

New Insight into the Preparation of Starch-Based Spherical Microgels with Tunable Volume

Shing-Yun Chang, Anson W. K. Ma, and Hsi-Mei Lai*

In this paper, novel, eco-friendly spherical cationic starch (CS) microgels are successfully prepared by partially gelatinizing CS granules, followed by stabilizing the structure with a cross-linker (sodium trimetaphosphate, STMP). Discrete and spherical swollen CS granules are first obtained by partially gelatinizing CS starch at 50 °C for 10 min, without the need for inverse emulsification. Various amounts of STMP are reacted with partially gelatinized CS granules to examine the effect of cross-linking density on the swelling behaviors. Depending on the degree of cross-linking, the average diameter of CS microgels in water ranges from 55 to 75 μm. The STMP cross-linking strengthens the structure of CS microgels through chemical cross-linking (via distarch monophosphate formation) and ionic cross-linking (via trapping unreacted STMP). Upon changing the environmental pH and ionic strength, it is found that the swelling volume of microgel is mainly controlled by the excess cationic groups and chemical cross-linking. Having a relatively stable swelling ratio within a wide pH range (3–9) and a good viscosity thickening ability, the CS microgel shows great potential as a natural thickener (texture stabilizer) in personal care products.

manipulated by varying polymer composition, cross-linking density, and environmental conditions (e.g., temperature and pH).^[2] The volume tunable microgel thereby has attracted considerable interests in multiple applications, such as stimuli-responsive drug carriers and thickeners in texture control of personal care products.^[3–5]

The microgel-based thickeners display an excellent development of viscosity upon absorbing water. They are extensively used in personal care products as texture stabilizers. However, they are mostly made from synthetic or half-synthetic polymers.^[4,5] With the growing environmental awareness in recent years, some bans on the use of plastic microbeads have been put into laws.^[6] The needs for environmental friendly materials to replace the fossil-fuel-based product become urgent. Microgels derived from naturally occurring biopolymers have been studied for decades.^[7–9] The conventional approaches to prepare micro-

1. Introduction

The term “microgel” has been coined to describe micro-sized, discrete, and cross-linked polymeric particles that swell in a good solvent.^[1] Different from hard microspheres, the soft nature of microgel shows a controllable volume, meaning that its physical properties (e.g., viscosity and swelling volume) can be

gels made of readily formed biopolymers include inverse emulsification, coacervation, and desolvation techniques. A critical step for all these approaches requires a phase separation on micro-scale to generate discrete emulsion droplets. Biopolymers inside droplets are subsequently cross-linked to form microgels and isolated with consecutive wash steps.^[3,9] In this case, the subsequent removal of oil phase (e.g., hexane and heptane) from microgels adds to the processing costs and increases the environmental footprint.

It is hypothesized that the unburst swollen starch granules formed during starch gelatinization keep most of starch molecules inside the granules. They could behave like the discrete starch droplets in the inverse emulsification process adopted by Dziechciarek et al.,^[10] and more recently Li et al.^[11] Therefore, a straightforward method for generating the micron-sized spherical microgels was proposed in this study. The partially gelatinized cationic starch granules were carefully prepared and then mechanically stabilized with cross-linker (STMP). The degree of cross-linking and composition within the microgels were identified. The swelling ratio and size distribution of microgels with varying cross-linking densities were studied at different pHs and ionic strengths. The corresponding rheological properties of microgels were investigated to assess its thickening ability.

S.-Y. Chang, Prof. H.-M. Lai
Department of Agricultural Chemistry
National Taiwan University
Taipei 10617, Taiwan
E-mail: hmlai@ntu.edu.tw

A. W. K. Ma
Department of Chemical and Biomolecular Engineering
University of Connecticut
Storrs, CT 06269, USA

A. W. K. Ma
Polymer Program
Institute of Materials Science
University of Connecticut
Storrs, CT 06269, USA

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/star.201800288>.

DOI: 10.1002/star.201800288

2. Experimental Section

2.1. Materials

Native corn starch was supplied from GuTong Ltd. (Chiayi, Taiwan), composed of 13.48 wt.% moisture, 0.39 wt.% crude lipid, 0.06 wt.% protein, and 0.06 wt.% ash. The cationic reagent (65% aqueous solution of 3-chloro-2-hydroxypropyl-trimethyl ammonium chloride, CHPTAC) was purchased from TCI America (Portland, OR, USA). The cross-linker (sodium trimetaphosphates, STMP) was purchased from Sigma–Aldrich (St. Louis, MO, USA). The staining reagent (0.1N iodine solution) and phosphate-buffered saline (PBS) (10×, pH 7.4) with an ionic strength of 1.7M were the products of Fisher Scientific (Waltham, MA, USA). All chemicals and solvents used were of analytical grade.

2.2. Degree of Substitution and Pasting Properties of Cationic Starch (CS)

Cationic starch was prepared following the method reported by Chang and Lai.^[12] The nitrogen content (%) was determined by the combustion method^[13] using an elemental analyzer (vario MICRO, Hanau, Germany). The degree of substitution (DS) of CHPTAC on cationic starch was calculated to be 0.148 using the following equation (Equation (1))

$$DS = \frac{(162.15 \times \% \text{ nitrogen})}{1401 - (151.64 \times \% \text{ nitrogen})} \quad (1)$$

where 162.15 is the averaged molecular weight of the anhydroglucose unit; 1401 is the atomic weight of nitrogen multiplied by 100; and 151.64 indicates the molecular weight of the substituted, chloride-free CHPTAC group.

