

The Effects of Neutralization on the Dynamic Rheology of Polyelectrolyte Microgel Mucilages

John C. Harrington

Ashland Water Technologies, Wilmington, Delaware 19808

Received 18 March 2011; accepted 2 February 2012

DOI 10.1002/app.36946

Published online in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The dynamic rheological properties of a model poly(acrylic acid) microgel mucilage in the close-packed concentrated region (reduced concentration $cQ > 1$) were evaluated as a function of the degree of neutralization, $\alpha = [\text{NaOH}]/[\text{COOH}]$. As the parent microgel is neutralized, up to an order of magnitude increase is observed in the swelling ratio Q , dynamic modulus, and yield properties. Four regions were observed where the dynamic rheological properties exhibited a different power law dependence with increasing α . The dynamic yield strain does not change remarkably with increased neutralization, whereas the dynamic yield stress increases more

than 10-fold. This supports a mechanism where the yield strain depends on geometric considerations, whereas the yield stress reflects the stress required to force microgels past adjacent microgels. A linearity observed between modulus and dynamic yield stress with increased neutralization suggests a concerted expansion and affect on the rheological properties with the microgel core and emanating polymer chains. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: microgels; polyelectrolytes; polymer rheology; solution properties; viscoelastic properties

INTRODUCTION

Crosslinked polyelectrolyte microgels are used as rheological additives in diverse applications, such as industrial and consumer formulations, personal care, and pharmaceuticals.^{1–6} The crosslinked structure provides a high elasticity and yield stress which aids in suspending materials or stabilizing formulations, and a highly shear-thinning region above the yield stress which imparts ease of spreading or flow. The polyelectrolyte microgels are typically poly(acrylic acid), where the weak carboxylic acid is readily ionized with a suitable base, providing chain expansion and an increase in rheological properties due to mutual repulsion of the charge groups.¹ Ketz et al. described these materials as discrete microgels at dilute concentrations, which form a close-packed lattice structure above a critical concentration C^* .⁷ The discrete microgel structure is different from a polyelectrolyte gel, which is comprised of a continuous matrix of crosslinked polyelectrolyte. Piau explained concentrated solutions of microgels as glasses of individual elastic sponges, which display elastoviscoplastic flow properties.⁸

The close-packed lattice structure is a biphasic system, comprised of a continuous water phase and a discontinuous microgel polymer phase, with the discontinuous phase dominating the liquid macroviscosity. The microviscosity of the continuous water phase can be up to several orders of magnitude lower than the macroviscosity, and increases with polymer concentration and degree of neutralization.⁹ Mapping the 2D trajectories of fluorescent particles introduced into a microgel mucilage demonstrated that particles become “trapped” within the microgels, and can “escape” into the continuous phase, eventually becoming “trapped” again.¹⁰ The particle diffusion and trajectory decreases with increased polymer concentration as the system becomes closer packed, and the fraction of the continuous water phase decreases.

The polyelectrolyte microgels exhibit unique properties compared with noncrosslinked polyelectrolytes as a function of concentration. Above the critical overlap concentration C^* , noncrosslinked polymers interpenetrate and form entanglements which provide a moderate viscosity increase, but relax within the experimental time frame. Polyelectrolyte microgels above C^* cannot interpenetrate to the same degree, and form a highly concentrated close-packed structure, resulting in a dramatic viscosity increase and the development of a yield stress.⁷ A recoverable strain above C^* with the polyelectrolyte microgels suggests some degree of particle deformation and interpenetration.

Correspondence to: J. C. Harrington (jcharrington@ashland.com).

A higher degree of crosslinking with the microgel provides a higher modulus and viscosity, along with a stronger gel, as the dynamic modulus was less variant with frequency.^{2,3,11} A lower intrinsic viscosity is observed with a higher degree of crosslinking, resulting in a higher C^* , requiring a higher microgel concentration to form a close-packed structure.^{11,12} The crosslink density determined by dynamic oscillation experiments are a decade lower than predicted by swelling experiments, which is attributed to network defects in the crosslinked system. A "star-like" structure is proposed based upon these network defects, comprising a highly crosslinked microgel core with dangling polymer chains emanating from the core.^{12,13} This simplified depiction is for illustrative purposes only, as the dimensions and composition of the core relative to the emanating chains have not been determined.

Although the yield stress increases with higher concentration,^{3,7,13,14} the yield strain is generally independent of concentration. This suggests a physical model where with increased concentration, a larger force is required to disrupt the close-packed lattice to permit fluid flow, whereas the strain required to move microgels past adjacent microgels was independent of concentration and depends only on geometric considerations.⁷

Rheological studies of these microgels have used steady-state rotational,^{5,7,8} dynamic oscillation experiments,² or both,^{3,4,7} with the dynamic oscillation experiments considered to be more effective in probing the material microstructure and dynamics.^{2-4,7}

The change in rheological properties upon microgel neutralization has been documented. The shear and dynamic viscosity increase as the pH increases from native pH to a pH of ~ 6 , are constant from pH 6 through pH 8, then decrease as the pH is further increased from 8 to 12.^{1,3,4,9,15} The dynamic yield and modulus properties have been evaluated at a nominal number of pH or α values. The microgels at neutral pH demonstrate a higher modulus, viscosity, and yield stress than at the native, or un-neutralized, microgel pH. However, these materials at native pH exhibit a less frequency dependent G' and a lower $\tan \delta$ than the polymer at neutral pH, suggesting more elastic properties with the un-neutralized parent microgel.^{2,3}

This study was undertaken to understand the effects of neutralization on the dynamic rheological properties of a model polyelectrolyte microgel, using a wide range of neutralization values.

