

Rheological Study of Self-Crosslinking and Co-Crosslinking of Ammonium Zirconium Carbonate and Starch in Aqueous Solutions

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ABSTRACT: Different from common hydrogel systems formed by a polymer and a crosslinker, a hydrogel consisting of both self-crosslinkable ammonium zirconium carbonate (AZC) and co-crosslinkable starch was investigated in this study using rheological measurements. The evolution of viscoelastic properties of AZC solutions and AZC-starch mixtures was characterized, and the crosslinking kinetics was determined. It was found that for both AZC self-crosslinking and AZC-starch co-crosslinking, the initial bond formation rate and the gel strength exhibited a power law scaling with polymer concentrations. The competition reaction between self-crosslinking and co-crosslinking indicates that the gelation kinetics

strongly depends on the AZC concentration but less depends on starch concentration. The temperature dependence of crosslinking was described by the Arrhenius plots which demonstrate a good linearity. It was determined that the activation energy of AZC self-crosslinking was approximately 145–151 kJ/mol, and the activation energy of AZC-starch co-crosslinking was 139 kJ/mol. The effect of solution pH on the crosslinking process was also studied. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1019–1029, 2011

Key words: starch; crosslinking; hydrogels; rheological measurements; kinetics

INTRODUCTION

As a common energy reserve in many plants, starch is a widely available and heavily used biopolymer with attractive properties, in particular biodegradability and biocompatibility. In many applications, crosslinked starch is superior to uncrosslinked native starch with regards to mechanical, thermal and chemical resistance.¹ Starch crosslinking can be accomplished via either covalent crosslinking or noncovalent intermolecular interactions. Noncovalent crosslinking, such as hydrogen bonding, is very versatile and reversible, which enables the engineering of polymer networks with controlled mechanical properties. By varying crosslinker dosage, starch concentration, pH, and temperature, the extent of crosslinking could be controlled.² Crosslinked starch hydrogels have many applications, in food, paper-making, oilfield, and pharmaceutical industries.^{2–4}

Ammonium zirconium carbonate (AZC) is a common crosslinker for starch. Figure 1(a) represents its chemical structure. AZC can react with polymers

containing hydroxyl groups by forming hydrogen bonds, such as starch and cellulose [Fig. 1(b)].⁵ As a result, AZC has already been widely used as an insolubilizer in paper coatings.^{6,7} Recently, we found that by using AZC as a bridging agent, large amounts of starch hydrogel could be grafted on wood fiber surfaces, which improved the fiber to fiber bonding capability.⁴ The reaction mechanism depicted in Figure 1(b) suggests that the crosslinking reaction can also occur between AZC molecules. Although the chemistry and application of AZC have been investigated intensively, the kinetics of AZC self-crosslinking and AZC-starch co-crosslinking has not been studied. Improved understanding of AZC-starch crosslinking is a prerequisite for further optimizing existing processes in paper coating, fiber modification and other applications.

Hydrogel networks can be formed either by self-association of polymers or by adding an appropriate crosslinking agent.⁸ When aqueous AZC solutions (one component system) are heated, the AZC molecular structure changes: CO₂ and NH₃ are released, while new hydrogen bonds are formed via inter- and intramolecular interactions [Fig. 1(b)]. As a result of this self-association, a crosslinked hydrogel network can be formed, which will be referred to as a heat-induced AZC gel in this report. For pre-cooked starch solutions at a low starch concentration (less than 3% by weight), self-association between

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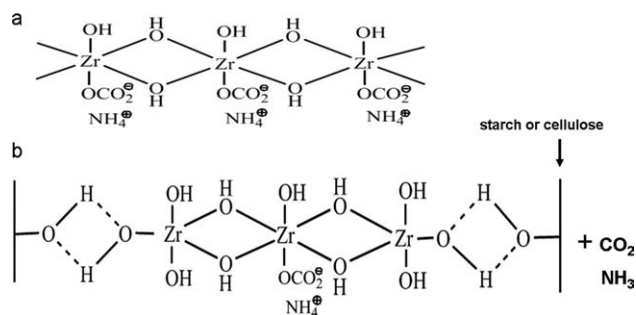


Figure 1 Chemical structure of AZC (a) and the microstructure formed by AZC and polymers containing hydroxyl groups (b).

starch molecules is not sufficient to form a hydrogel network. To obtain a crosslinked polymeric network in these dilute solutions, a crosslinker like AZC has to be induced. With the addition of AZC in a starch slurry, interchain hydrogen bonding occurs between starch molecules and AZC, and a crosslinked starch hydrogel network can be formed. In blends of AZC and starch, both AZC self-association and AZC-starch co-association can occur at elevated temperatures. Therefore, unlike other common polymer-crosslinker systems, AZC-starch gels are expected to contain two types of networks, i.e., heat-induced AZC networks and AZC-crosslinked starch networks. To develop a thorough understanding of the formation of these mixed gels, studies on the formation of the individual gels should first be conducted.

During the crosslinking process, bonds are formed between polymer molecules, resulting in changes of the viscoelastic properties of the polymer solution over time. A common method to study the kinetics of crosslinking processes is to monitor the evolution of moduli of the polymer solution. Using such dynamic rheometry experiments, the kinetics of starch and protein gelation processes have been studied.⁹ Some rheological parameters, such as gel time and gel strength, could be represented as a function of concentration and temperature. Gaunet¹⁰ suggested that for some thermoreversible gels, the modulus depends on concentration with a third power relation.

The classical theory of rubber elasticity predicts that the network modulus is proportional to the bond density,^{11–15} i.e.

$$G = q \nu k T + G_0 \quad (1)$$

Where q is a coefficient between 0.4 and 1,³ ν is the bond density, k is the Boltzmann constant, and T is the absolute temperature. G_0 represents the initial modulus of polymers before gelation. Essentially, G_0 is the contribution of chain entanglement to modulus, and is normally a very small value.