Following the CS concentration (2.5 wt.%, on a dry basis) and the heating program modified from the official pasting method^[14] reported in Kuo and Lai,^[15] a rheometer (AR-G2, TA instrument, New Castle, UK) equipped with a Couette (two concentric cylinders) fixture and solvent trap was used to obtain the viscosity profile of cationic starch. In addition, the transient viscosity profiles of the CS suspensions at 0.5 wt.% were measured at 50, 60, and 70 °C, respectively, for 10 min, followed by cooling to 35 °C at a rate of 2.5 °C min⁻¹. In the official pasting method,^[14] a paddle speed of 160 rpm corresponds to a shear rate of 240 s⁻¹ for the Couette fixture (inner radius = 14 mm; outer radius = 15 mm) used in this study.

2.3. Preparation of CS Microgels

CS was dispersed in distilled water to prepare a suspension with a concentration of 0.5 wt.%, and then transferred to a water bath at 50 °C under continuous stirring with a stir-bar at 150 rpm for 10 min to perform the partial gelatinization. Based on the cross-linking method in Li et al.^[16] with some modifications, stock STMP solution was added into the partially gelatinized CS suspension containing 0.1% NaCl (w/v) at different STMP/CS weight ratios (0, 0.01, 0.03, 0.05,

0.1, 0.2, 0.3, and 0.4). The pH was adjusted to 10.0–10.2 with the addition of 0.01M NaOH. After mixing, the suspensions were placed in an oven at 40 °C for 3 h. The previous study suggested a reaction time of 3 h was sufficiently long for accessible STMP to react (Figure S1, Supporting Information). To collect the CS microgels, absolute ethanol was added into the mixture to achieve an ethanol concentration of 30 v/v%; meanwhile, the mixture turned turbid. After centrifugation at 3000 rpm for 10 min, the supernatant was carefully decanted. The precipitates were re-suspended and centrifuged with 50 and 60% ethanol until the supernatant showed a pH of 7–8. The final precipitates were immersed in 95% ethanol overnight to dehydrate. Then, the dehydrated CS microgels were recovered by filtration and the residual ethanol was removed by a final wash with acetone. After oven-drying at 40 °C for 6 h, dried CS microgels were stored in a desiccator before measurements. As a control experiment, the partially gelatinized CS undergoing the same procedures in the absence of STMP, was denoted as “CS000.” Experimental cross-linked CS microgels were named after their STMP/CS ratio; for example, “CS02” represented CS microgel samples cross-linked with a STMP/CS ratio of 0.2.

2.4. Thermo-Gravimetric Analysis (TGA) of CS Microgels

The residual weight of dried CS microgels from different batches were examined with a thermo-gravimetric analyzer (Q500, TA instrument, New Castle, UK). Weighed dried CS microgels (10 mg) were heated in a furnace injected with N₂ (60 mL min⁻¹), with a heating rate of 10 °C min⁻¹, from 25 to 700 °C. The residual weight percentage (wt.%, on a dry basis) was recorded as a function of temperature.

2.5. Phosphorus Content and Phosphorus Characterization

The phosphorus content (P_{total} , wt.%) was analyzed according to the EPA Method.^[17] The digested solution from dried CS microgel (40 mg) was diluted until the nitric acid (HNO₃) concentration became less than 2%, and then filtered through a 0.45-μm filter. Inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7700× with a He collision cell, Agilent, Delaware, USA) was utilized to determine the phosphorus content in this work. Standards and quality control checks were prepared from independent high purity standards (Spex-Certiprep, Metuchen, NJ, USA and VHG Labs, Inc., Manchester, NH, USA).

To characterize the phosphorus compounds present in the CS microgels, the ³¹P nuclear magnetic resonance (NMR) analysis was used to identify all phosphorus from different compounds. The enzymatic digestion was carried out to concentrate the sample while keeping the viscosity sufficiently low before the ³¹P NMR analysis. The details of enzymatic digestion^[18] were described in Supporting Information. The ³¹P NMR data were acquired with an AVANCE 300 MHz instrument (Bruker, USA), operating at 121.49 MHz for ³¹P. The ³¹P NMR experiments were performed at 27 °C using a delay of 2 s between pulses (pulse width 11.1 μs), and a sweep

width of 37 878 Hz. The spectra were processed and analyzed using TopSpin 3.5.

The weight percentage of phosphorus from either unreacted STMP ($P_{\text{unreacted}}$) or distarch monophosphate (P_{distarch}) in dried CS microgels was calculated based on the total phosphorus content (P_{total}) of the CS microgels from ICP analysis. Since the peak area in ^{31}P NMR spectrum reflected the amount of phosphorus, the weight percentage of phosphorus from unreacted STMP, $P_{\text{unreacted}}$, was given by $P_{\text{unreacted}}(\text{wt.}\%) = P_{\text{total}}(\text{wt.}\%) \times \frac{\text{Peak area of } P_{\text{unreacted}}}{\text{Total peak area}}$.