An un-neutralized poly(acrylic acid) parent microgel was systematically neutralized to the poly(acrylic acid-co-sodium acrylate) microgel. Eighteen levels of neutralization were used, with α ranging from 0.0001 to 10.0. The dynamic rheological properties dependence on the degree of neutralization of a model microgel was reported, and a mechanism of

the effects of neutralization on polyelectrolyte microgels is presented.

EXPERIMENTAL

Sample preparation

A poly(acrylic acid) microgel powder (Aldrich, Product No. 306231, Milwaukee, WI) was used as received. Poly(acrylic acid) is a weak acid which can be readily ionized, and thus, is a good candidate for evaluating neutralization effects.¹ The microgel powder moisture content was determined to be 6.0% via thermo-gravimetric analysis. A 2.66% active mucilage was prepared by dissolving the powder into nano-pure water ($<2 \mu\text{S}/\text{cm}$) using an overhead mechanical stirrer equipped with a U-shaped paddle (Cole Parmer, Vernon Hill, IL) at 200 rpm. The mucilage was mixed for 6 h until a homogenous material was obtained. The pH of the parent microgel mucilage was determined to be 2.3 (Orion 230A, Mettler-Toledo, Columbus, OH). The mucilages were stored in a dark environment at 4°C to minimize the potential of polymer degradation. A microgel concentration of 2% was used for all mucilages. Eighteen separate poly(acrylic acid-co-sodium acrylate) microgel mucilages were prepared from the poly(acrylic acid) microgel parent by adding calculated amounts of sodium hydroxide (Aldrich, Milwaukee, WI) and nano-pure water to the parent microgel mucilage to achieve the desired degree of neutralization at a 2% microgel concentration. The solutions were centrifuged at 4000 rpm for 2 min before conducting rheological experiments to eliminate air bubbles. The degree of neutralization α is defined as the molar equivalents of sodium hydroxide added per acrylic acid monomer, $[\text{NaOH}]/[\text{COOH}]$. The effective charge density and degree of ionization of the resultant polyelectrolyte microgels are likely lower than the calculated degree of neutralization due to counterion condensation.¹⁶

Mucilage characterization and rheology

The swelling ratio Q was determined via analytical ultracentrifuge.¹² The mucilage was centrifuged (Avanti J-21I, Beckman Coulter, Brea, CA) for 2 h at 25,000 rpm ($77,600 \times g$). The swelling ratio Q is calculated by the weight ratio of swollen to dry microgel. The molecular weight between crosslinks M_C was determined by swelling experiments using the Flory-Rehner equation:

$$-\left[\ln(1 - V_r) + V_r + \chi V_r^2\right] = \rho V_s M_C^{-1} [V_r^{1/3} + 0.5V_r] \quad (1)$$

where V_r is the equilibrium swollen microgel volume fraction, χ is the microgel-solvent interaction

parameter, V_s is the solvent molar volume, ρ is the microgel density, and M_C is the number average molecular weight between crosslinks. A χ value of 0.44 was used.

Rheological tests were conducted with a Paar Physica UDS 200 Dynamic Spectrometer (Anton Paar, Ashland, VA) using a parallel plate geometry with a 50 mm diameter and a 1 mm gap. The temperature was controlled at a constant 25°C using a Peltier plate. The mucilage sample was placed into the geometry using a syringe with the tip removed to eliminate any shear effects during sample loading. The mucilage was allowed to remain unperturbed for 20 min before testing to allow for relaxation of loading stresses⁷; no change in modulus properties was noted after 2 min equilibration. A thin film of Drakeol 5 light mineral oil (Penreco, Karns City, PA) was applied to the solution surface to minimize water evaporation.

Dynamic oscillation experiments were used exclusively, as they are reported to provide a better means to probe microgel dynamics.^{2,3} Frequency sweep experiments were conducted at frequencies ranging from 0.063 to 63 radians per second (ω) at a strain (γ) level of 0.2%, which was determined to be in the linear viscoelastic region for all polymer solutions at several test frequencies. A γ sweep was then conducted at a constant ω of 6.3 radians per second, with γ increasing from 0.1% to 1000%. The storage modulus (G') and loss modulus (G'') were determined from the oscillatory data using the instrument software according to:

$$G' = (\tau_0/\gamma_0) \cos \delta \quad (2)$$

$$G'' = (\tau_0/\gamma_0) \sin \delta \quad (3)$$

where τ_0 is the stress amplitude, γ_0 is the strain amplitude, and δ is the phase angle shift between the stress and strain amplitude.¹⁷

