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# Effect of crosslinker length on the elastic and compression modulus of poly(acrylamide) nanocomposite hydrogels

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**Abstract.** Polymer hydrogels have shown to exhibit improved properties upon the addition of nanoparticles; however, the mechanical underpinnings behind these enhancements have not been fully elucidated. Moreover, fewer studies have focused on developing an understanding of how polymer parameters affect the nanoparticle-mediated enhancements. In this study, we investigated the elastic properties of silica nanoparticle-reinforced poly(acrylamide) hydrogels synthesized using crosslinkers of various lengths. Crosslinker length positively affected the mechanical properties of hydrogels that were synthesized with or without nanoparticles. However the degree of nanoparticle enhancement was negatively correlated to crosslinker length. Our findings enable the understanding of the respective roles of nanoparticle and polymer properties on nanoparticle-mediated enhancement of hydrogels and thereby the development of next-generation nanocomposite materials.

## 1. Introduction

Previous studies, both experimental and computational, have established that the addition of nanoparticles to polymer systems can have a large impact on their properties, even for very low nanoparticle weight fractions [1-6]. Despite the extensive efforts that have led to elaborate correlations among various properties of polymer systems and nanoparticles on the enhancements of the polymer properties, a complete understanding of the mechanisms in which nanoparticles act to enhance polymer properties is lacking [7-8]. While several hypotheses have been proposed to explain the mechanisms behind the enhancements, one hypothesis that has gained significant support is that strong polymer-nanoparticle interactions can facilitate the formation of additional crosslinks within the polymer network, which thereby leads to enhancements in polymer properties [9-12]. However, it is not clear how the formation of the additional ‘pseudo’ crosslinks affects hydrogel microarchitecture; for instance, the relative effects of nanoparticle mediated crosslinks on the ordered and disordered regions of a polymer are largely unknown.

In this study, we used chemically crosslinked polyacrylamide (pAAM) hydrogels incorporating silica nanoparticles (SiNPs) as a model system to experimentally study the role of polymer-nanoparticle interactions in enhancing the mechanical properties of hydrogels. Furthermore, we examine the effect of polymer properties, specifically by varying the crosslinker length, on the enhancements in polymer mechanical properties due to the addition of nanoparticles. We expected that determining the effect of polymer properties on the degree of nanoparticle-mediated enhancements would reveal if the nanoparticles impact both ordered and disordered regions of the hydrogel network or if they are selective to one region, thereby shedding light on the mechanisms behind the



nanoparticle-mediated enhancements in hydrogel mechanical properties. Our data obtained using unconfined compression and rheological characterization of pAAm-SiNP composites showed enhancements in the elastic properties of hydrogels upon the addition of nanoparticles, consistent with previous investigations [11-14], irrespective of the choice of the crosslinker. Our data also demonstrates that the degree of nanoparticle-mediated enhancements was strongly dependent on the crosslinker length, with statistically similar moduli for neat pAAm hydrogels and pAAm-SiNP hydrogels prepared with the longest crosslinker used in this study.

## 2. Experimental procedure

### 2.1. Materials

All the materials for the polymerization reaction, acrylamide (AAm, monomer), initiator, ammonium persulfate (APS, initiator), N,N,N',N'-tetramethylethylenediamine (TEMED, catalyst), N,N'-methylenebis(acrylamide) (bisacrylamide, crosslinker) and poly(ethylene glycol) diacrylates of various chain lengths ( $n = 2, 4,$  and  $17,$  crosslinker) were purchased from Sigma Aldrich (St. Louis, MO) and used as received. Tris-HCl buffer (pH 7.2) was obtained from Life Technologies (Carlsbad, CA) and binzil silica nanoparticle colloid solution with mean particle size of 4 nm was obtained as a gift from AkzoNobel Pulp and Performance Chemicals Inc. (Marietta, GA).

### 2.2. Polymerization reaction

Chemically crosslinked poly(acrylamide) hydrogels were prepared as previously reported [14]. Briefly, AAm and crosslinker stocks were diluted to their desired concentrations in pH 7.2, 250 mM Tris-HCl buffer, followed by the addition of TEMED (0.1% of the final reaction volume) and 10% w/v APS solution (1% of the final reaction volume). For nanocomposite hydrogels, various amounts of silica nanoparticles were added to the reaction mixture prior to the addition of APS and TEMED. Polymerization reactions were performed at 25 °C between parallel plates (of a mold or the rheometer cell) to minimize exposure to air as oxygen inhibits the free radical polymerization reaction.

