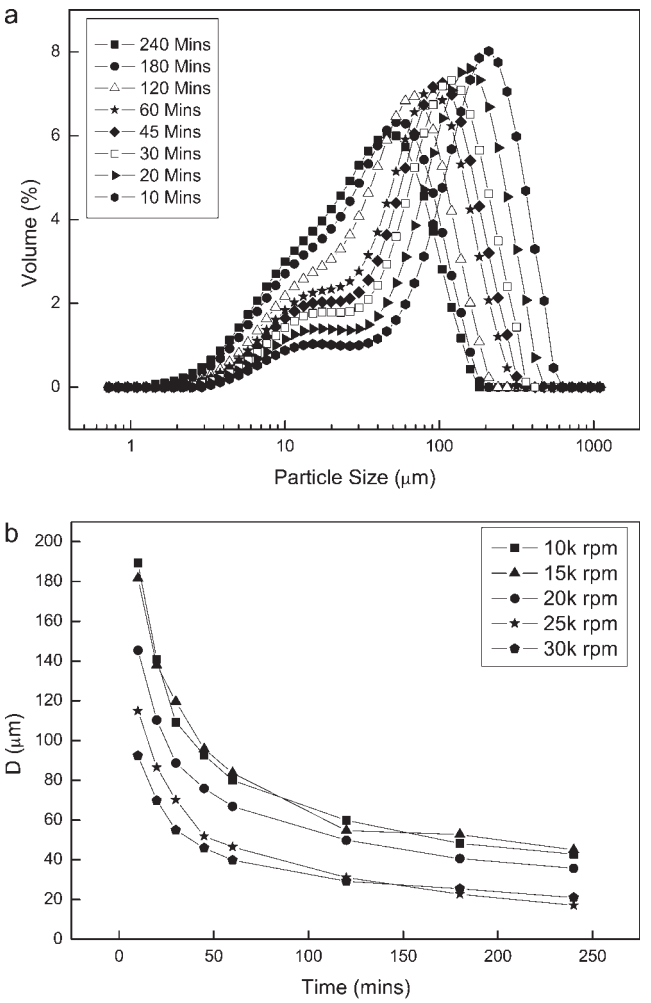

Figure 6 (a) Particle size distribution plots of hydrogel **3** over a 4-h period at 10 krpm. (b) Comparison of the average particle size at different shear rates over a 4-h period for system 3.

decreases with time, since the volume of the 10 μm microgels increases while the volume of the 100 μm microgels decreases. If the duration of cutting was extended the particle size distribution could therefore be expected to become monomodal.

The same trend for **3** was observed for **4** with regards to the effect of shear rate and duration of cutting on the particle size distribution as **1**, **2**, and **3** [Fig. 7(a,b)]. However, as for **3** the particle size distribution is consistently bimodal throughout the 4-h period of cutting. The average microgel particle size of **4** remains larger at all cutting speeds.

DISCUSSION

The effect of crosslinking density on the Young's modulus of the bulk hydrogels is clearly visible in Figure 1. As the crosslinking density is increased the Young's modulus increases from 13 to 210 kPa. These values are comparable with those found in literature[56] for hydrogels, such as poly(2-hydroxyethyl methacrylate-*co*-acrylic acid), which were in the range of 34 kPa at low crosslinking densities and rising to 380 kPa as the crosslinking density was increased.

In contrast to commonly used emulsion/precipitation polymerization techniques, our mechanical cutting technique enables the concentration and particle size distribution of the microgel suspensions to be easily controlled, which allows to tailor the rheology of the microgel suspensions by changing its pH. This is not the case for microgel suspensions prepared via emulsion polymerization techniques, which produce microgels in the nanometer range and occasionally up to several micrometers in size. Emulsion/precipitation polymerization techniques require the use of surfactants and there are limitations to the concentrations of microgels that can be obtained. The particle size is not easily varied, as the concentration of a surfactant can be used to a certain extent[19] to control the colloid size, but a range of surfactants is needed to synthesize