The plateau modulus (G_N) was determined from ω sweep data as the G' value where G'' is at a minimum.¹⁷ The dynamic critical stress σ_c and critical strain γ_c were determined from the amplitude sweep as the respective stress and strain values at the onset of the nonlinear G' elastic response. The dynamic yield stress σ_Y and yield strain γ_Y were determined from the amplitude sweep as the respective stress and strain values where G' has decreased in value to where it is equal to G'' .¹⁸

RESULTS

Microgel mucilage identification and characterization

Sample identification, degree of neutralization, and swelling ratio Q for the 19 microgel mucilages are listed in Table I. The degree of neutralization α was

TABLE I
Mucilage Identification and Properties

Sample ID	α^a	Q^b	cQ^c
PMG.0	0.0	52.65	1.05
PMG.0001	0.0001	55.50	1.11
PMG.001	0.0010	62.27	1.25
PMG.0018	0.0018	59.40	1.19
PMG.0032	0.0032	69.28	1.39
PMG.005	0.005	75.34	1.51
PMG.01	0.010	97.9	1.96
PMG.018	0.018	131.33	2.63
PMG.032	0.032	164.72	3.29
PMG.05	0.05	301.19	6.02
PMG.1	0.10	393.72	7.87
PMG.18	0.18	560.02	11.20
PMG.32	0.32	561.35	11.23
PMG.5	0.50	558.19	11.16
PMG1.0	1.0	423.53	8.47
PMG1.8	1.8	190.45	3.81
PMG3.2	3.2	124.18	2.48
PMG5.0	5.0	94.71	1.89
PMG10.0	10.0	70.85	1.42

^a $\alpha = [\text{NaOH}]/[\text{COOH}]$, the equivalents of sodium hydroxide per acrylic acid monomer.

^b $Q = \text{swelling ratio}$; ratio of swollen to dry microgel.

^c $cQ = \text{reduced concentration at 2\% microgel}$.

0 for the un-neutralized microgel parent, and ranged from 0.0001 to 10.0 for the neutralized microgels. Four levels of neutralization were prepared per decade of neutralization, equally spaced on a logarithmic scale. The sample nomenclature used throughout this report for the un-neutralized polyelectrolyte microgel parent is PMG.0. The neutralized microgels are identified by the degree of neutralization, for example, $\alpha = 0.001$ is PMG.001, $\alpha = 0.1$ is PMG.1, and $\alpha = 1.0$ is PMG1.0, respectively.

The value of Q for the un-neutralized parent microgel was 52.65, and increased a decade to 560 for the highest level of neutralization. The reciprocal equilibrium swollen microgel volume fraction V_r^{-1} was determined to be 57.4, resulting in a M_C of 2.6×10^5 g/mol per eq. (1).

Dynamic rheological properties

Frequency sweep data of G' and G'' using a representative $\alpha = 0.0, 0.01, \text{ and } 1.0$ are illustrated in Figure 1. The un-neutralized microgel parent is highly elastic before neutralization, albeit at a much lower modulus compared with the neutralized microgels. As the degree of neutralization is sequentially increased, a concurrent increase of modulus is observed. G' is a decade larger than G'' and is largely invariant with frequency at all levels of neutralization. A terminal region where the microgel exhibits liquidlike properties with $G' < G''$ was not evident at low frequencies. The G' and G'' values of PMG1.0, the sample with the highest illustrated level

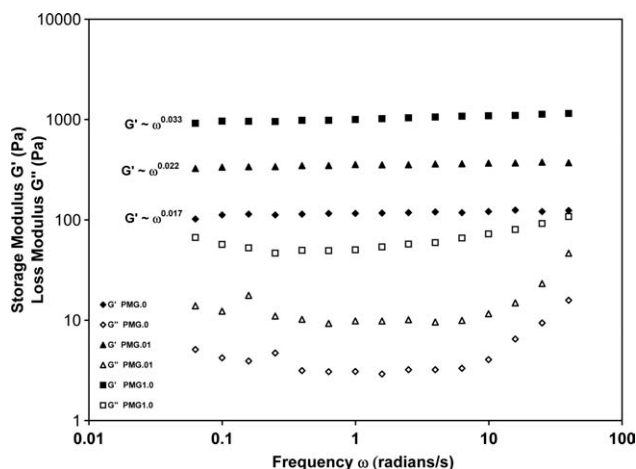


Figure 1 Storage G' and loss modulus G'' as a function of frequency ω for the degree of neutralization $\alpha = 0, 0.01,$ and 1.0 .

of neutralization, are approximately a decade higher than the un-neutralized parent PMG0.