### 2.3. Compressive modulus measurements

Compressive modulus measurements for the pAAm hydrogels were performed as previously reported (Zaragoza, 2015). Briefly, we first prepared pAAm hydrogel disks using an acrylic mold (1.6 mm height and 6.5 mm in radius) by pipetting 210  $\mu$ L of a well-mixed reaction mixture into individual molds. After complete gelation (gelation usually occurs within 20 minutes), pAAm hydrogel discs were removed from the mold, wiped gently with tissue paper to remove any excess water, before adding the samples to the Mach-1 mechanical testing system (Biomomentum, Canada). The pAAm gel disks were compressed under unconfined conditions and at room temperature at 0.1 mm/s to 50% of sample thickness, and the compressive modulus was determined by calculating the slope of the linear region of the stress-strain curves (typically between 10–15% strain). The compressive moduli are reported as average of three independent measurements.

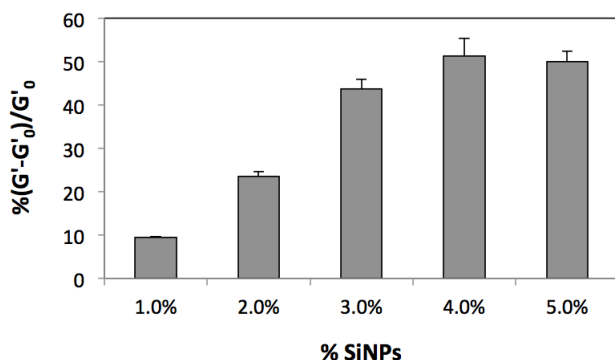
### 2.4. Rheological characterization

Rheological measurements of pAAm hydrogels were carried out, as previously described, using the MCR302 rotational rheometer (AntonPaar, Austria). Briefly, 500  $\mu$ L of a well-mixed reaction mixture was pipetted onto the lower plate of the rheometer and the upper plate was lowered until the desired gap distance (1 mm) was achieved. Amplitude sweeps at a constant frequency of 1 Hz were then carried out to ensure measurements were carried out in the linear viscoelastic regime of the acrylamide hydrogels. Next, dynamic sweep tests over frequencies ranging from 0.1-100 Hz. Final hydrogel parameters were determined by following the gelation for 90 minutes at 1 Hz and 1% strain for all samples. The elastic moduli are reported as average of three independent measurements.

### 3. Results and discussion

#### 3.1. Effect of nanoparticles on hydrogel elastic modulus

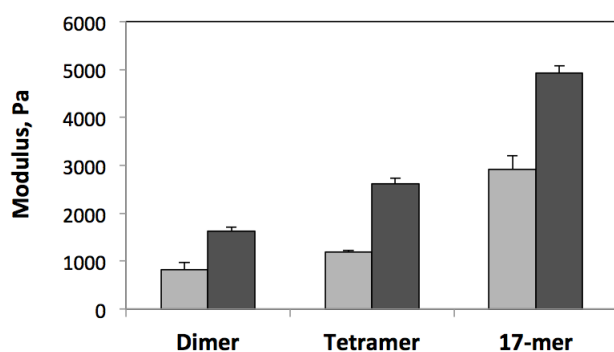
Poly(acrylamide) (pAAm), synthesized using 10% w/v acrylamide and 0.5 w/v bisacrylamide, was used as the model because of its widespread application and availability, ease of synthesis, and previous use in experimental analyses. Commercially available silica nanoparticles (4 nm diameter) were used due to their reported ability to strongly interact with pAAm chains and thereby influence various pAAm hydrogel properties [14]. Elastic moduli of the hydrogels prepared with and without SiNPs were tested using rotational rheology, which indicated that bisacrylamide-crosslinked pAAm hydrogels exhibit enhancements in mechanical properties upon the addition of SiNPs at weight fractions as low as 1% w/v [Figure 1]. The SiNP-mediated enhancements increase linearly with nanoparticle concentration and plateau at 4% w/v SiNPs. The observed results are attributed to the formation of “pseudo-crosslinks” facilitated by strong nanoparticle-polymer interactions and eventual saturation in crosslinker density [12, 14, 15].