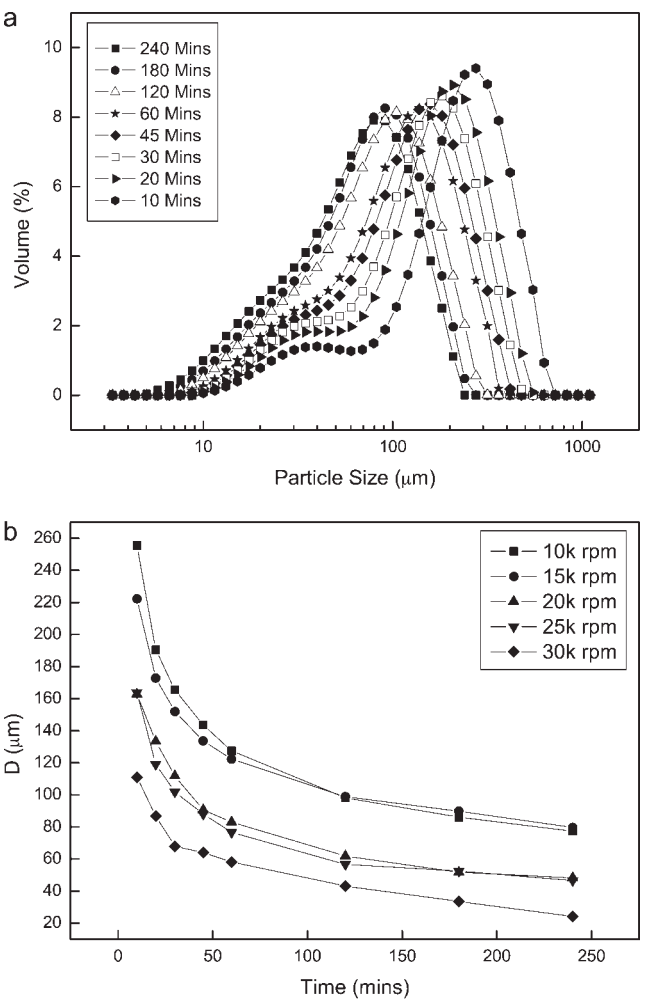

Figure 7 (a) Particle size distribution plots of hydrogel **4** over a 4-h period at 10 krpm. (b) Comparison of the average particle size at different shear rates over a 4-h period for system **4**.

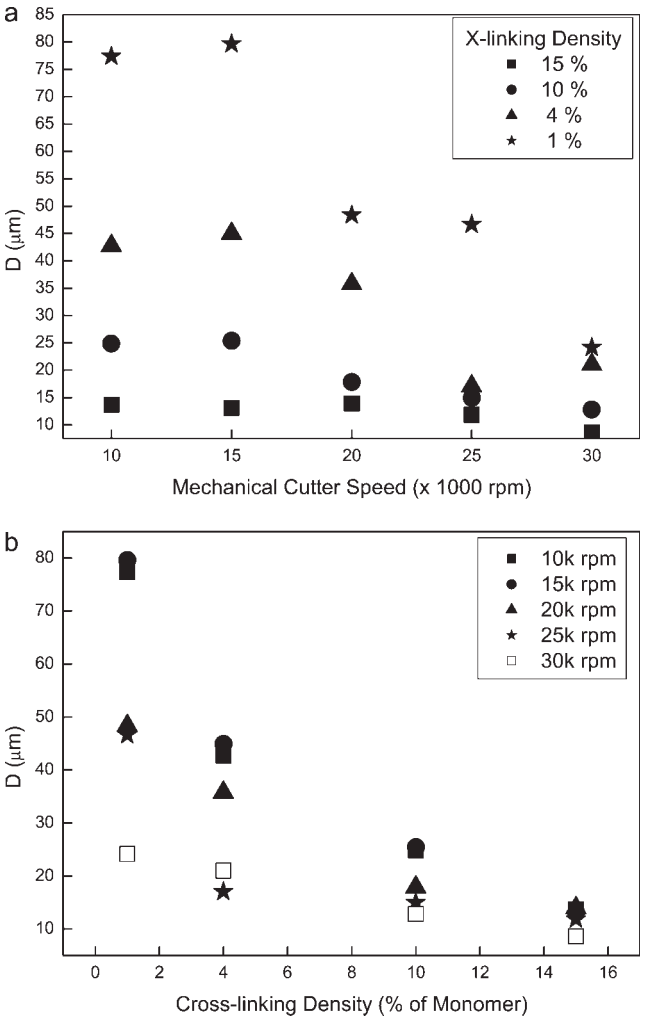

Figure 8 (a) Comparison of the effect of mechanical cutter speed on the de Brouckere Mean diameter of hydrogel suspensions after 4 h. The size of the symbol represents the error. (b) Comparison of the effect of crosslinking density on the de Brouckere Mean diameter of hydrogel suspensions after 4 h. The size of the symbol represents the error.

microgels of different sizes.[28,37] Surfactants have been shown to interact with the polymer colloid and influence the properties of the resulting suspension.[57]

All four investigated microgel systems show that as the duration or the speed of the mechanical cutting increases the mean microgel particle diameter decreases. The average particle diameter of the highly crosslinked (15% MBA) hydrogel **1** decreases by 37% as the speed of the mechanical cutter is increased from 10 to 30 krpm when compared with the particle size at 10 min. However, the particle diameter of **4**, which has a lower crosslinking density (1% MBA), decreases by 69% as the speed of the mechanical cutter is increased from 10 to 30 krpm. The average particle size of **2** and **3** decreased by 49 and 60%, respectively, as the mechanical cutting speed was increased from 10 to 30 krpm.