A linear viscoelastic region is observed at low strain amplitude levels for G' and G'' with the three representative microgels, as shown in Figure 2. G' in the linear region increases with increased neutralization, with G' for PMG1.0 being approximately a decade higher than the G' for PMG0. As the strain amplitude increases to values in the range of 1%, G' becomes nonlinear, indicating the critical strain γ_C has been attained. With further increases in strain amplitude above 10%, G' decreased remarkably in magnitude. Concurrent with the decrease in G' at γ_C , a gradual increase in G'' occurs. As γ further increases above γ_C , a maximum storage modulus G'_{max} is observed, which generally occurs around 57% strain amplitude. At γ of $\sim 100\%$, G' decreased in value to equal G'' , identified as the dynamic yield strain γ_Y . This indicates the transition from an elastic

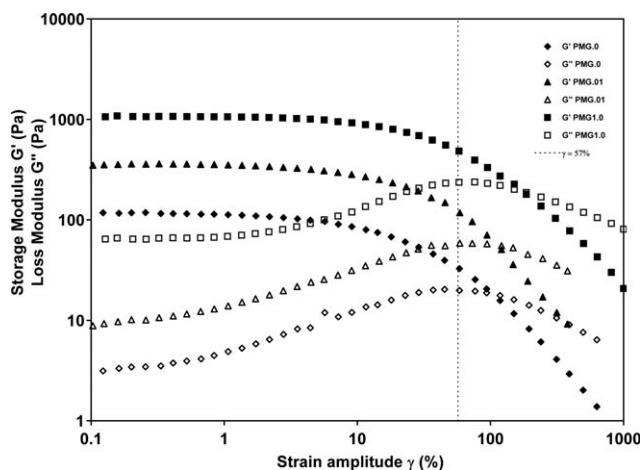


Figure 2 Storage G' and loss G'' modulus as a function of oscillatory strain amplitude γ . The vertical dotted line represents $\gamma = 57\%$.

state to a viscous state due to disruption of the closed packed structure.¹⁸ At the highest γ value of 1000%, G' had decreased up to two orders of magnitude from the initial value in the linear viscoelastic region. The data in Figure 2 illustrate that γ_C , G'_{max} , and γ_Y do not increase notably with increased neutralization.

G' and G'' were then evaluated as a function of the stress amplitude, which exhibited a different net effect with microgel neutralization than the strain amplitude. The presence of an initial linear viscoelastic region, followed by a decrease in G' and the development of G''_{max} , as was observed with the strain amplitude experiments, was also observed with the stress amplitude. However, Figure 3 illustrates that τ_C , G'_{max} , and τ_Y are highly dependent upon the degree of neutralization, in direct contrast to the strain amplitude which is not affected to a great extent by increasing α . With increased neutralization, a higher stress amplitude is required for τ_C , G'_{max} , and τ_Y , which increased a respective 24 times, 17.5 times, and 18 times as α increases from 0 to 1.0. These are approximately a decade higher than the strain amplitude responses of a 3.3 times increase for γ_C , a 1.7 times increase for G'_{max} , and 1.9 times increase for γ_Y under the same neutralization conditions.

The effects of neutralization on the specific rheological properties for all 19 samples were then evaluated. Figure 4 illustrates G_N , Figure 5 illustrates the dynamic strain responses γ_C and γ_Y , and the dynamic stress responses τ_C and τ_Y are shown in Figure 6.

Below $\alpha = 0.0018$, the rheological properties of the neutralized microgels are generally equal to or slightly greater than the un-neutralized microgel PMG-0. A slight increase in G_N and τ_Y is observed with α less than 0.0018 when compared with PMG0. As the level of neutralization increases, a critical

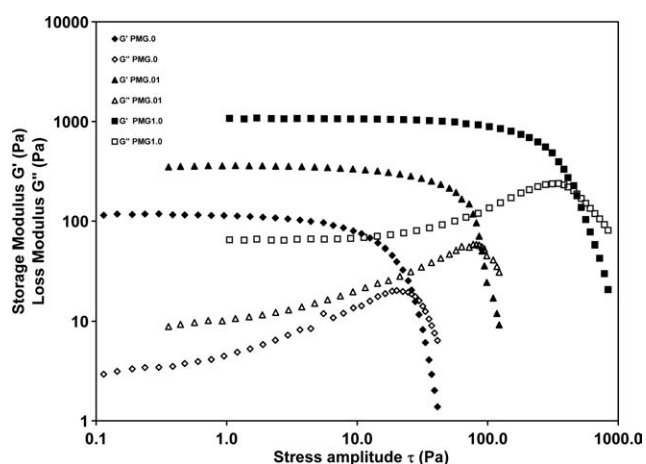


Figure 3 Storage G' and loss G'' modulus as a function of oscillatory stress amplitude τ .

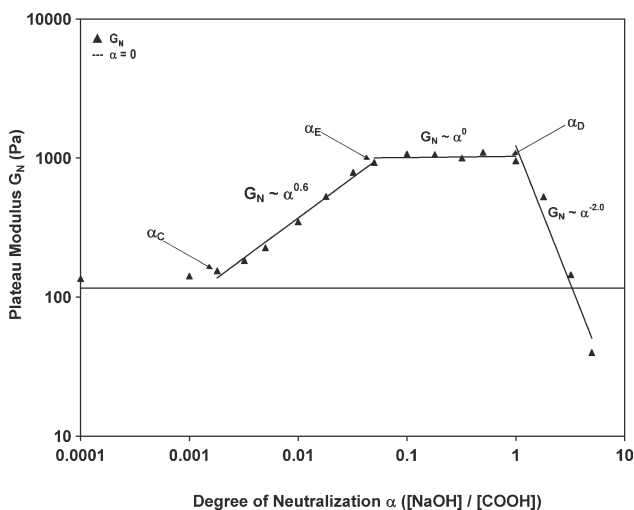


Figure 4 Plateau modulus G_N as a function of the degree of neutralization α . The solid lines between the neutralization transitions represent the least squares best fit.

