



Viscoelasticity of near-critical silica-polyacrylamide hydrogel nanocomposites



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ABSTRACT

The sol-gel transition of silica-polyacrylamide hydrogel nanocomposites is studied when approaching the gel point by independently varying the nanoparticle (NP) and chemical crosslinker concentrations. Time-concentration-superposition (TCS) principles are applied to ascertain the effect of NPs on dynamics at the gel point. Doping dilute and concentrated polyacrylamide (PA) solutions with silica NPs indicates that these particles do not crosslink PA; neither do they form percolating networks. Nevertheless, silica NPs interact with PA to influence the storage and loss moduli to a much greater degree than expected for passive fillers. Interestingly, when silica NPs are embedded in very weakly chemically crosslinked PA (with a bis crosslinker concentration that would otherwise not form PA hydrogels), they significantly enhance the effective degree of crosslinking, forming viscoelastic solids. From TCS analysis of dynamics at the gel point, the bond probability is found to scale with the NP volume fraction as $p \sim \phi^{1.5}$, whereas chemical crosslinking furnishes a bond probability that is linear in the crosslinker concentration.

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1. Introduction

Hydrogels have widespread biomedical applications [1]. Their tuneable mechanical properties and similarities to biological tissues make them attractive for tissue engineering [2] and drug delivery [3]. However, chemically crosslinked hydrogels (CCHs) are usually soft, and stiff CCHs are brittle. The mechanical properties of CCHs depend on a heterogeneous microstructure [4–6] that arises from a broad distribution of polymer chain lengths between irreversible, randomly distributed chemical crosslinks.

Chemically crosslinked polyacrylamide (PA) hydrogels are one of the most widely studied [4,5,7,8]. These are typically synthesized by free-radical polymerization of acrylamide, and are often crosslinked using bisacrylamide (bis). Because of the high propensity of bis to react with itself, bis accumulates in clusters that reduce its overall crosslinking efficiency [4,8]. Therefore, PA hydrogels comprise nondraining clusters that are rich in bis with a surrounding “dilute phase” that is depleted of bis.

One promising technique to overcome the foregoing limitations of chemical crosslinking is to embed nanoparticles (NPs), thus forming hydrogel nanocomposites (HNCs). Depending on the NP-

polymer interaction, NPs may increase the shear modulus of a gel, similarly to the Einstein enhancement of the shear viscosity of a Newtonian solvent. Mahaut et al. [9] showed that, for viscoelastic materials with an elastic modulus in the range 0.3–3 kPa, containing (micrometer scale) polystyrene or glass particles with diameters in the range 80–140 μm , the elasticity enhancement factor G'/G'_0 is independent of the particle-size and the continuous medium (G'_0 is the storage modulus without NPs), proposing

$$G'/G'_0 \approx \frac{1}{(1 - \phi/\phi_m)^{2.5\phi_m}}, \quad (1)$$

where ϕ is the particle volume fraction, and $\phi_m \approx 0.57$ is a least-squares fitting constant. Such a correlation is expected to be valid when there is a negligible influence of the (rigid) particles on the (compliant) continuous-phase microstructure. This may occur when the particles are large compared to the distance over which they disturb the microstructure (as in the experiments underlying Eqn. (1)) or when the physicochemical interaction between the particles and polymer is weak. When polymer adsorbs strongly, for example, polymer bridging of NPs has been shown to impart a significantly greater elasticity enhancement [10,11].

Crosslinking polymers with NPs often produces hydrogels with desirable mechanical properties. For example, hydrogel nanocomposites with large storage moduli, in contrast to stiff chemically

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crosslinked hydrogels, have an unusually large elongation at breaking [12]. However, it is not always known *a priori* whether adding NPs to polymer solutions enhances the viscoelasticity by polymer bridging of NPs, or decreases the entanglement density by polymer adsorption on the NP surfaces and depletion in the NP interstitial spaces [13].

Among the NPs that have been used to form HNCs, such as clay [14], carbon nanotubes [15] and gold [16], silica is one of the most commonly applied and well studied. Unique properties of silica NPs arise from the surface silanol groups, which can dissociate to form negatively charged groups in water. With a well-studied surface chemistry, silica NPs form covalent and/or hydrogen bonds with several polymers, including acrylamide. For example Petit et al. [11] crosslinked a poly(acrylamide-*co*-sodium acrylate) backbone with poly(N-isopropylacrylamide) stickers (PNIPA) using silica NPs to form a viscoelastic solid. Lin et al. [17] reinforced a stiff chemically crosslinked poly(N,N-dimethylacrylamide) (PDMA) ($E \approx 25$ kPa) with silica NPs to achieve an elasticity enhancement factor of 7 with less than 7 v% NPs. Moreover, several studies have modified the silica surface chemistry to form HNCs with PA by grafting other polymers to the NP surface [18–20].