From eq. (1) it can be seen that the gel strength G is proportional to the bond density. The time derivative of eq. (1) can be written as:

$$dG/dt = q k T dv/dt \quad (2)$$

The above expression shows that the rate of modulus change is proportional to the rate of bond formation at a given temperature.¹² Therefore, tracking the changes of modulus can provide us with some inherent information about bond formation in the network of interest. The bond formation rate is expected to depend on polymer and crosslinker concentrations, and on reaction conditions like temperature and pH. Power-law scaling between bond formation rates and concentration has been reported in literatures, but the values of the scaling exponent were found to vary with reaction systems and conditions.³

For the crosslinking/gelation process, the temperature dependence of reaction rate can be described by the Arrhenius equation^{16,17}:

$$dG/dt = A^* \exp(-E_a/RT) \quad (3)$$

where A^* is an experimental factor, E_a refers to the experimental activation energy, R is the gas constant, and T is the absolute temperature. Ahmed et al.¹⁷ determined the activity energy E_a of basmati rice starch by utilizing the above relationship.

The objective of this article is to study the mechanism and kinetics of AZC self-crosslinking and AZC-starch co-crosslinking by monitoring the evolution of the modulus for AZC solutions and AZC-starch blends. Power-law scalings for the initial bond formation rate and the gel strength were determined as a function of starch and AZC concentration. The temperature dependence of crosslinking was described by an Arrhenius expression, and the activation energy values of AZC self-crosslinking and AZC-starch co-crosslinking were determined. The effect of solution pH on the crosslinking process was also studied.

EXPERIMENTAL

Materials

Native corn starch (B200) was provided by Grain Process (Muscatine, Iowa USA). Starch suspensions at 1–3% solid content by weight were precooked at 95°C for 40 min using a rotary evaporator. An ammonium zirconium carbonate aqueous solution containing 1–2% tartaric acid as stabilizer was purchased from Aldrich, USA.

Turbidity test and CO₂ release tests

The turbidity of polymer solutions was measured with a Digital Direct-Reading Turbidimeter (Orbeco-

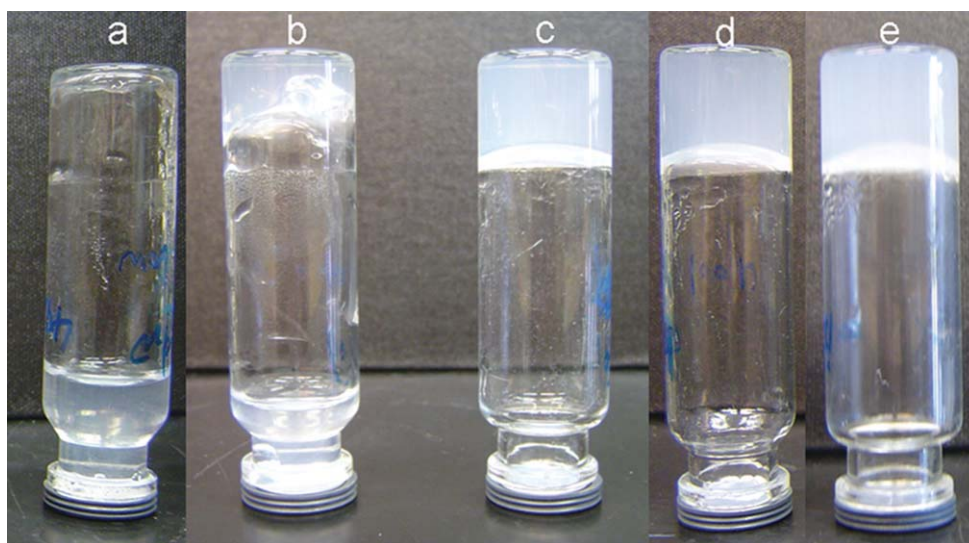


Figure 2 3-h inversion tests for different samples (reaction 1 h at 60°C: a. 2000 ppm AZC in water; b. 6000 ppm AZC in water; c. 10,000 ppm AZC in water; reaction 1 h at 70°C: d. 6000 ppm AZC in water, e. 6000 ppm AZC in 1% starch). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Hellige, Sarasota, FL). The amount of carbon dioxide release during gelation was determined using a multisampling method with headspace gas chromatograph. Details about the multisampling method can be found in a previous publication.¹⁸

Rheological characterization

Rheological measurements were conducted by using an MCR 300 controlled stress rheometer (Anton Paar) with a standard couette geometry (CC17: the inner diameter of cup is 18.08 mm and the diameter of the bob is 16.66 mm) in small deformation oscillatory mode. A predetermined amount of the crosslinker (AZC solution) was mixed with 20 mL DI water or starch solution at room temperature and pH was adjusted to the desired value with 5% NaOH solution or 5% HCl solution. After stirring for 5 min, 4.72 mL sample was transferred into the measuring cup of the rheometer. A thin layer of low viscosity silicon oil was applied on the top of sample to prevent moisture losses during measurements at high temperatures. Storage modulus G' and loss modulus G'' were measured over time at a frequency of 1 Hz and a strain amplitude of 5%, which was within the linear viscoelastic regime for all samples.

RESULTS AND DISCUSSION

As a crosslinking agent, AZC can react with polymers containing hydroxyl groups [Fig. 1(b)]. Similarly, with relatively large number of hydroxyl groups in its molecule, self-assembly between AZC molecules can also occur. Therefore, in a one-component system of AZC solutions, AZC self-crosslinking

can occur. In a two-component system of AZC-starch blends, both AZC self-crosslinking and AZC-starch co-crosslinking exist, and these two associations might compete with each other. For a qualitative study, visual observations and turbidity tests were conducted. For the quantitative investigation, the crosslinking (or gelation) process was characterized using rheological measurements.