2.6. Swelling Ratio Measurement

To measure the swelling ratio, a given buffer (5 mL) was added into the centrifuge tubes containing CS microgels (10 mg). According to the kinetic swelling curve (Figure S2, Supporting Information), it took 6 h for CS000 to achieve the equilibrium swelling ratio while soaking in PBS ($i = 0.0017\text{M}$). After centrifugation (3000 rpm, 30 min), the supernatant was carefully removed. The swelling ratio (g g^{-1}) was defined as the weight of swollen CS microgels (sediment) divided by the weight of the dried CS microgels.

2.7. Microscopic Observation and Particle Size Distribution Analysis

After CS microgels (ca. 0.05 w/v%) swelled in either water or PBS for 6 h, suspensions were taken and stained with iodine solution (0.01N KI/I₂) at a 1:40 volume ratio. The morphology of stained microgels in a hanging drop slide without a coverslip was studied using an optical microscope (Olympus

BX50, Tokyo, Japan). The particle size analysis was done by calculating the diameters of at least 300 particles in optical microscopy images with ImageJ. The frequency of each diameter interval was normalized by dividing the number of particles counted for a given diameter interval by the total number of particles. The median diameter (d_{50}) and the range between d_{90} and d_{10} (span) were extracted from the cumulative distribution to quantify the average size and polydispersity of CS microgels, respectively.

2.8. Rheological Properties of CS Microgel Suspensions

Steady shear measurements were carried out on a MCR 702 rheometer (Anton Paar, Graz, Austria) equipped with a Couette geometry. The gap between the outer cup and the inner bob is 1 mm. CS microgel suspensions with concentrations ranging from 0.01 to 3 g dL^{-1} (i.e., w/v%) in a given buffer solution were prepared and hydrated overnight. The steady shear measurements at 25 °C were performed to record the apparent shear viscosity of CS microgel as a function of decreasing shear rate from 100 to 1 s^{-1} . Steady shear viscosity at each shear rate was recorded as the temporal viscosity varied less than 5%. In this study, the apparent shear viscosity at a shear rate of 10 s^{-1} was arbitrarily chosen for calculating the specific volume.

The relative viscosity (η_r) is defined as the suspension viscosity divided by the suspending medium viscosity and varies depending on the volume fraction (ϕ) of particles in suspension. The volume fraction (ϕ) is equal to the product of specific volume k (mL g^{-1}) and mass concentration c (g mL^{-1}). The concentration (c) was known, but the specific volume (k) of the swollen microgel particle was not known a priori. The k value of CS

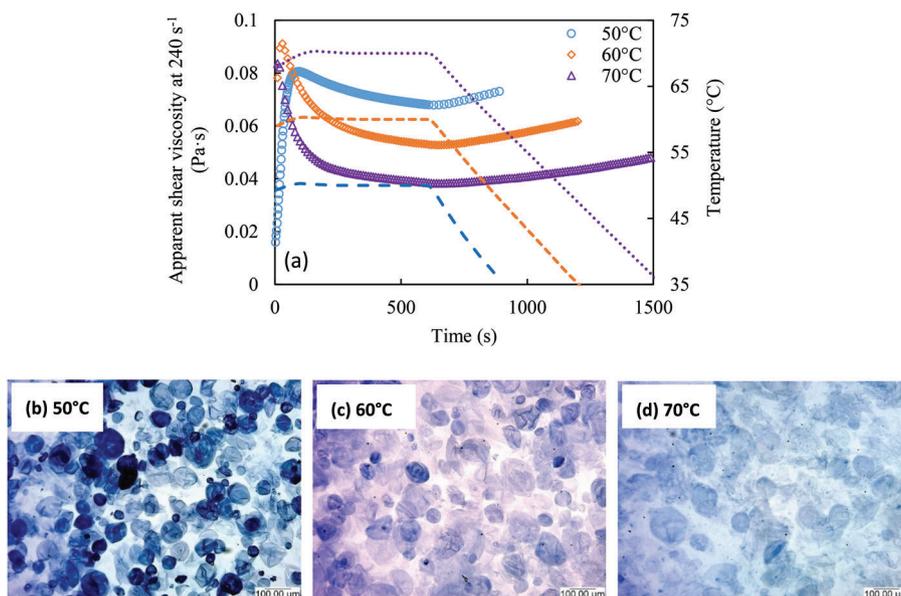


Figure 1. The transient viscosity profile of a CS suspension (0.5 wt.%) (a), where the temperature was initially kept constant for 10 min at 50 °C (open circle), 60 °C (open diamond), and 70 °C (open triangle), respectively. Dotted line represents the temperature profile. The corresponding optical micrographs of CS after heat treatment at 50 °C (b), 60 °C (c), and 70 °C (d). The samples were stained with an iodine solution.