**Figure 1.** Percent relative elastic modulus of pAAm hydrogels as a function of 4 nm SiNP concentration. The values for relative elastic modulus were calculated by normalizing the modulus for pAAm-SiNP hydrogels ( $G'$ ) to the modulus for control pAAm gels ( $G'_0$ ). Error bars indicate standard deviation of triplicate measurements.

#### 3.2. Effect of crosslinker length on hydrogel mechanical properties

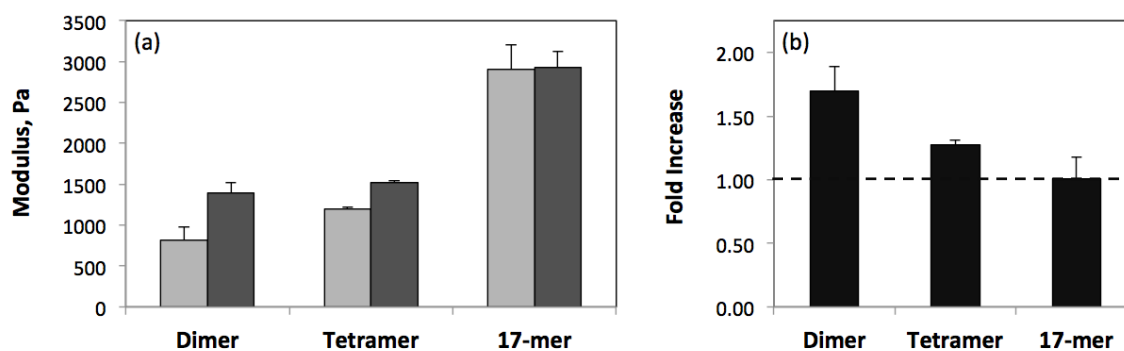
Next, we used PEG diacrylates as crosslinkers instead of bisacrylamide since PEG diacrylates are commercially available in various chain lengths and therefore allow assessment of crosslinker length on hydrogel properties. Mechanical testing revealed a length dependent increase in mechanical properties. Specifically, rheological tests indicated that the longer the PEG chain length, the higher the viscoelastic modulus of the resulting hydrogel (Figure 2), with the dimer crosslinker leading to the lowest value in elastic modulus. These findings are corroborated by unconfined compression tests which showed that pAAm hydrogels crosslinked with 17-mer PEG exhibited highest modulus followed by those crosslinked using tetramer and dimer crosslinkers (Figure 2). To account for these observations, we hypothesize that the longer crosslinkers lead to increases in the ordered structure within the hydrogel network, which in turn leads to increases in hydrogel mechanical properties. Our findings and hypothesis are consistent with previous studies that indicate that hydrogel modulus can be controlled by varying crosslinker length [16, 17]. Further experiments including X-ray diffraction are necessary to confirm mechanisms by which crosslinker length affects hydrogel properties.



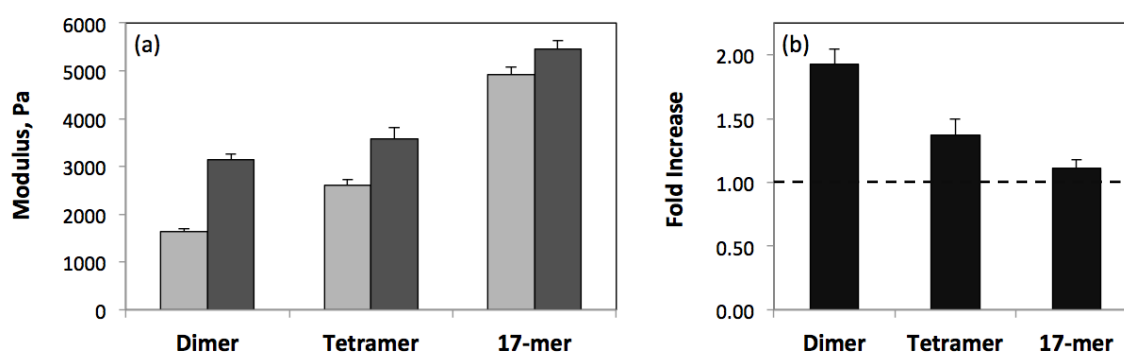
**Figure 2.** Variation in elastic (light grey) and compressive (dark grey) modulus of pAAm hydrogels crosslinked with PEG diacrylate crosslinkers of varying chain length. Error bars indicate standard deviation of triplicate measurements.