Visual observation

At elevated temperatures ($>60^{\circ}\text{C}$), the crosslinking between individual AZC molecules can result in a weak hydrogel. The gel strength, corresponding to the degree of crosslinking, is highly dependent on the reaction temperature and AZC concentration in the solution. Figure 2 demonstrates different samples in inverted vials. After 1 h reaction at 60°C, the initially clear AZC solution with low concentrations (2000 ppm and 6000 ppm) became sticky and opaque, but no stable gel was formed [Fig. 2(a,b)]. At a higher concentration of 10,000 ppm [Fig. 2(c)], a stable gel was formed. If a higher reaction temperature (70°C) was applied, the 6000 ppm AZC sample could also be converted to a stable gel after 1 h [Fig. 2(d)].

If AZC is added to a starch solution, there are two competitive crosslinking reactions: AZC self-crosslinking, and AZC-starch co-crosslinking. With the involvement of AZC-starch co-crosslinking, whether an enhanced gel network can be achieved is one concern for this study. The inversion test result shows qualitatively that a stable hydrogel was also formed for the AZC-starch mixture [Fig. 2(e)].

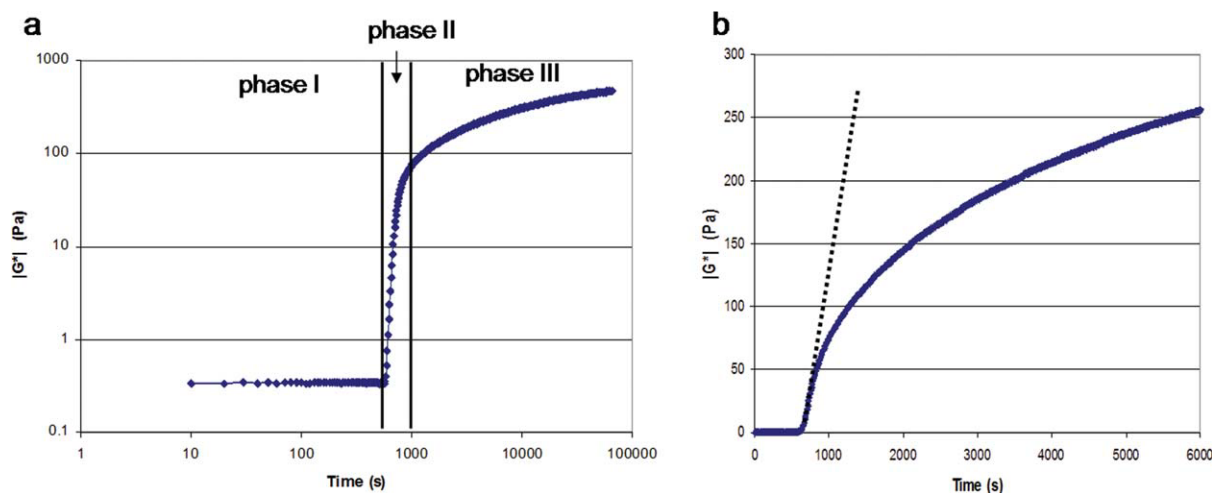


Figure 3 Typical profiles of the evolution of the complex modulus (a: 3-phase profile; b: a $|G^*|$ profile with a tangent line) (6000 ppm AZC in water, 80°C, pH 9). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The initial AZC solutions at room temperature were clear. With the proceeding of crosslinking upon heating, the solution became turbid. The turbidity measurement results of the solutions (not shown here) increased first, and then leveled off. Turbidity is a visual reflection of the crosslink process, which apparently leads to microscopic phase separation. It was also found that for the same reaction times, the higher the AZC concentration, the higher the turbidity of the crosslinked gels.

Rheological characterization

Starch self-association

One objective of this study is to investigate the network of starch crosslinked by AZC. Before conducting the study on the two-component system, the self-association of the starch in aqueous solutions was investigated to provide a benchmark.

It is well known when an uncooked raw starch slurry is heated to an elevated temperature (80–90°C), a significant viscosity increase occurs due to the swelling of starch granules. The viscoelastic behaviors of starch cooking have been studied extensively and some kinetic models have been established.^{9,19} In this study, the starch sample used is precooked starch. The rheological measurement results show that both the loss and storage moduli of the starch solution (3%) remained virtually constant at low values, indicating the lack of measureable changes of rheological properties over time for cooked starch solution. In other words, the self-association of starch molecules in such a diluted solution is negligible.

AZC self-crosslinking

As demonstrated in the inversion tests, self-crosslinking of AZC would occur at elevated tempera-

tures, and a weak hydrogel would be formed. According to the rheological measurement (the plot of storage modulus G' and loss modulus G'' is not shown here) the G'' of the initial AZC solution was larger than G' indicating a liquid-like sample. After reaction for a short time, G' increased quickly and overtook G'' at a certain point, indicating the transition of sol–gel. For simplification, the absolute value of complex modulus $|G^*|$ was calculated²⁰ and chosen as a characteristic parameter to describe the gelation process¹⁵:

$$|G^*| = [(G')^2 + (G'')^2]^{0.5} \quad (4)$$

Figure 3(a) is a typical evolution profile of the absolute value of complex modulus for AZC self-crosslinking. The profile shows that the gelation process consists of three phases. Phase I represents an initial plateau, during which G' and G'' remain virtually constant, with G'' being much larger than G' (not shown here), indicating that the polymer sample is a viscous liquid. This phase is also called the induction period.¹² Normally, the induction time is the period prior to the gel point, during which crosslinking between polymer molecules can occur, but no global crosslinked network is formed yet. The induction period has been reported by many researchers for different polymers^{21,22} and is generally dependent on crosslinker dosage, pH and temperature (more detail will be discussed in the following sections). Following Phase I, the complex modulus exhibits a period of rapid increase, referred to as the fast gelation phase (Phase II). In Phase III, the increase rate of the complex modulus decreases, eventually reaching a plateau, indicating completion of the gelation process. Similarly, Sarvestani²² proposed three regions during the gelation of