neutralization α_C is encountered at $\alpha = 0.0018$, where the rheological properties G_N , τ_C and τ_Y increase remarkably. These rheological properties can be fit to a power-law dependence as a function of neutralization above α_C , as $G_N \sim \alpha^{0.6}$, $\tau_C \sim \alpha^{0.8}$, and $\tau_Y \sim \alpha^{0.7}$. The α_C transition for the strain responses occurs in the range of $\alpha = 0.005$, a slightly higher α than the stress responses. The strain responses also exhibit a lower power-law exponent than the stress responses, as $\gamma_C \sim \alpha^{0.4}$ and $\gamma_Y \sim \alpha^{0.3}$.

An equilibrium neutralization α_E occurs for the rheological properties, beginning in the range of $\alpha = 0.05$ to 0.10 , and terminates at $\alpha = 1.0$. In this equilibrium region, the rheological properties G_N , τ_C , and γ_C are invariant with α . The yield responses, τ_Y and γ_Y , are highly invariant with neutralization in this region, with a slight positive slope.

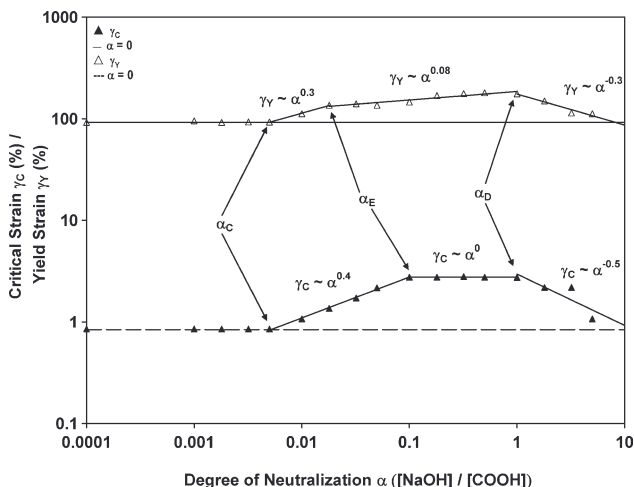


Figure 5 Dynamic critical strain γ_C and yield strain γ_Y as a function of α .

Finally, a degradative neutralization α_D is encountered at $\alpha = 1.0$, where the further addition of sodium hydroxide neutralizing agent produces a decrease in values for all rheological responses. The decrease in values above α_D for the modulus and stress responses is greater than the increase between α_C and α_E , as $G_N \sim \alpha^{-2}$, $\tau_C \sim \alpha^{-2.6}$, and $\tau_Y \sim \alpha^{-2.3}$. The decrease in values for the strain responses above α_D is consistent with the increase above α_C , as $\gamma_C \sim \alpha^{-0.5}$ and $\gamma_Y \sim \alpha^{-0.3}$. It is noted that all rheological properties for $\alpha = 5.0$ are lower than the un-neutralized parent microgel. Furthermore, addition of excess sodium hydroxide to a calculated $\alpha = 10.0$ produced a mucilage that was qualitatively of low viscosity, which is likely due to counterion condensation. A linear viscoelastic region was not measurable with this sample, and as such no subsequent rheological characterizations were conducted.

DISCUSSION

The published literature explains the rheological properties of polyelectrolyte microgels in terms of a close-packed lattice structure, which behaves as an elastic solid above a reduced concentration cQ of 1.^{19,20} Below this concentration, the swollen particles do not interact. The value of cQ for the un-neutralized parent microgel is above 1, indicating the system is in the close-packed concentration region. With increased concentration, the microgel becomes closer packed, resulting in an increase in modulus and viscosity.²¹ The G' storage modulus changes with concentration (C) can be fit to a power-law as $G' \sim C^x$, with $x = 0.9$ for an un-neutralized poly(acrylic acid) microgel,³ and x ranging from 0.6 to 0.75 for fully neutralized, poly(acrylic acid) microgels.^{3,7}

Polyelectrolytes expand when ionized due to interchain and intrachain electrostatic charge

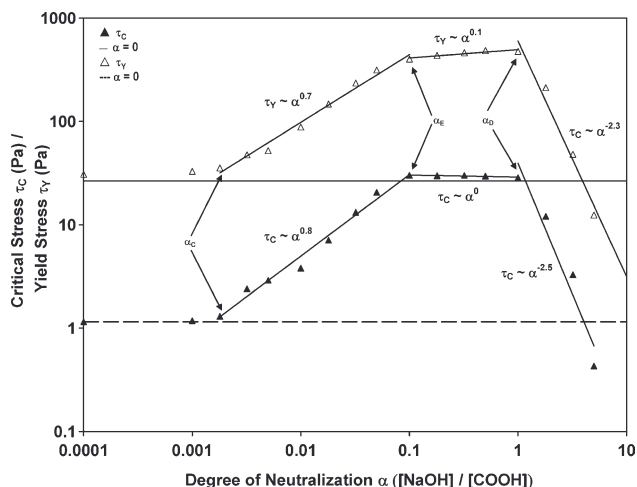


Figure 6 Dynamic critical stress τ_C and yield stress τ_Y as a function of α .