### 3.3. Effect of crosslinker length on nanoparticle-mediated enhancements in hydrogel properties

Finally, we explored the effect of adding nanoparticles to hydrogels synthesized using crosslinkers of various lengths. We selected 3% (w/v) SiNPs as it led to the highest level of enhancements within the linear regime for Bis-crosslinked pAAM hydrogels (Figure 1). Consistent with previous results, addition of nanoparticles enhanced the elastic modulus of pAAM hydrogels crosslinked with the various PEG diacrylates. However, the degree of enhancement was inversely correlated to crosslinker length (Figure 3a), with statistically similar values of elastic modulus for hydrogels crosslinked using the longest crosslinker (i.e., 17-mer PEG diacrylate) prepared with or without nanoparticles (Figure 2). In contrast, we observed >50% enhancement in elastic modulus for pAAM hydrogels crosslinked using the PEG dimer upon the addition of SiNPs (Figure 3). Similar trends, i.e., decrease in the degree of SiNP-mediated enhancement with increasing crosslinker length, were also observed for unconfined compression (Figure 4). The observed saturation in SiNP-mediated increases in modulus suggests that modifying either parameter, i.e. increasing nanoparticle concentration or crosslinker chain length may have a similar effect on hydrogel mechanical properties and can be attributed to the hypothesis that both chemical crosslinkers and nanoparticle-based pseudo crosslinkers lead to enhancements in hydrogel modulus by increasing the ordered structure of the polymer network [12, 14, 18].



**Figure 3.** (a) Elastic modulus of pAAM hydrogels prepared with or without 4 nm SiNPs and PEG diacrylate crosslinkers of varying chain length – control pAAM hydrogels (light grey) and pAAM-SiNP hydrogels (dark grey). (b) Fold increase in the modulus of pAAM hydrogels due to the addition of 4 nm SiNPs. Error bars indicate standard deviation of triplicate measurements



**Figure 4.** (a) Compressive modulus of pAAM hydrogels prepared with or without 4 nm SiNPs and PEG diacrylate crosslinkers of varying chain length – control pAAM hydrogels (light grey) and pAAM-SiNP hydrogels (dark grey). (b) Fold increase in the modulus of pAAM hydrogels due to the addition of 4 nm SiNPs. Error bars indicate standard deviation of triplicate measurements

#### 4. Conclusions

In this work, we performed experiments that improve our understanding of the role of nanoparticles on the mechanical properties of hydrogels. Using poly(acrylamide) hydrogels incorporating silica nanoparticles as the model system, we first demonstrated that the addition of nanoparticles led to significant enhancement in hydrogel mechanical properties, possibly due to the formation of additional pseudo-crosslinks in the hydrogel network. Next, using PEG diacrylate of various chain lengths we show that pAAM hydrogels crosslinked with longer chain crosslinkers presented higher elastic and compressive moduli, relative to those crosslinked using shorter crosslinkers. We hypothesize that longer crosslinks lead to an increase in the ordered structure of the hydrogel network, although further experiments using X-ray diffraction are necessary to confirm the hypothesis. Finally, our results also demonstrate that the degree of nanoparticle-mediated enhancements was inversely correlated to the length of the crosslinker. In combination, our data indicates that nanoparticles and crosslinkers act similarly in that they both lead to an increase in the ordered structure of the polymer network, thereby leading to saturation in the enhancements in hydrogel mechanical properties afforded by (covalent or pseudo) crosslinking. Therefore, for the pAAM hydrogels crosslinked with the 17-mer PEG diacrylate crosslinkers, we observe statistically similar elastic and compression modulus values for hydrogels prepared with or without nanoparticles. It is however important to note that nanoparticles contribute to additional crosslinking only for systems characterized by strong polymer-nanoparticle interactions. The implications of these results are two-fold: first, the data demonstrates that nanoparticle-mediated enhancements in polymer mechanical properties are strongly dependent on the crosslinker length and not simply its interactions with the polymer backbone. Second, since previous studies have indicated that chemical crosslinkers improve polymer mechanical properties by increasing the ordered structure within the polymer network, saturation of nanoparticle enhancements at longer crosslinker length indicates that nanoparticles behave similarly to chemical crosslinkers, i.e., they impact the ordered regions of the hydrogel network. Overall, these results suggest a new understanding of the roles of chemical crosslinkers and nanoparticles in mechanical reinforcement of polymer nanocomposites.

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