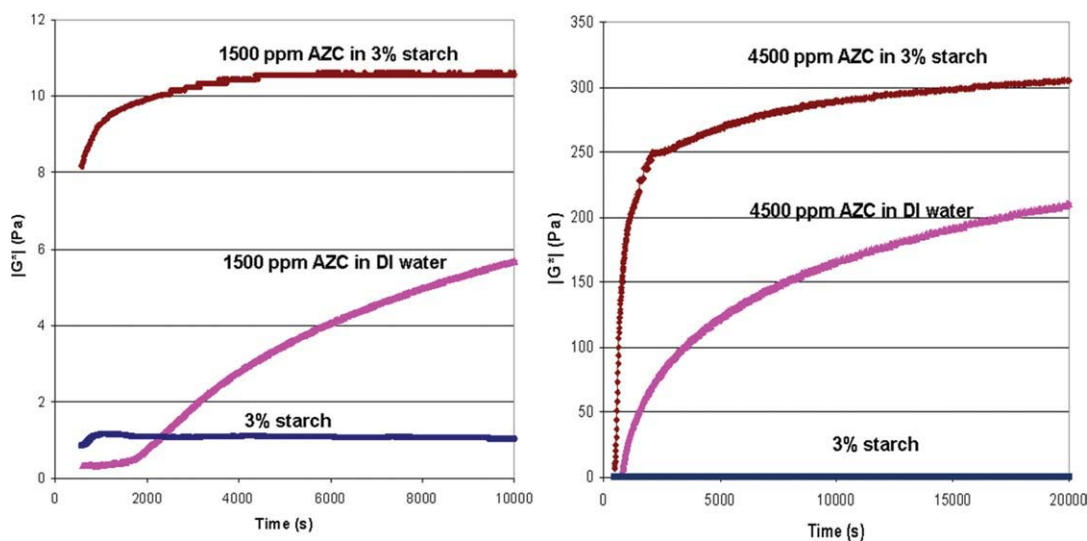


Figure 4 $|G^*|$ profiles for different reaction systems (80°C, pH 9). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

poly(lactide-*co*-ethylene oxide-*co*-fumarate) hydrogels. Calvet²¹ studied the gelation of polyacrylamide and also defined three phases, and the data were fitted with a modified Hill equation. The gelation of gelatin, on the other hand, has been divided into four phases.²³ By analyzing the profiles of complex modulus, the kinetics of gelation can be quantified.

AZC-starch co-crosslinking

The rheological changes for two-component blends of AZC and starch were characterized using the same methodology as for the pure AZC solutions. The $|G^*|$ profiles in Figure 4 show a direct comparison between the pure solutions and the two-component solution for two different AZC concentrations. It can be seen that the two-component solution exhibits a faster initial increase of $|G^*|$ and a higher $|G^*|$ value after a given reaction time, which indicates a synergistic effect. This means that the development of the whole gel network is attributed not only to the self-crosslinking of AZC, but also to the co-crosslinking of AZC with starch.

Kinetic study of AZC self-crosslinking and AZC-starch co-crosslinking

To characterize the kinetics of gelation, modulus evolution curves have been analyzed by many researchers in various ways. In this study, we focus on the change of complex modulus. Equation (2) shows the link between the rate of bond formation dv/dt and the rate of change of the complex modulus, $d|G^*|/dt$, which is the slope of complex modulus curve in the linear growth region.³ For the gelation of polyacrylamide crosslinked by trivalent chromium ions, Prud'homme¹² measured the maxi-

imum rate of change of G' with respect to time, and considered it the maximum rate of crosslink formation. In Sarkar's¹⁴ study on kinetics of methylcellulose gelation, the fastest rate of increase in G' was used as a measure of the rate of gelation. In this study, a similar method was applied, i.e., the maximum slope of the initial increase of $|G^*|$ was determined [the dotted line in Fig. 3(b)], and chosen to reflect the initial bond formation rate.

Normally, a plateau value of $|G^*|$ at long times can be used to represent the final strength of the network of interest. Figure 3(a) shows that after the initial rapid increase (Phase II), the growth of $|G^*|$ indeed slows down, approaching a plateau. However, for lower AZC concentrations and lower reaction temperatures, the time needed for $|G^*|$ to reach a plateau was found to be extremely long. Under some conditions, a plateau could not be observed even after 20 h. For most of our gelation studies, 5–6 h were long enough to observe the viscoelastic property changes and longer observation times were not necessary.

Effect of crosslinker and polymer concentrations

Effect of AZC concentration for AZC self-crosslinking

For a single component system, the gelation/self-crosslinking process highly depends on the polymer concentration. In this study, the evolution profiles of $|G^*|$ for AZC samples at different concentrations (600–6000 ppm) were obtained (Fig. 5). It can be seen that increasing the AZC concentration resulted in faster increase of $|G^*|$ at short times. The maximum slopes of the initial portions of the curves were determined, and are plotted in Figure 6 (right),