repulsion. Flory derived the expansion of a polyelectrolyte e_x as a function of the degree of polyelectrolyte ionization i as $e_x \sim i^2$.²² It is noted that the degree of ionization is related to α , but is lower than α due to counterion condensation.¹⁶ The polyelectrolyte expansion results in an increase in hydrodynamic volume and chain entanglements, and a concurrent change in the rheological properties.^{23–26} The charge repulsion does not fully explain the polymer expansion, as the charged species may also be screened by proximal counter-ions. The charged species within the polymer network will achieve an equilibrium state, with a higher concentration of counter-ions within the polymer network than in the external phase. The higher internal concentration of counter-ions will result in an osmotic pressure differential between the polymer network and the external aqueous phase, thus providing an osmotic pressure mechanism for polymer expansion. The mechanisms of charge repulsion or osmotic pressure are mutually related, resulting in identical results if the expansive forces were evaluated quantitatively.²²

Experimental results for noncrosslinked polyelectrolytes with α ranging from 0.05 to 0.50 demonstrate a power law relationship $G' \sim \alpha^x$, where x ranges from 0.35 to 0.70, and x decreases with increased concentration.²⁷ It is noted that at an equivalent 2% concentration, $x = 0.62$, consistent with this study.

The swelling of a polyelectrolyte gel is determined by the total free energy ΔF of the system

$$\Delta F = \Delta F_{\text{mix}} + \Delta F_{\text{el}} + \Delta F_{\text{ion}} \quad (4)$$

where ΔF_{mix} is the free energy of mixing, ΔF_{el} is the elastic energy, and ΔF_{ion} .²² Above $\alpha = 0.0018$, in the region where the rheological properties increase with neutralization, the ionic contribution is greater than the elastic contribution, which permits the microgel to swell with increased neutralization. The system becomes closer-packed, resulting in an increase in dynamic modulus and yield properties. The power law exponent x from $G' \sim \alpha^x$ was determined in previous studies to range from 0.40 to 0.45 for the neutralization of poly(acrylic acid) microgels.^{3,4,28}

The experimentally determined M_C of 2.6×10^5 g/mol is in agreement with reported swelling experiments of 1.0×10^5 g/mol to 2.4×10^5 g/mol.¹¹ Tetrafunctional allyl pentaerythritol would yield an approximate crosslinking level of 0.03%.

Although the dynamic modulus and yield will increase with concentration and neutralization, an equilibrium region, such as that which occurs between $\alpha = 0.10$ and $\alpha = 1.0$, is a function of neutralization only. Increasing the microgel concentration or volume fraction will not produce an equi-

librium region. Equation (4) suggests that in the equilibrium region the total free energy of the system is zero. As the gel expands at lower levels of neutralization due to a greater ionic contribution, there is a balance between the expansive ionic forces (increasing neutralization) and the contractive elastic forces in the equilibrium region. The equilibrium region is not a maximum packing region, which would result in a remarkable increase in modulus and viscosity.⁷

The degradative neutralization α_D was encountered at $\alpha = 1.0$ for all rheological responses. The values of cQ above α_D are greater than 1, suggesting the mucilage is in the close-packed region. It is noted that this transition occurs at a stoichiometric balance between carboxylate functional groups and hydroxide equivalents, where α is unity. The effective charge f will be lower than α due to counter-ion condensation, and f for poly(acrylic acid) will achieve a plateau value in the approximate range of 0.25 at α values greater than 0.80.¹⁶ The decrease in magnitude for the rheological responses with an excess of sodium hydroxide neutralizing agent is due to counterion condensation. In this region, the expansive ionic forces are negligible. The decrease in rheological properties above $\alpha = 1.0$ is specific to inorganic bases such as sodium hydroxide and is not observed with organic bases such as triethanolamine.³

The G' power-law exponents as a function of frequency for these polyelectrolyte microgels are very low (Fig. 1), with $G' \sim \omega^{0.017}$ for PMG0 and $G' \sim \omega^{0.033}$ for PMG1.0. A slight increase in power-law exponents is observed with neutralization, consistent with previous studies.^{2,3} Thus, while the modulus of the ionized polymer PMG1.0 is a decade greater than the un-neutralized parent PMG0, a slightly greater frequency dependence or “softer gel” is observed with the neutralized polymer. The modulus frequency dependence for polyelectrolyte microgels decreases with the level of crosslinking or concentration.