Mechanical enhancement from silica NPs (without any surface modification) in PA hydrogels has been controversial. Lin et al. [21] and Ye et al. [22] embedded silica NPs in stiff chemically crosslinked PA hydrogels to investigate the mechanical properties, finding that silica NPs weakly increase the elastic modulus, similarly to rigid fillers that have no attraction to the polymer: According to [23], $G'/G'_0 \approx 1 + 2.5\phi + 14.1\phi^2$, which is equivalent to Eqn. (1) when $\phi < 0.35$. To explain these results Lin et al. [21], argued that there is no interaction between silica and PA, and they referred to Petit et al. [11] to support their claim that PA does not adsorb on silica. However Petit et al. [11], did not study the PA interaction with silica; they studied the interaction of PA-sodiumacrylate copolymer (a negatively charged polyelectrolyte) with silica NPs, which electrostatically repel each other. Other studies have measured the adsorption of PA on silica, finding a maximum adsorption of ≈ 0.15 mg m⁻² [22,24]. Although this is much weaker than the adsorption of PDMA and PNIPA on silica (≈ 1 mg m⁻² [11]), it still suggests an attractive interaction between silica and PA. The silica-PA interactions are due to (i) a hydrophobic interaction, since silica and polymer are less polar than water, and (ii) weak hydrogen bonds between silica-silanol groups and polymer-carbonyl functional groups [24]. These hydrogen bonds play a secondary role in strengthening the otherwise weak hydrophobic interaction between silica and polymer.

Di Michele et al. [25] showed that silica NPs in PA hydrogels have an attractive inter-particle potential that can be tuned with the hydrogel stiffness. For a PA hydrogel with $G' \approx 12$ Pa, silica NPs aggregate, forming clusters, whereas with $G' \approx 240$ Pa, silica NPs are mainly separated, also forming dimers, triplets and small NP chains. Di Michele et al. [25] attributed the attractive forces in soft gels to either polymer depletion or polymer bridging, whereas the repulsive force was attributed to the elasticity of polymer coils squeezed between the particles.

Following Di Michele et al. [25], Adibnia et al. [26] showed that silica NPs can increase the storage modulus of very soft PA gels ($G' \approx 1.5$ Pa) by two orders of magnitude, forming viscoelastic solids with a frequency-independent storage modulus at low frequencies. For stiff gels ($G' > 0.5$ kPa), however, the enhancement was very weak, as expected by Eqn. (1) for passive fillers. Therefore, whereas well-dispersed silica NPs in stiff gels do not produce significant NP crosslinking, the NP clusters, which are formed in soft gels from an enhanced inter-particle attraction, act as multifunctional crosslinks that significantly enhance the storage modulus, similarly to the clusters in CCHs. Note that NP aggregates, even for passive fillers,

increase the elastic modulus much more ($\approx 50\%$ more) than well dispersed particles [27]. The storage-modulus enhancement reported by Adibnia et al. [26] is much greater than for passive aggregates, and has therefore been attributed to the adsorption of PA on silica.

The foregoing studies investigated the effect of silica NPs on PA hydrogels as a viscoelastic solid, but it remains unknown if silica NPs can crosslink PA without a chemical crosslinker. Neither is it known how NPs contribute to the sol-gel transition, either with chemical crosslinking or without it. To answer these questions, this study uses time-concentration superposition (TCS) principles [13,28,29] to examine the sol-gel transition in PA-silica HNCs. Our previous study [8] suggested that dynamics at the gel point are similar for different materials having similar gelation mechanisms. Here, we seek to quantify how NPs change dynamics at the gel point, and to establish whether NPs alter the dynamics during the sol-gel transition.

The sol-gel transition is characterized by the storage G' and loss G'' moduli having the same power-law scaling

$$G' \sim G'' \sim \omega^\Delta,$$

where ω is the angular frequency, and Δ is the critical relaxation exponent. Near the sol-gel transition, many viscoelastic quantities diverge as powers of $\epsilon = |p - p_c|/p_c$, the proximity of the bond probability p from the critical bond probability p_c at the gel point. Below the gel point, the zero shear viscosity scales as

$$\eta_0 \sim \epsilon^{-k},$$

whereas above the gel point the equilibrium shear modulus scales as

$$G \sim \epsilon^z.$$

Moreover, the transition from a liquid or solid to a viscoelastic material, *i.e.*, crossing the gel point from either below or above, is accompanied by a divergence of the longest relaxation time.

$$\tau \sim \epsilon^{-y}.$$

Using scaling analysis from percolation theory Martin et al. [30], showed that the foregoing exponents are related as

$$y = z + k \text{ and } \Delta = z/y.$$

Many experimental values for these exponents were reviewed by Adibnia and Hill [8], indicating $0.7 \leq k \leq 1.4$ and $0.6 \leq \Delta \leq 0.8$ for different polymerization methods.

Three sets of TCS are performed in this study to compare NP and chemical crosslinking during the sol-gel transition. We use NPs as crosslinkers to study the possibility of gelation without chemical crosslinking, also investigating the possibility of NP percolation (available as SI). Despite an attractive interaction between silica and PA, a viscoelastic solid is unexpected without chemical crosslinking. Therefore, we seek to elucidate how the sol-gel transition dynamics change with NPs in the presence of a chemical crosslinker. We also investigate dynamics at the gel point by crosslinking an HNC using silica NPs when the concentration of chemical crosslinker is insufficient to form a gel on its own.

2. Materials and methods

HNCs were prepared by mixing acrylamide (40 w% aqueous solution, Fisher Scientific, U.S.A.), bisacrylamide (2 w% aqueous solution, Fisher Scientific, U.S.A.), and silica NPs (NexSil-125, 40 w% colloidal suspension, Nyalcol Nanotechnologies Inc., U.S.A.) as

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