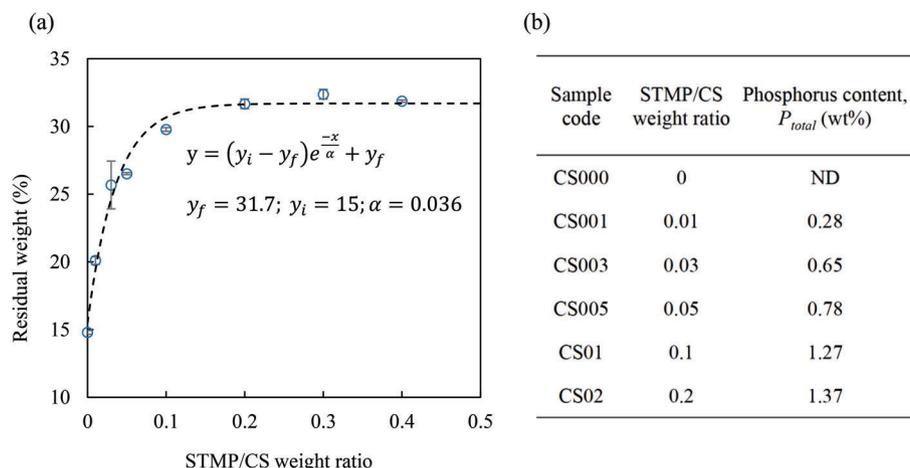


Figure 2. a) The TGA of CS microgels with STMP/CS weight ratios from 0 to 0.4. Black dash lines were empirical curve fits with an exponential function. The error bar represents the standard deviation of data in triplicate. b) The phosphorus content (P_{total}) of CS microgels with STMP/CS weight ratios from 0 to 0.2 (determined by the ICP method). ND: not determined.

microgel was determined by fitting the experimental η_r at different concentrations (c) with the Batchelor equation (Equation (2)) within the dilute regime ($\phi < 0.15$)^[2] (Figure 5 insets). For comparison, the relative viscosity profiles of CS microgel were plotted together with the profiles of hard spheres (having the same k)^[19] (Supporting Information) (Figure 5).

$$\eta_r = 1 + 2.5 kc + 5.2(kc)^2 \quad (2)$$

where η_r is the relative viscosity, k is the specific volume (mL g^{-1}), and c is the concentration (g mL^{-1}).

3. Results and Discussion

3.1. Preparation and Partial Gelatinization of CS

It was known that the charged groups on polymers will reduce the tendency of polymer chains' association, thus a good reversible swelling/de-swelling behavior could be maintained during applications.^[12,20] The CS granule with DS of 0.148 was prepared and used as the starting materials to generate starch soft granules. Next, disassociating most of the crystalline structure in the CS raw granules while keeping the granules intact was essential and critical. Heat treatment was used to partially gelatinize starch granules from the raw granules.

During heating in the presence of excess water, starch granules underwent gelatinization where the raw granules swelled and formed a viscous solution.^[21] Given the peak temperature of 50 °C observed in CS (Figure S3, Supporting Information), various holding temperatures (50, 60, and 70 °C) were adopted to heat CS (0.5 wt.%) for 10 min. As shown in Figure 1a, the paste viscosity rapidly increased upon heating and quickly reached its maximum viscosity, followed by a decrease in viscosity. The higher peak viscosities for 60 and 70 °C, compared to 50 °C, was attributed to the higher disassociation degree of crystalline structure inside the starch granules, which resulted in larger swollen granules and consequently a higher viscosity due to a higher hydrodynamic volume fraction. Swollen starch granules prepared from higher heat treatment temperatures (60 and 70 °C) were more susceptible to shear-induced breakdown due to their larger size (Figure 1c and d). A larger degree of viscosity reduction was therefore observed at higher holding temperatures. This explanation was consistent with optical micrographs showing that most of the swollen starch granules remained intact after a heat treatment temperature of 50 °C (Figure 1b). Based on the transient viscosity profiles, a heat treatment temperature of 50 °C was chosen to partially gelatinize the CS granules while keeping the envelopes intact. This decision considered the trade-off between the disassociation degree of crystalline and the mechanical integrity of the partially gelatinized granules.

Table 1. Phosphorus compounds and their fractions in CS microgels with STMP/CS ratios of 0.01, 0.03, and 0.2

	P_{total}^a (wt.%)	$P_{unreacted}^b$ (wt.%)	$P_{unreacted}/P_{total}$	$P_{distarch}$ (wt.%)	$P_{distarch}/P_{total}$
CS001	0.28	0.21	0.77	0.07	0.23
CS003	0.65	0.53	0.82	0.12	0.18
CS02	1.37	0.99	0.72	0.38	0.28

^{a)} P_{total} is the weight percentage of total phosphorus weight over dried CS microgel weight, as determined from ICP analysis. ^{b)} According to the peak area in ³¹P NMR spectrum and the known total phosphorus content, the weight percentage of phosphorus from unreacted STMP ($P_{unreacted}$) is calculated.