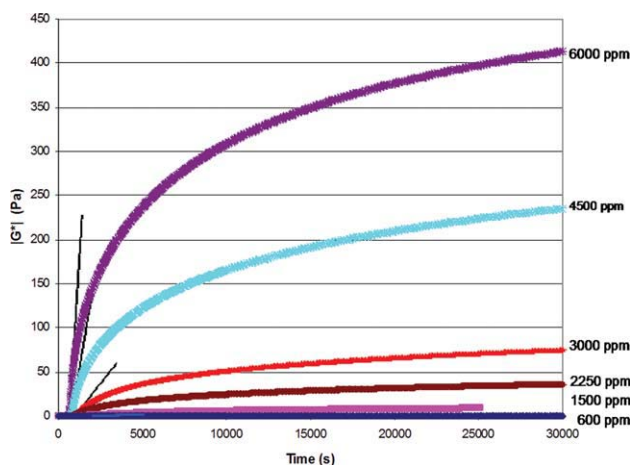


Figure 5 Profiles of $|G^*|$ for AZC self-crosslinking at different AZC concentrations (80°C, pH 9) (the straight lines represent the tangent at short times). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

which shows a good power-law scaling between $d|G^*|/dt$ and AZC concentration, C_{AZC} :

$$d|G^*|/dt \sim (C_{AZC})^{3.0} \quad (5)$$

The power-law exponent of 3.0 for the kinetics of AZC self-crosslinking suggests that three AZC polymer chains participate in the formation of the primary junction zones. The C^3 power-law dependence of gelation rates was also reported in the literatures for other gelation systems. For example, a power-law of 2.7 was reported for the polyacrylamide-glyoxal gelation system.³ It was also reported that the maximum gelation rate of methylcellulose (MC) following a power-law relationship for MC concentration with an exponent of 3.3.¹⁴

In addition, Figure 5 also shows that with increasing AZC concentrations, higher $|G^*|$ values were reached for the same reaction time. This is because at higher AZC concentration, a more densely cross-linked network can be formed.²⁴ The values of $|G^*|$ at 20,000s were chosen and plotted against C_{AZC} (Fig. 6 left). It can be seen that, the $|G^*|_{20,000}$ plot exhibits a good power law relationship between gel strength and AZC concentration:

$$|G^*|_{20,000} \sim (C_{AZC})^{2.9} \quad (6)$$

The power-law scaling of modulus with concentration has been reported by many researchers with different values of the exponent n ($2 \sim 3$). Aguilera⁹ reported an exponent close to 3.1 for whey protein isolate. Gaunet¹⁰ found that for some thermoreversible gels, the relationship between polymer modulus and concentration follows a power law with exponent 3. For the rest of this study, the value of $|G^*|$

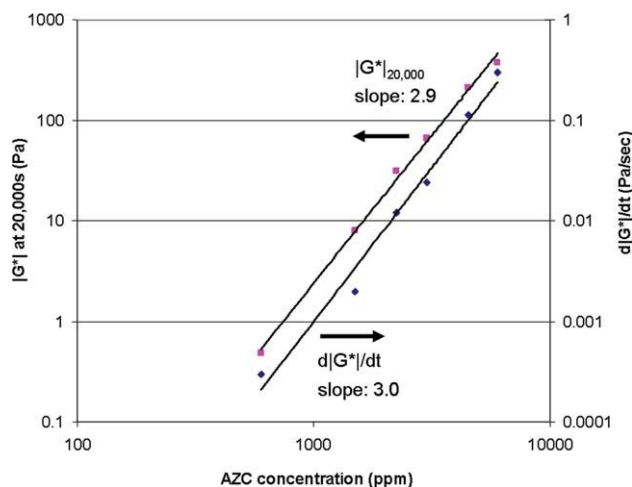


Figure 6 The initial rates of increase of $|G^*|$ (right) and the values of $|G^*|$ at 20,000 s (left) versus AZC concentration for AZC self-crosslinking at 80°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

at 20,000s, $|G^*|_{20,000}$, was chosen to represent the “gel strength”. It should be noted that the gel strength at 20,000s only provides a snap shot of the gel network and not the actual ultimate gel strength. For the gelation at low temperatures, for example, the system at 20,000s had only reached the early stages of gelation.²⁵

Effect of AZC concentration on co-gelation of AZC and starch

In the AZC-starch system, both starch-AZC co-crosslinking and AZC self-crosslinking can occur. Therefore, the amount of AZC in the mixture is expected to play an important role in the gelation process. From Figure 7, it can be seen that increasing the

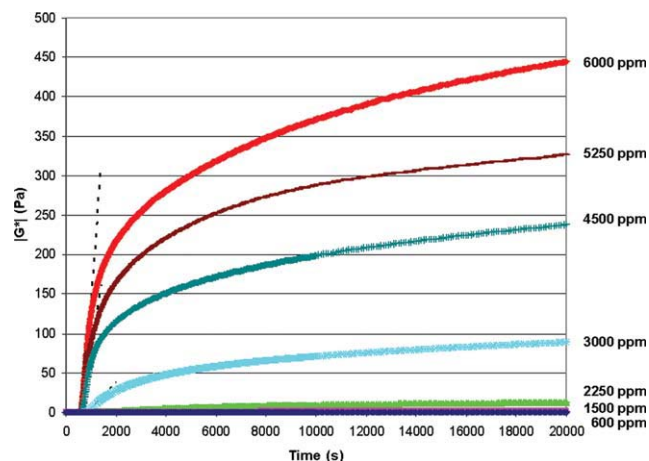


Figure 7 Effect of AZC concentration on the co-gelation of AZC and starch (1% starch, 80°C, pH 9). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

AZC concentration leads to faster increase of $|G^*|$. This is expected because the crosslinking reaction rate depends on the reactant concentration. The dependence of the initial slopes (i.e., the initial gelation rate) on AZC concentration was determined, and it was found that the co-gelation of AZC and starch followed the power-law scaling of

$$d|G^*|/dt \sim (C_{AZC})^{5.3} \quad (7)$$

The high power law (5.3) for the concentration dependence of the gelation rate is a surprising finding, which indicates the simple models (C^2 and C^3) are not applicable for the co-gelation of AZC and starch. Unlike the self-gelation of AZC which involves three AZC chains in the formation of junction zones, the AZC-starch junction zones might involve around three associated double helices according to Oakenfull's "domain model".²⁶ The high power law may be associated with higher-order aggregates of helices. In the process of co-gelation of AZC and starch, preaggregation, and nonrandom co-operative process, such as nucleation and growth, might occur.²⁷ Although Oakenfull's explanation of high power laws has been challenged by other researches,^{26,28} no other satisfactory explanation has been proposed so far. The high power laws (>4) for the dependence of gelation rates versus polymer concentrations were also reported in the literatures. Oakenfull and Scott²⁹ found that the power law exponent n was 4.5 for *l*-carrageenan and 12.5 for *k*-carrageenan respectively. The gel time reflecting the initial gelation rate was found to follow a C^6 concentration dependence for the gelation of maltodextrin aqueous solutions.³⁰