The lower the crosslinking density of the hydrogel to be cut, the larger the particle diameter at any given speed and duration of mechanical chopping [Fig. 8(a,b)]. The lower crosslinked hydrogels have a lower compression modulus (Fig. 1) and are more extensible and may deform more easily in the mechanical cutter resulting in larger particles.

Swelling and its pH dependence

The effect of pH on the particle size of all four systems was investigated and the results are summarized in Figure 9(a,b). The particle size increases as the pH is increased until a maximum size is reached at about pH 8. These results can be explained by taking into account the ionization of the carboxylic acid groups and the Donnan equilibrium.[58] As the pH increases around the pK_a of the MAA repeating unit ($pK_a = 4.35$) the increased ionization of the carboxylic acid groups raises the osmotic pressure within the gel, until at about pH > 10 the ionic strength of the system causes the osmotic pressure to decrease, giving a maximum in size at near neutral pH.

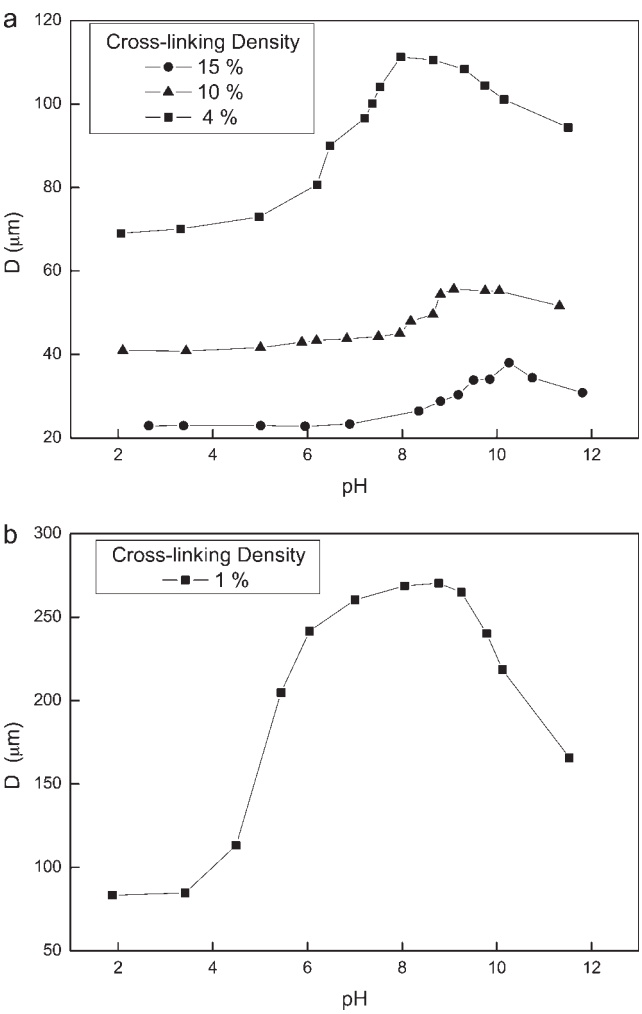

Figure 9 (a) Effect of pH on the mean particle size of the 15–4% crosslinked systems. (b) Effect of pH on the mean particle size of the 1% crosslinked system.

The amount of swelling of the microgels is dependent on the degree of crosslinking. As expected, the higher the crosslinking density the lower the degree of swelling,[1,2] owing to the crosslinks restricting the chain expansion. As shown in Figure 2(b) the swelling of the microgel particles takes approximately 30–45 s. The particle size was also monitored over a period of several days [Fig. 2(a)], indicating that the swelling equilibrium position is reached within a minute. Research[59] has been carried out on the transport of water through hydrogel membranes that gave diffusion coefficients of 2–7 $\times$ 10^7 cm^2/s and permeabilities of 0.7–6.5 cm/s. These results indicate that it is possible for the microgel particles to reach equilibrium within the measured time of 30–45 s.

CONCLUSIONS

High shear mechanical cutting yielded surfactant-free hydrogel dispersions. The sizes of the resulting microgel particles, characterized by light scattering, were in the region of 10–250 μm. The mechanical cutting technique allows for the particle size to be controlled simply by altering the speed of the mechanical cutter and/or the duration of cutting. As the speed of the mechanical cutter or the duration of cutting is increased the particle size decreases. The lower the degree of crosslinking of the hydrogel, the lower the compression modulus, and the larger the particle size of the resulting microgel at any given speed or duration of cutting. The lower crosslinked and, therefore, more flexible hydrogels probably deform in the mechanical cutter rather than being torn into smaller particles. The microgels swell with increasing pH, having a maximum particle size between pH 8 and 10. The lower the crosslink density the larger the swollen particle. The time needed for these particles to swell to equilibrium is approximately 30–45 s.

The rheological properties of the microgel suspensions are much more easily controlled. The intended applications of these microgel systems are in oil recovery; therefore, large volumes of microgel suspensions are required and cost is paramount. This new technique is much better suited for the intended application than other techniques such as emulsion/inverse emulsion polymerization.

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