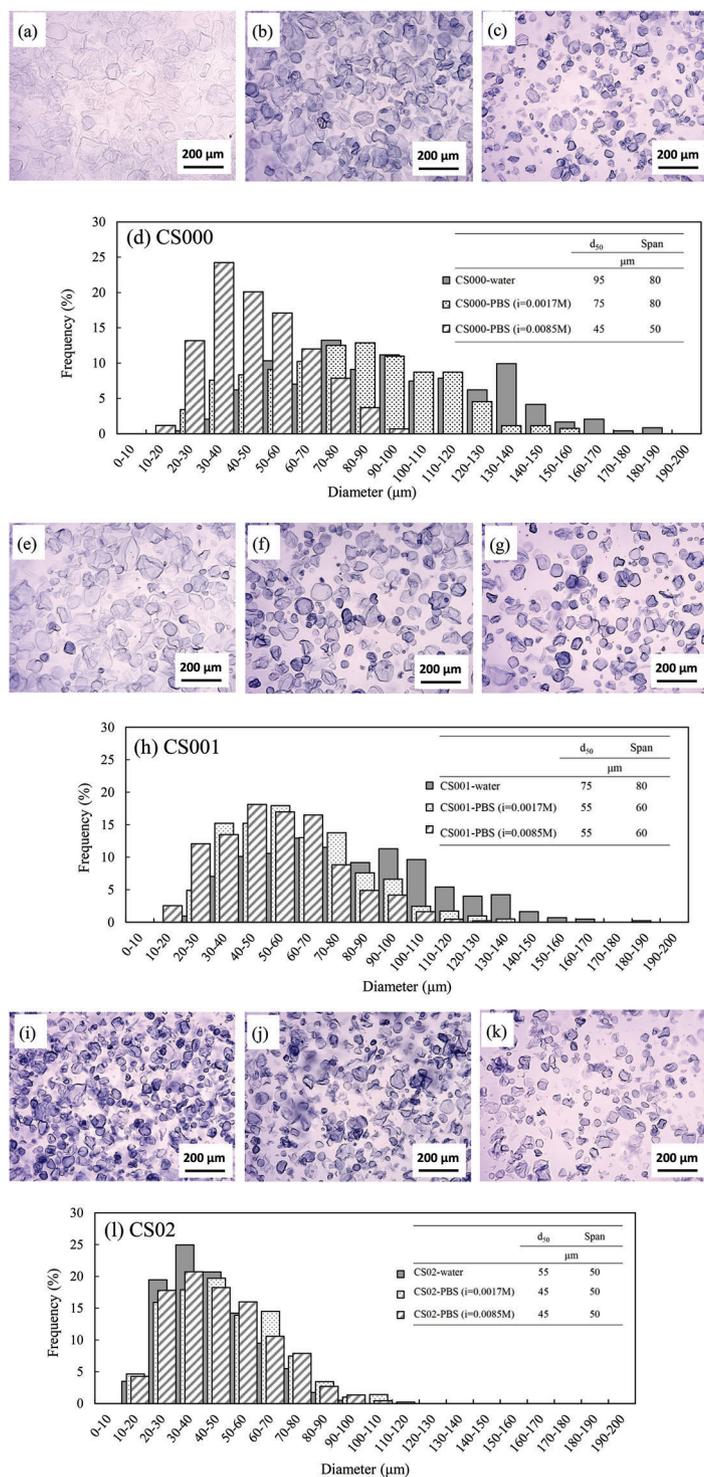


Figure 3. Micrographs of CS microgels with STMP/CS ratios at: 0 (a–c), 0.001 (e–g) and 0.2 (i–k), after swelling for 6 h in pure water (a, e, and i), and in PBS solutions with ionic strengths of 0.0017M (b, f, and j) and 0.0085M (c, g, and k). The samples were stained with iodine solution. The histograms of frequency distribution versus CS microgels diameter with STMP/CS ratios at: 0 (d), 0.01 (h), and 0.2 (l) after swelling in pure water and in PBS ($i = 0.0017$ and 0.0085M).

3.2. STMP Cross-Linking of CS Microgels

To sustain the granular shape with swelling/de-swelling characteristics as the environmental conditions vary, the structure of partially gelatinized CS granules needed to be strengthened. Sodium trimetaphosphate, an effective food-grade cross-linking reagent,^[22] was introduced. Cross-linking reaction was generally performed in alkaline conditions (pH 9–11) which facilitated the formation of the covalent form of STMP cross-linking (distarch monophosphate).^[23,24]

The residual weight of CS microgels at 700 °C obtained from TGA allowed a quick estimation of STMP content remained in CS microgel. The residual weight initially showed an upturn as the STMP/CS ratio increased, then started leveling off above a STMP/CS ratio of 0.1 (Figure 2a). The leveled-off value of residual weight is 31.7%, deduced by exponential curve fitting. As a result, the highest amount for STMP to react with CS seems to occur at a STMP/CS weight ratio of 0.1. Similarly, the total phosphorus contents (P_{total}) increased significantly with the increasing STMP/CS weight ratio up to 0.1 (Figure 2b).

To verify the type of phosphorus, the ^{31}P NMR spectra of CS microgels with STMP/CS ratios at 0.01, 0.03, and 0.2 were collected. The two peaks at the chemical shift of –21 and 0 ppm represented the phosphorus of unreacted STMP and distarch monophosphate, respectively^[23] (Figure S4, Supporting Information). The presence of unreacted STMP indicated a substantial amount of unreacted STMP remaining in CS microgels, although CS microgel has been submitted to successive washing steps. It may be due to the ionic cross-linking between STMP and cationic starch which made the removal of unreacted STMP difficult. The ^{31}P NMR spectra confirmed both the ionic cross-linking of unreacted STMP and chemical cross-linking through the formation of distarch monophosphate in CS microgels. The individual phosphorus amount of unreacted STMP and distarch monophosphate ($P_{\text{unreacted}}$ and P_{distarch}) and the weight fractions were calculated and listed in Table 1. $P_{\text{unreacted}}$ and P_{distarch} increased as expected when the STMP/CS ratio increased from 0.01 to 0.2. However, when normalized by the total phosphorus content, the phosphorus weight fractions from unreacted STMP and distarch monophosphate (i.e., $P_{\text{unreacted}}/P_{\text{total}}$ and $P_{\text{distarch}}/P_{\text{total}}$) were rather insensitive to the STMP/CS ratio. This implied that only 18–28% of phosphorus in STMP was able to form the chemical cross-linking under our experimental conditions (pH 10.0, 40 °C) independent of the STMP/CS weight ratios utilized.