Figure 7 also shows that the higher the AZC concentration, the higher the values of $|G^*|$ after a fixed reaction time. The dependence of the gel strength at 20,000s on AZC concentration was determined, and it was found that the power law exponent was 3.4, which is close to the widely reported third power law scaling.

$$|G^*|_{20000} \sim (C_{AZC})^{3.4} \quad (8)$$

Effect of starch concentration on co-gelation of AZC and starch

Besides the AZC concentration, the effect of starch concentration on gelation of AZC/starch blends was also studied. For a fixed amount of AZC, the initial reaction rate was found to depend on the amount of starch in the system. The higher the starch concentration, the more likely it is for an AZC molecule to react with starch. In Figure 8, a faster increase of $|G^*|$ for the systems with higher starch concentration was observed. By plotting $d|G^*|/dt$ versus

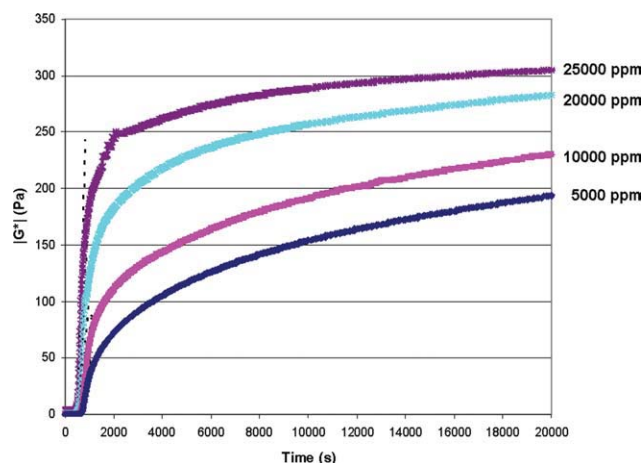


Figure 8 $|G^*|$ profiles at different starch concentrations for AZC-starch gelation (AZC concentration 4500 ppm, 80°C, pH 9). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

starch concentration (not shown here), it was found that the maximum rate of $|G^*|$ change followed a power law relationship with starch concentration:

$$d|G^*|/dt \sim (C_{starch})^{1.0} \quad (9)$$

The results indicate that the crosslinking of starch by AZC is a first order reaction. A similar result was reported by Omari¹³ who found that the gelation rate of scleroglucan (a polysaccharide) was dependent on the polymer concentration with a 1.4 power relationship. For the hydroxypropyl guar-titanium system,³¹ the exponent is 0.7. The dependence of the gelation rate on polymer concentration was found to follow a power law with a coefficient of 1.25 for gelation of xanthan with trivalent metal ions.³² However, the exponent is dependent on the structure and confirmation of the polymers. Normally, the values of the exponent for flexible polymers are much larger than that for rigid polymers, such as polysaccharides. An exponent value around 2.7 was reported for polyacrylamide with different crosslinkers.¹²

Figure 8 also shows that $|G^*|$ (at 20,000s) increases with the increase of the starch concentration. This is because the addition of starch in the blends increased the probability of starch to AZC reaction. The $|G^*|_{20,000}$ versus starch concentration also demonstrated a power law relationship:

$$|G^*|_{20,000} \sim (C_{starch})^{0.3} \quad (10)$$

The small exponent value of starch concentration indicates that the final strength of the crosslinked network is not highly dependent on the starch concentration.

TABLE I
Dependence of the Initial Bond Formation Rate and Gel Strength on Different Parameters

Crosslinking system	AZC solution	AZC-starch blend	
	AZC concentration	AZC concentration	Starch concentration
$d G^* /dt$	$(C_{AZC})^{3.0}$	$(C_{AZC})^{5.3}$	$(C_{starch})^{1.0}$
$ G^* _{20,000}$	$(C_{AZC})^{2.9}$	$(C_{AZC})^{3.4}$	$(C_{starch})^{0.3}$

The dependence of the initial bond formation rate (corresponding to $d|G^*|/dt$) and the gel strength (at 20,000s) for both the pure AZC solutions and AZC-starch blends are summarized in Table I. The results reveal different levels of significance of various parameters of the gelation process. AZC self-crosslinking is a third power process with respect to AZC concentration, both for the initial bond formation rate and gel strength (at 20,000s). However, with an exponent of 5.3, the initial bond formation rate of AZC-starch blends has a much stronger dependence on AZC concentration than the pure AZC solutions. The efficiency of AZC as crosslinking agent is strongly enhanced by the presence of starch molecules. Somewhat surprisingly, the starch concentration has a relatively less impact on the gelation rate. This may be because that starch is a rigid polymer with a much higher molecular weight than that of AZC, and no starch self-gelation can occur in the system. Therefore, the smaller and more reactive AZC molecules demonstrate a dominate role during the cogelation of AZC and starch.

For practical applications, the dosage of AZC should be minimized for saving the chemical cost.

For example, in the case of fiber surface modification via starch grafting by using AZC as a crosslinking agent, more native starch with a lower cost rather than AZC should be grafted onto fiber surfaces to improve the fiber-fiber bonding capability.⁴ However, the results shown in Table I indicate that the initial crosslinking rate and gel strength are mainly attributed to the AZC concentration. The impact of starch concentration on the reaction kinetics is relatively less significant. The lower the dosage of AZC applied in the reaction system, the lower the gel strength of hydrogels. If the level of AZC is too low, a hydrogel might not be formed, and a large amount of starch grafting onto fibers might not be achieved.

