In situ viscoelasticity and in situ thermo-responsiveness in acrylic acid-based soft hydrogels

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Abstract. This study was aimed at understanding any effects that the presence of acrylic acid dimer could have on thermo-mechanical properties of acrylic acid-based hydrogels. Polymeric hydrogels were systematically synthesised and characterised on the basis of having different concentrations of acrylic acid dimer. The materials show a reversible thermo-responsive behaviour, when heated in situ using light transmittance approaches. The point of cloudiness is significantly influenced as a consequence of the presence of the acrylic acid dimer material. Increasing the amount of the dimer additive up to 2% improves the light transmittance (%) of the soft gels by up to 70%, at 140°C, suggesting that a potential method of altering the lower critical solution temperature of the soft gels is to alter the polymer backbone through copolymerization. As the amount of dimer was increased up to 2%, the values of storage modulus (G’) were increased by up to 75%, leading to greater viscoelasticity and stronger gel compositions.

1. Introduction

Hydrogels are polymers that can absorb water, thereby swelling without dissolution [1]. This property arises from the structure of the gels which is based on a three dimensional network, created by physical interactions and chemical cross-linking of the polymer structure [2]. Many hydrogels are created using acrylic acid (AA) as a monomeric component, for various applications [3-5]. Stimuli responsive hydrogel materials, based on hydrophilic polymers such as poly (acrylic acid), have drawn interest from academia and industry, due to their responsive behaviour to external stimuli such as temperature change, changes to the ionic strength and pH [6]. Rheometric, viscoelastic characterisations are often necessary in order to provide understanding of the behaviour of soft gel materials. In such materials, the storage modulus (G’) and loss modulus (G”) are parameters that are investigated in order to establish the frequency dependency of the gel structure, the stiffness and the energy dissipation events [7]. These are useful in the interpretation of soft gel characteristics such as mechanical rigidity and relaxation. The cloud point and optical properties of hydrogels are influenced by the spatial inhomogeneity in the gel networks. These arise due to a number of factors such as differences in the reactivity ratios of the monomer(s) and cross-linker(s), cyclisation resulting in structural loop formation, microgel formation, diffusion controlled reactions, crosslink density, pH of the composition, ionic strength and the nature of any cations, present as the counter ion [8].

In this study, controlled, small quantities of AA-dimer were used in a range of gel-precursor formulations in order to monitor the contribution of the presence of this AA-dimer to the viscoelastic properties and the thermo-responsiveness of the resulting soft gel materials.
2. Experimental
The gel-precursor solutions were prepared by using methylene bis-acrylamide (MBA) as crosslinker (0.05%), UV Irgacure IR1170 as photoinitiator (0.01%), acrylic acid as monomer (10%) and water as solvent. The solutions were prepared containing known amounts of the AA-dimer, covering dimer loadings of 0, 0.05, 0.1, 0.25, 0.5, 1.0 and 2.0% of the total formulation. Each solution was stirred, using a magnetic bar, for 5 minutes, then filtered, using 0.2 micron syringe filter. pH of the aqueous solutions were measured using HI1230 portable pH meter from HANNA Instruments. Ultra-Pure water (conductivity of 0.06 μS/cm and resistivity of 16.6 MΩ) was used for pKa calculations.

In situ photo-crosslinking reactions and rheology were performed using a TA−Instruments DHR2 with photo-curing bottom plate fixture attached to the rheometer. With these, an Omnicure S200S lamp source was used, emitting radiation through a clear glass bottom window. Radiation intensity was fixed at 8 mW/cm2, for 30 minutes cure, while a Smart Swap steel parallel plate fixture with 20 mm diameter was employed using an initial gap size of 2 mm. Frequency sweeps were carried out in the materials’ LVR region using a strain value of 0.1%, for the frequency range 20 Hz to 0.02 Hz.

In situ thermo-responsive characteristics were studied using a PerkinElmer Lambda-25 UV-VIS Spectrophotometer, equipped with a cell heating accessory from Pike Technology. Measurements on UV cured gel samples were carried out using 10mm crimp sealed vials designed to withstand temperatures of up to 170 °C. The transmittance of the hydrogel samples was recorded as a function of temperature by scanning the sample in the visible region of the spectrum (400-700 nm).

3. Results and Discussion

3.1 Effect of AA-dimer on viscoelasticity of the soft gels

| Carboxylic Acid | Conc. (M) | pH | pKa values |
|----------------|-----------|----|------------|
|                |           |    | This work  | Literature |
| AA             | 0.14      | 2.60 | 4.34       | 4.23       |
| AA-dimer       | 0.14      | 3.05 | 5.24       | 4.99       |

The evolution of the elastic (G’) and viscous (G”) moduli for the soft gels, during the photo-polymerisations, are represented in Figure 1. Increasing the amount of AA-dimer in the liquid formulations does not significantly affect the cure patterns. It was also observed that minor differences exist in the cure kinetics. An increase in the AA-dimer loading slightly slows down the initial structure development. Such minor differences can be expected since increasing the AA-dimer loading slightly affects the pH of the liquid formulations, prior to the photo-polymerisation. In addition, it is anticipated that the molar ratio of the photo-initiator/AA monomer is marginally affected by the presence of AA-dimer in the formulations when used as additive, although AA and AA-dimer and have different pKa values, as discussed with respect to Table 1. As Figure 1 and Figure 2 show, the amount of AA-dimer in the formulations affects the mechanical properties of the soft gels which are formed from the photo-polymerisation. This indicates that, by copolymerising AA with AA-dimer, the micro-structure and the mechanical properties of the soft gels can easily be influenced.