3.3. Morphologies and Swelling Ratio of CS Microgels Responding to Environmental Changes

The swelling of hydrogels was known to be driven by osmotic pressure. For an ionic gel system like the CS microgels. The unequal concentration of mobile ions inside and outside the charged CS microgel (i.e., the concentration

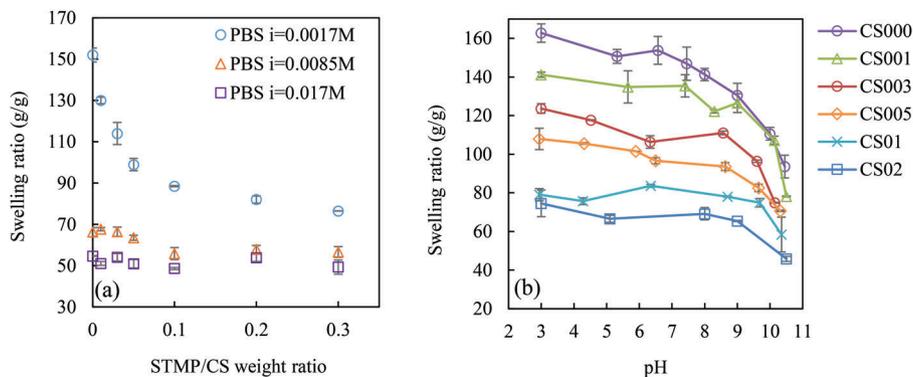


Figure 4. Swelling ratios of CS microgels with various STMP/CS ratios in PBS with various ionic strengths (a) and in NaCl solutions with an ionic strength of 0.002M and a pH value ranging from 3 to 11 (b). The error bar represents the standard deviation of data in triplicate.

of counter-ions accompanying the immobilized charged groups and the concentration of ions outside network) principally contributed to osmotic pressure.^[25,26] Basically, the higher the osmotic pressure, the larger extent of microgel swelling. Taking all factors into account: (1) increasing the environmental ionic strengths (at a given pH) reduced the difference in mobile ion concentration inside and outside CS microgel, resulting in smaller osmotic pressure and thus limiting swelling; (2) the presence of cross-linking enhanced the structure of CS microgel to resist swelling^[26]; (3) the environmental pH (at a fixed ionic strength) affected the ionization degree of charged groups in CS microgels, namely the quaternized amino groups and phosphate groups of unreacted STMP. At a pH value above or below pK_a , the charged groups became de-ionized, which led to fewer accompanying counter-ions and a decrease in osmotic pressure, limiting the swelling.

To explore the effect of ionic strengths while keeping the pH constant, PBS – a common buffer in biological research – was chosen and diluted (200 and 1000 times) to suspend the CS microgels. The CS000 and the slightly cross-linked CS001 showed their highest extent of swelling when dispersed in water (Figure 3a and e). An increase in ionic strength limited the swelling volumes (Figure 3b, c, f, and g), significantly reducing their median size and polydispersity (Figure 3d and h). However, the swelling volume of highly cross-linked CS02 barely changed with the environmental ionic strengths (Figure 3i–l). Likewise, it was hard to observe the influence of STMP cross-linking in CS microgels as the swelling was limited in PBS with excess salt ($i = 0.0085M$) (Figure 3c, g, and k). The structural strengthening in the CS microgels via STMP cross-linking can only be visualized either in water (Figure 3a, e, and i) or in PBS ($i = 0.0017M$) (Figure 3b, f, and j). A similar trend was observed when the microgels were suspended in NaCl solutions with different ionic strengths (Figure S5, Supporting Information).

The experimental swelling ratio of CS microgels versus pH at a fixed ionic strength ($i = 0.002M$) (Figure 4b) was similar over a wide range from pH 3 to 9, and decreased sharply above pH 9. This trend basically followed the ionization curve of quaternized amino groups ($pK_a \approx 9.8$)^[27] and there was no significant restriction of ionic cross-linking observed. This finding was explained by the abundance of cationic groups relative to anionic groups in CS microgels. The cationic group hence dominated the pH-dependent swelling behavior of CS microgels.

3.4. Rheological Properties of CS Microgel Suspensions

The relative viscosities of CS001 and CS02 in water and in PBS ($i = 0.0017M$ and $0.0085M$) at a shear rate of 10 s^{-1} were plotted as a function of concentration (Figure 5). All relative viscosity data show an inflection point, indicating a transition from dilute to overlap region. The specific volume k (mL g^{-1}), as determined from rheological data fitting (Figure 5 insets), is the