Effect of reaction temperatures

For the crosslinking/gelation process, the temperature dependence of reaction rates can be described by an Arrhenius type eq. (3) in which the rheological parameter change rate dG/dt is used to express the reaction rate.¹⁷ The Log form of eq. (3) can be written as:

$$\ln(dG/dt) = \ln(A^*) - E_a/RT \quad (11)$$

Therefore, by plotting $\ln(dG/dt)$ versus $1/T$, the activation energy E_a can be determined from the slope if a linear relationship exists.

In this study, the isothermal gelation of AZC and AZC-starch blends was conducted over a temperature range of 50–90°C. Figure 9 presents the $|G^*|$ profiles for different reaction temperatures. It was found that the induction period became significantly shorter with the increase of temperature. For AZC self-crosslinking (Fig. 9 left) at 90°C, the induction

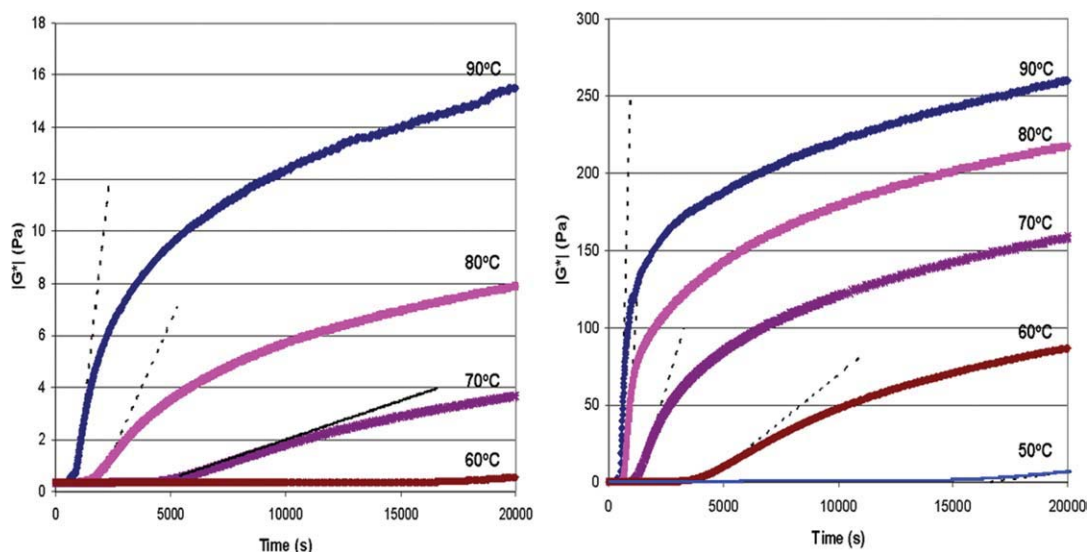


Figure 9 Effect of temperatures on the gelation process (left: 1500 ppm AZC in water; right: 4500 ppm AZC in 1% starch). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

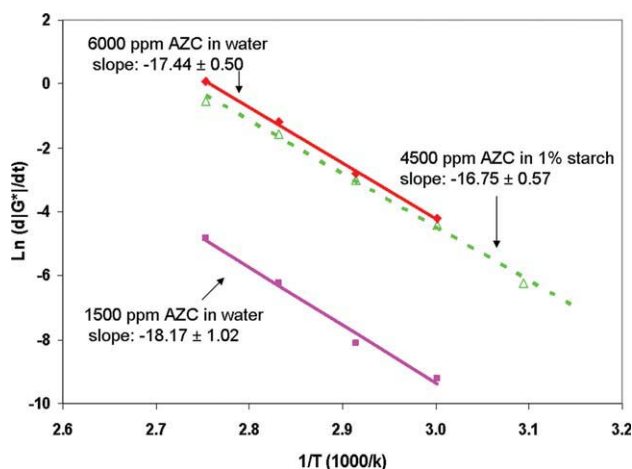


Figure 10 The Arrhenius plots of the initial $d|G^*|/dt$ on the isothermal gelation of AZC and AZC/starch blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

time is only 600s, while it is around 4800s at 70°C. A similar result was reported for the gelation of polyacrylamide.²¹

For the both reaction systems, the initial bond formation rate ($d|G^*|/dt$) and the gel strength at 20,000s are highly dependent on temperature. Figure 9 shows that the higher the temperature, the faster $|G^*|$ increase, and the larger the value of $|G^*|$ at a similar time. The maximum slopes of the initial increase portion of the curves at different temperatures were determined, and the Arrhenius plots of $d|G^*|/dt$ versus $1/T$ were obtained (Fig. 10). It can be seen that, for both AZC self-crosslinking (the solid lines) and AZC-starch co-crosslinking (the dash line), the plots exhibit a good linearity. By using the slopes of the lines (i.e., $-E_a/R$), the activation energy values were calculated. For the system of AZC self-crosslinking at different AZC concentrations (1,500 ppm and 6,000 ppm), the activation energy values are 145 ± 9 kJ/mol and 151 ± 4 kJ/mol respectively. According to the collision theory of reaction rates, the activation energy is the energy barrier for the reaction of individual molecules. Therefore, theoretically, the activation energy is independent of polymer concentrations. However, the Arrhenius equation is an empirical equation. The parameter used here, the complex modulus is a macro description of polymer network. Therefore, slight difference of the activation energy values obtained for the systems with different concentrations is possible. The activation energy of AZC-starch co-crosslinking determined from the plot in Figure 10 is 139 ± 5 kJ/mol which is slightly lower than that of AZC self-crosslinking. This means that the energy barrier of the reaction between AZC and starch molecule is close to that of the reaction between AZC and AZC mole-

cules. Therefore, from the point of molecule reactions, the preference of AZC to AZC and AZC to starch is comparable. In addition, the values of activation energy obtained are of the same order as those of starch or other polysaccharide gelation which are within the range of 30-138 kJ/mol.^{13,17,33}