The intrinsic crosslink densities of PMG0 and PMG1.0 are equivalent, and any increase in modulus with increased neutralization is due to additional microgel interactions resulting from microgel expansion. Polymer chain expansion due to neutralization will result in a more stretched polymer chain segment between crosslinks compared with the un-neutralized microgel.²⁹ The material will also take up more solvent with neutralization, and the ionized polymer will contain more intra-polymer water than the neutral polymer. It is proposed that the decreased entropy of the stretched chain segments between crosslinks and the additional intra-polymer water with the neutralized material causes the slight increase in dynamic modulus time dependence compared with the un-neutralized parent microgel.

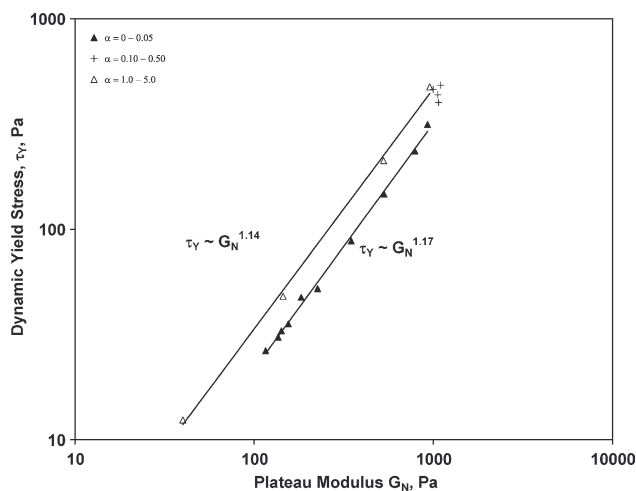


Figure 7 Plot of plateau modulus G_N and dynamic yield stress τ_Y . The solid lines represent the least squares best fit.

The polyelectrolyte microgel has been depicted as possessing a central crosslinked core with linear chains emanating from the core, somewhat analogous to a star shaped polymer structure. This model is based upon a calculated difference in crosslink density between swelling and dynamic shear modulus experiments, where a decade lower value for the shear modulus was thought to be due to the presence of network defects.¹² The dimensions and composition of the core relative to the emanating chains have not been determined.

Figure 7 illustrates a plot of G_N and τ_Y , where a power-law is noted between the modulus and yield stress as the neutralization increases from $\alpha = 0$ to α_E , with $\tau_Y \sim G_N^{1.17}$. Above α_D , the power-law between the modulus and yield stress was $\tau_Y \sim G_N^{1.14}$. Microgel suspensions containing varying crosslink densities demonstrated different slopes in plots of G_N versus rotational τ_Y , where a steeper slope was obtained with lower crosslink density.³⁰ This was attributed to an interpenetration of dangling surface chains, which provided a higher yield stress at a given modulus. The authors concluded that the crosslink density on the inner portion of the material affects modulus and that yield stress is affected by the dangling chains on the particle surface. The material depiction of these microgels is consistent with the present crosslinked polyelectrolyte, exhibiting a central core and emanating chains. Assuming a similar effect of crosslink density and dangling chains on the respective rheological properties, the linear response plot of G_N and τ_Y in Figure 7 suggests an affine contribution from crosslinked core and linear chain expansion upon neutralization. If neutralization were to have a different or varied effect on the core versus the emanating chains with neutralization, an inflection would be

observed in G_N and τ_Y plots. The linear response plot over a wide range of neutralization, occurring both with the modulus and yield stress increasing above α_C and above α_D where the rheological properties are decreasing, suggests a concerted expansion and effect on the rheological properties between the core and emanating chain species.

The close-packed lattice structure for microgels has demonstrated an increased yield stress with higher concentration, whereas the yield strain has been shown to be invariant with concentration.⁷ This was explained to occur due to geometric considerations, in that the stress required to force polymer particles past neighboring particles and induce flow increases with higher concentration as the lattice becomes closer-packed.³¹ The strain required to induce flow in the close-packed lattice is independent of concentration, depending only on the geometric requirement to force particles past proximal particles to induce flow. Spherical models determined an $\sim 57\%$ yield strain in a close-packed lattice.^{7,32} This study demonstrated a similar affect on yield stress and strain with increased neutralization as was observed with increased concentration, as the yield stress increased with higher neutralization, but the yield strain was consistent at all levels of α . Thus, chain expansion upon neutralization causes the system to become closer-packed and increases the yield stress. The yield strain is not affected by increased neutralization, depending solely on the geometry required to force particles past proximal particles and induce flow.

A G'' strain hardening phenomena was noted in both concentration and neutralization studies with crosslinked polyelectrolytes, with a maximum G'' occurring in the range of 57% strain, consistent with geometric models.⁷ As G'' reflects the effective volume occupied by the mechanically active entanglements, the strain hardening phenomena depends upon interparticle interactions, specifically interparticle distance.³³ With increased strain, neighboring particles are forced closer to one another, increasing the concentration of dangling chains per volume and decreasing the interparticle distance. Once the particles have been forced past adjacent particles, the interparticle distance and concentration of dangling chains decreases, as measured by the resultant decrease in G'' .