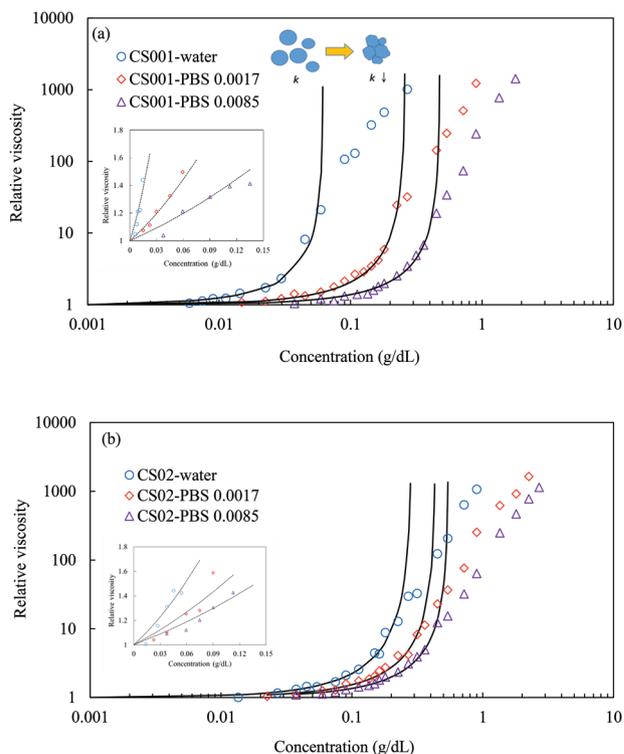


Figure 5. Relative viscosity at a shear rate of 10 s^{-1} as a function of concentration (g dL^{-1}) of CS microgels with STMP/CS ratios at: 0.01 (a) and 0.2 (b), prepared in water and in PBS with an ionic strength of 0.0017 and 0.0085M. Solid curves represent the hard sphere model. The diluted regimes were zoomed in as the inserted plots where the specific volume was deduced with the Batchelor equation (dash line). The deformable CS microgels de-swell upon close-packing was illustrated in (a).

Table 2. The parameters obtained from the curve fits on the relative viscosity of CS microgels with STMP/CS ratios of 0.01 and 0.2, suspended in water and in PBS (pH 7.4) with an ionic strength of 0.0017 and 0.0085M.

Samples	k (mLg ⁻¹) ^{a)}	C^* (g dL ⁻¹) ^{b)}
CS001 in water	810	0.25
CS001 in PBS ($i = 0.0017M$)	230	0.87
CS001 in PBS ($i = 0.0085M$)	115	1.53
CS02 in water	262	0.85
CS02 in PBS ($i = 0.0017M$)	150	1.78
CS02 in PBS ($i = 0.0085M$)	110	2.47

^{a)} Specific volume (k) is from the Batchelor equation (Figure 5 insets). ^{b)} C^* is defined as the concentration (g dL⁻¹) required to reach a relative viscosity of 1000. The unit of g dL⁻¹ is equivalent to the unit of w/v%.

hydrodynamic volume occupied by 1 g of dried microgel in a suspension. As shown in Table 2, increasing ionic strength and/or the cross-linking density reduces the specific volume (k). The smaller the k value, the smaller the swelling ratio (Figure 4) and consequently the lower the apparent shear viscosity of CS microgel suspension at a given concentration (Figure 5 and Figure S6, Supporting Information).

As shown in Figure 5a and b, the relative viscosities of CS001 and CS02 at different ionic strengths followed closely the hard sphere model from the dilute regime up to the inflection point, but at high concentrations the viscosities of the microgels were consistently lower than the theoretical values if hard spheres were assumed, suggesting the deformable nature of the microgels (illustration in Figure 5a).^[28,29] The deformability might arise from the limited reactivity of STMP to form chemical cross-linking as mentioned in Section 3.2.

The concentration (C^*) needed for reaching an arbitrary relative viscosity of 1000 was defined as a benchmark for the viscosity thickening ability of CS microgels. As shown in Table 2, the higher the specific volume of CS microgel, the smaller the C^* . For instance, CS001 had a lower C^* than CS02 in a given solution, implying a smaller amount of CS001 was required to attain the same viscosity than CS02. In this case, CS001 has a

better thickening ability than CS02. Nevertheless, the viscosity thickening ability of CS001 and CS02 was both comparable to commercial natural thickeners, such as xanthan gum with a C^* of 0.5–1 w/v%^[30] and carboxymethyl cellulose with a C^* of 1–1.5 wt.%.^[31]

4. Conclusion

This paper reported the preparation of starch-based microgels using cationic starch, taking advantage of the starch envelopes that were spherical, as well as its charged interior structure that facilitates the swelling/de-swelling. Unlike the conventional inverse emulsification to produce discrete starch droplets, partial gelatinization of cationic starch granules was used to produce discrete and soft CS spheres, followed by stabilizing the swollen granules with STMP cross-linking. The STMP cross-linking in CS microgel was composed of both ionic and chemical cross-linking. The preparation and the structure of CS microgel were concluded and illustrated in Figure 6.

As evidenced in the changes of morphology, size distribution, and swelling ratio of CS microgels under various environments, a moderate STMP cross-linking was desired for stabilizing the structure of CS microgel while keeping the volume tunable for responding to environmental changes. In this study, ionic cross-linking showed relatively little effect on the swelling ratio, and the pH response of the microgels was dominated by the abundant cationic groups.