Effect of pH

The chemistry of AZC is very sensitive to the solution pH.¹³ It was reported that the active pH range of AZC is 6–10. The crosslinking studies were conducted at different pH values. Figure 11 shows that the induction time is shorter at the lower pH values. This is because at a low pH, AZC is not stable, and the self-decomposition occurs (forming crystalline metal), which might trigger crosslinking. It was found that increasing pH value led to higher gel strengths i.e., the values of $|G^*|$ at 20,000s in Figure 11 (with an exception of pH 10). Omari¹³ also reported that the gel formation could be enhanced by increasing pH for the scleroglucan-zirconium system. The low gel strength at pH 10 is likely caused by zirconium hydrolysis which was enhanced in alkaline media.¹³ With respect to the final gel strength, pH 9 is the optimal reaction condition, which agrees well with the results from our previous publication.⁴ A similar result was obtained for the effect of pH on the starch-AZC co-crosslinking.

Comparison of reaction rates in different reaction systems

The mechanism of the AZC reaction with polymers containing hydroxyl groups [Fig. 1(b)] shows that CO_2 is generated when AZC reacts with starch or

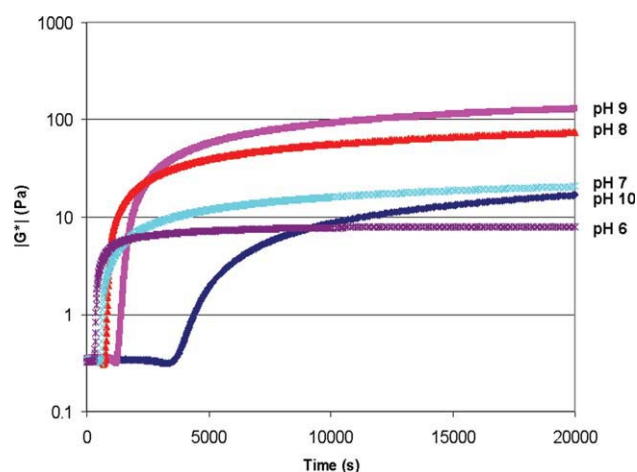


Figure 11 The effect of pH on AZC self-association (AZC concentration 4500 ppm, 80°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

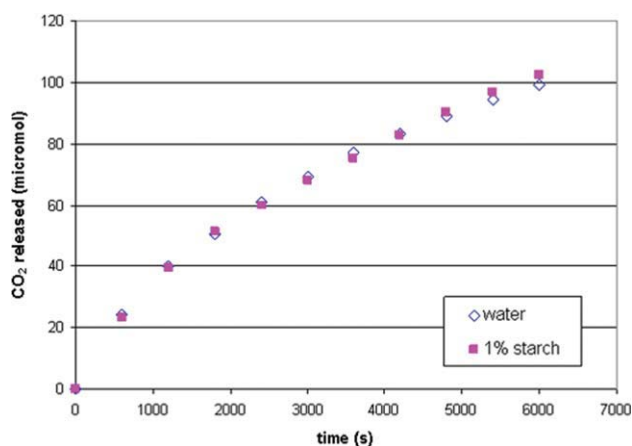


Figure 12 The release of CO₂ over time for different reaction systems (3000 ppm AZC in water and in 1% starch at 80°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with itself. The release rate of CO₂ should be proportional to the rate of link formation. In this study, GC headspace multiple sampling was used to monitor the release of CO₂ over the reaction time. Figure 12 represents the CO₂ release curves for two different crosslinking systems. It can be seen that AZC self-crosslinking and AZC-starch co-crosslinking have a similar CO₂ release rate, which means AZC self-crosslinking and AZC-starch co-crosslinking have a similar reaction rate. The reaction preference of AZC with AZC and the reaction preference of AZC with starch are comparable, which agrees with the results of activation value determination. It should be noted that the reaction rate revealed by CO₂ release represents the interaction between individual molecules, AZC-AZC, and AZC-starch. However, starch has a much higher molecular weight and lower mobility than AZC in aqueous solutions, the probability of collision between AZC and starch is primarily dominated by AZC diffusion. Therefore, during the gelation process, a higher power law dependence of the gelation rate on AZC concentration was demonstrated compared with that on starch concentration.

Figure 12 shows that at an elevated temperature, the reaction can occur immediately after the addition of AZC in the water or starch. However, the initial generated links between molecules are not enough to form a gel in the system, and as a macro level characterization the value of $|G^*|$ observed is kept constant at a low level for a time period [i.e., the induction period in Fig. 3(a)] before the rapid increase of $|G^*|$, which represents the development of the crosslinked hydrogel network. The above result indicates that the gel network development shows some delay following the link formation, i.e., CO₂ release.

CONCLUSIONS

In this study, the evolution of complex modulus (absolute value) for the pure AZC solution and the AZC-starch mixture solution in water was characterized. The kinetics of the crosslinking processes (the gelation) for the two systems was determined. It was found that the dependence of both the initial bond formation rate and the gel strength exhibited a power law scaling with both AZC and starch concentrations. The development of the crosslinking network is highly dependent on the AZC concentration. The effect of starch concentration on the gelation rate is relatively less significant for AZC-starch mixture solution. The temperature dependence of the crosslinking rate depicted in the Arrhenius plots shows a good linearity. The activation energy of AZC self-crosslinking is approximately 145–151 kJ/mol, while the activation energy of AZC-starch co-crosslinking is 139 kJ/mol. The CO₂ release rates show that AZC self-crosslinking and AZC-starch co-crosslinking have a similar reaction (i.e., link formation) rate. The reaction preference of AZC with AZC and the reaction preference of AZC with starch are comparable. Furthermore, the gel network development shows some delay following the link formation, i.e., CO₂ release.

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