According to Figure 1 and Figure 2, those gels with greater amounts of AA-dimer are stiffer than those containing no AA-dimer or smaller amount of AA-dimer. For practical reasons, the stronger the soft gels the better, for their potential application in different areas (biomedical, tissue engineering, et al.). Since G’ is significantly greater than G” value, viscoelastic solid behaviour is clearly demonstrated by the gels. In Figure 2, the elastic moduli were less dependent on frequency as a result of increase in the amount of AA-dimer. This lesser frequency dependence of the modulus indicates greater ‘gel’
character. The significance of these results is that the viscoelastic properties of soft gels-based on AA can be optimised by using small amounts of AA-dimer as a dopant material.

![Graph showing viscoelastic properties](image)

**Figure 1.** *In situ* cure profile (1Hz, 0.1% strain at RT), showing the evolution of the elastic moduli $G'$ (filled symbols) and loss moduli $G''$ (open symbol), for compositions containing different amounts of AA-dimer underwent photo-polymerisation

![Graph showing elastic and loss moduli](image)

**Figure 2.** Frequency sweep data showing the elastic moduli $G'$ (filled symbols) and loss moduli $G''$ (open symbols) as a function of the applied frequency from the soft gels that contain various amounts of AA-dimer. The strain was 0.1% and the run temperature was 25°C

### 3.2 Effect of AA-dimer on thermo-responsiveness of the soft gels

The effects of temperature change are among the more commonly exploited stimuli in responsive polymeric soft gels [10]. Figure 3 shows a reversible temperature dependent light transmittance. Figure 4 shows the dependence of light transmittance on the amount of AA-dimer used in formulation. It is proposed that the presence or absence of AA-dimer strongly affects the hydrophilic/hydrophobic nature of the polymer, hence the optical transitions (clear/cloudy) are controlled by balance between the hydrophilic and hydrophobic interactions. At elevated temperatures, the carboxyl groups of poly
(carboxyethyl acrylate) would remain protonated, leading to a reduction of the hydrophobic complexation by Mg$^{2+}$ ions by maintaining their hydrophilic interactions with water molecules via hydrogen bonding. This phenomenon is illustrated by Figure 5, showing intra-molecular hydrogen bonding and the inter-molecular bonding between the Mg$^{2+}$ and the COO- groups of either the poly(acrylic acid) or the poly(carboxyethyl acrylate) species that are attached to the polymer backbone. Below the critical temperature, poly(acrylic acid) soft gels are clear and transparent suggesting that hydrophilic interactions such as hydrogen bonding between water and the polar functional groups that are present in the matrix, such as –COOH and –C=O, are dominant. However, as the temperature is increased, these hydrophilic interactions are reduced, allowing cations such as Mg$^{2+}$ to complex with the carboxylate ions. This complexation of Mg$^{2+}$ ions causes the composition to become more hydrophobic in nature, leading to precipitation or phase separation, resulting in cloudiness.

**Figure 3.** Light transmittance at 450 nm as a function of temperature f for the soft gel that had no AA-dimer added during formulation. Measurements were carried out while the sample was heated in-situ.

**Figure 4.** % Light transmittance at 450 nm and cloud point dependence of on AA-dimer content of the soft gels. The light transmittance measurements were carried out at 140°C, the samples being heated in-situ.
As the content of AA-dimer was increased, the optical clarity of the soft gel at 140°C was markedly increased, reaching 100% light transmittance when 2% AA-dimer was present in the polymerisation. The carboxyl groups in the polymer backbone are capable of making strong hydrogen bonds with water molecules both in ionised and protonated form and it may be due to these strong enthalpic interactions that poly(acrylic acid) hydrogels show very high lower critical solution temperature (LCST). The LCST of poly(acrylic acid) hydrogels has previously been shown to be controlled by manipulating a number of parameters such as pH, ionic strength, nature of cation and anion, and by co-polymerising with hydrophobic or hydrophilic (ionic, non-ionic) monomer [11-12].

![Figure 5](image.png)

**Figure 5.** Illustration of the potential interactions, physical and chemical, in soft gels created from AA and containing AA-dimer, with MBA being the crosslinking agent

### 4. Conclusions

The viscoelastic properties and the thermo-responsive characteristics of soft hydrogels containing AA-dimer were successfully investigated. Both properties were influenced by AA-dimer that was present in the composition. A correlation was observed showing that superior viscoelastic properties of the soft gels could be achieved with an increase in the AA-dimer content. For gel composites containing no or little AA-dimer, a very hazy, semi-opaque gel was observed at 140°C, in contrast to the transparent gel material that was observed having 2% loadings of the AA-dimer in the formulation, at the same temperature.

### 5. References

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