Having an advantage of pH insensitivity (pH 3–9) plus its thickening ability, the moderately cross-linked CS microgels may be used as an alternative eco-friendly thickener for personal care products and related fields. Further studies will be pursued to evaluate the storage stability of CS microgels and the interaction with other ingredients for such applications.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgments

This work was supported by the Ministry of Science and Technology (MOST) grants 105-2320-B-002-023-MY3 and 105-2917-I-002-034, Taipei, Taiwan. The authors also thank Professor Montgomery T. Shaw (UConn) for helpful discussions and Anton Paar USA for providing the instrument and partial financial support.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

cationic starch, rheology, sodium trimetaphosphate (STMP), starch microgels, swelling behavior

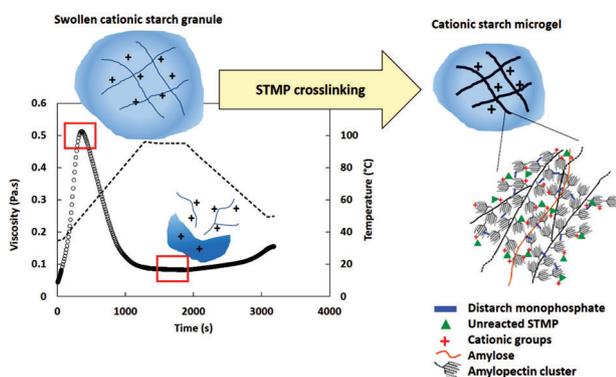


Figure 6. Illustration of the processes to prepare the CS microgel as well as the cross-linkings inside CS microgel.

Received: October 15, 2018

Revised: April 18, 2019

Published online:

-
- [1] N. B. Graham, A. Cameron, *Pure Appl. Chem.* **1998**, *70*, 1271.
- [2] F. A. Plamper, W. Richtering, *Acc. Chem. Res.* **2017**, *50*, 131.
- [3] H. M. Shewan, J. R. Stokes, *J. Food Eng.* **2013**, *119*, 781.
- [4] M. Hayase, in *Cosmetic Science and Technology: Theoretical Principle and Applications* (Eds: K. Sakamoto, R. Lochhead, H. Maibach, Y. Yamashita), Elsevier, UK **2017**, Ch. 10.
- [5] J. B. Thorne, G. J. Vine, M. J. Snowden, *Colloid Polym. Sci.* **2011**, *289*, 625.
- [6] H.R. 1321-Microbead-free waters act of 2015. *Congress. Gov.* Congress. Gov. USA. Retrieved 14 July **2017**.
- [7] H. M. Shewan, J. R. Stokes, *J. Colloid Interface Sci.* **2015**, *442*, 75.
- [8] S. H. Ching, N. Bansal, B. Bhandari, *Food Res. Int.* **2015**, *75*, 182.
- [9] T. Farjami, A. Madadlou, *Food Hydrocolloid.* **2017**, *62*, 262.
- [10] Y. Dziechciarek, J. J. G. van Soest, A. P. Philipse, *J. Colloid Interface Sci.* **2002**, *246*, 48.
- [11] Y. Li, J. M. Kleijn, M. A. C. Stuart, T. Slaghek, J. Timmermans, W. Norde, *Soft Matter* **2011**, *7*, 1926.
- [12] S.-Y. Chang, H.-M. Lai, *Food Hydrocolloid.* **2016**, *56*, 254.
- [13] AOAC Official Method 992.23. Combustion method. AOAC International, Gaithersburg, MD, USA, **2000**.
- [14] AACC Method 76-21.01. General Pasting Method for Wheat or Rye Flour or Starch Using the Rapid Visco Analyzer. AACC International, St. Paul, MN, USA, **2000**.
- [15] W.-Y. Kuo, H.-M. Lai, *Carbohydr. Polym.* **2007**, *69*, 544.
- [16] Y. Li, R. de Vries, T. Slaghek, J. Timmermans, M. A. C. Stuart, W. Norde, *Biomacromolecules* **2009**, *10*, 1931.
- [17] EPA. In: J. T. Crees, C. A. Brockhoff, T. D. Marin (Eds.), Method 200.8: Determination of trace elements in waters and wastes by inductively coupled plasma-mass spectrometry, Cincinnati, OH, USA, **1994**.
- [18] AOAC Method 991.43. Total dietary fiber enzymatic gravimetric method. AOAC International, Gaithersburg, MD, USA, **2000**.
- [19] I. M. Krieger, T. J. Dougherty, *Trans. Soc. Rheol.* **1959**, *3*, 137.
- [20] C.-N. Wu, H.-M. Lai, *Carbohydr. Polym.* **2019**, *208*, 201.
- [21] H. Han, J. Hou, N. Yang, Y. Zhang, H. Chen, Z. Zhang, Y. Shen, S. Huang, S. Guo, *Int. J. Biol. Macromol.* **2019**, *126*, 37.
- [22] K. Woo, P. A. Seib, *Carbohydr. Polym.* **1997**, *33*, 263.
- [23] K. Manoi, S. S. H. Rizvi, *Carbohydr. Polym.* **2010**, *81*, 687.
- [24] R. Shukri, Y.-C. Shi, *Food Chem.* **2017**, *214*, 90.
- [25] T. Colla, C. N. Likos, Y. Levin, *J. Chem. Phys.* **2014**, *141*, 234902.
- [26] C. Chang, M. He, J. Zhou, L. Zhang, *Macromolecules* **2011**, *44*, 1642.
- [27] J. A. Dean, *Lange's Handbook of Chemistry*, 13th ed., McGraw-Hill Book Co., NY **1985**.
- [28] R. Borrega, M. Cloitre, I. Betremieux, B. Ernst, L. Leibler, *Europhys. Lett.* **1999**, *47*, 729.
- [29] B. H. Tan, K. C. Tam, Y. C. Lam, C. B. Tan, *J. Rheol.* **2004**, *48*, 915.
- [30] D. Nordqvist, T. A. Vilgis, *Food Biophys.* **2011**, *6*, 450.
- [31] A. Benchabane, K. Bekkour, *Colloid Polym. Sci.* **2008**, *286*, 1173.