CONCLUSIONS

A model un-neutralized poly(acrylic acid) parent microgel at a reduced concentration $cQ > 1$ in deionized water is highly elastic, exhibiting properties of a close-packed structure. As the parent microgel is neutralized with sodium hydroxide, up to a 10-fold increase in dynamic modulus and yield properties was observed. Four regions were observed where

the rheological properties exhibit a different power law dependence as a function of the level of neutralization, as α increased from 0 to 10. Between $\alpha = 0.0018$ and $\alpha = 0.10$, the microgel swells with increased neutralization, resulting in an increase in dynamic yield properties as the system becomes closer packed. An equilibrium region occurs between $\alpha = 0.10$ and $\alpha = 1.0$ as the expansive ionic forces are balanced by the contractive elastic forces. As excess caustic neutralizing agent is added above $\alpha = 1.0$, a decrease in the rheological properties occurs due to counterion condensation.

Previous studies proposed that microgels are comprised of a central crosslinked core with emanating chains, where the core will affect the modulus and the exterior chains impact yield stress. A linearity of modulus and yield stress with increased α suggests a concerted affect on the rheological properties with the crosslinked core and the extended chain species. The dynamic yield stress increases with α , whereas the yield strain does not change with α . As was surmised with concentration effects, the yield strain is affected solely on the geometry required to force particles past adjacent particles, whereas increased stress is required as α increases to induce flow.

References

- Lochhead, R. In *Rheological Properties of Cosmetics and Toiletries*; Laba, D., Ed.; Marcel Dekker: New York, 1993; Chapter 8.
- Barry, B. W.; Meyer, M. C. *Int J Pharm* 1979, 2, 27.
- Kim, J. Y.; Song, J. Y.; Lee, E. J.; Park, S. J. *Colloid Polym Sci* 2002, 281, 614.
- Islam, M. T.; Rodriguez-Hornedo, N.; Ciotti, S.; Ackermann, C. *Pharm Res* 2004, 21, 1192.
- Taberner, T. S.; Martin-Villodre, A.; Pla-Delfina, J. M.; Herraiz, J. V. *Int J Pharm* 2002, 233, 43.
- Shah, A. J.; Donovan, M. D. *Pharm Sci Tech* 2007, 8, E1.
- Ketz, R. J.; Prud'homme, R. K.; Graessley, W. W. *Rheol Acta* 1988, 27, 531.
- Piau, J. M. *J Non-Newtonian Fluid Mech* 2007, 144, 1.
- Lochhead, R. Y.; Davidson, J. A.; Thomas, G. M. In *Polymers in Aqueous Media*; Glass, E. J., Ed.; American Chemical Society: Washington, DC, 1989; Chapter 7.
- Oppong, F. K.; Rubatat, L.; Frisken, B. J.; Bailey, A. E.; de Bruyn, J. R. *Phys Rev E* 2006, 73, 041405.
- Nae, H. N.; Reicher, W. W. *Rheol Acta* 1992, 31, 351.
- Carnali, J. O.; Naser, M. S. *Colloid Polym Sci* 1992, 270, 183.
- Geraint, G. P.; Barnes, H. A. *Rheol Acta* 2001, 40, 499.
- Barry, B. W.; Meyer, M. C. *Int J Pharm* 1979, 2, 1.
- Curran, S. J.; Hayes, R. E.; Afacan, A.; Williams, M. C.; Tanguy, P. A. *J Food Sci* 2002, 67, 176.
- Konop, A. J.; Colby, R. H. *Macromolecules* 1999, 32, 2803.
- Ferry, J. W. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.
- Lin, Y. C.; Koenderink, G. H.; MacKintosh, F. C.; Weitz, D. A. *Macromolecules* 2007, 40, 7714.
- Taylor, N. W.; Gordon, S. H. *J Appl Polym Sci* 1982, 27, 4377.
- Taylor, N. W.; Bagley, E. B. *J Polym Sci Polym Phys Ed* 1975, 13, 1133.
- Wolfe, M. S. *Prog Org Coat* 1992, 20, 487.
- Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
- Noda, I.; Tsuge, T.; Nagasawa, M. *J Phys Chem* 1970, 74, 22.
- Konno, A.; Kaneko, A. *Die Makromol Chem* 1970, 138, 189.
- Okamoto, H.; Wada, Y. *J Polym Sci Polym Phys Ed* 1974, 12, 2413.
- Yamaguchi, M.; Wakutsu, M.; Takahashi, Y.; Noda, I. *Macromolecules* 1992, 25, 470.
- Harrington, J. C. *J Appl Polym Sci* 2008, 107, 3310.
- Tiu, C.; Guo, J.; Uhlherr, P. H. T. *J Ind Eng Chem* 2006, 12, 653.
- Rubinstein, M.; Colby, R. H.; Dobrynin, A. V.; Joanny, J. *Macromolecules* 1996, 29, 298.
- Senff, H.; Richtering, W. *Colloid Polym Sci* 2000, 278, 830.
- Chen, L. B.; Zukoski, C. F. *J Chem Soc Faraday Trans* 1990, 84, 2629.
- Princen, H. M. *J Colloid Interface Sci* 1983, 91, 160.
- Cram, S. L.; Brown, H. R.; Spinks, G. M.; Hourdet, D.; Creton, C. *Macromolecules* 2005, 38, 2981.