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ARTICLE

Epidemic models for phase transitions: application to a physical gel

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ABSTRACT

Carrageenan gels are characterized by reversible sol–gel and gel–sol transitions under cooling and heating processes and these transitions are approximated by generalized logistic growth curves. We express the transitions of carrageenan–water system, as a representative of reversible physical gels, in terms of a modified Susceptible–Infected–Susceptible epidemic model, as opposed to the Susceptible–Infected–Removed model used to represent the (irreversible) chemical gel formation in the previous work. We locate the gel point T_c of sol–gel and gel–sol transitions and we find that, for the sol–gel transition (cooling), $T_c > T_{sg}$ (transition temperature), i.e. T_c is earlier in time for all carrageenan contents and moves forward in time and gets closer to T_{sg} as the carrageenan content increases. For the gel–sol transition (heating), T_c is relatively closer to T_{gs} ; it is greater than T_{gs} , i.e. later in time for low carrageenan contents and moves backward as carrageenan content increases.

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Sol–gel; gel–sol transitions; carrageenan; generalized logistic curve; gel point

1. Introduction

We were basically interested in the gelation of two types of systems; polyacrylamide (PAAm) and K-carrageenan. In the first case, (PAAm)–sodium alginate (SA) composite was prepared with different amounts of SA and studied by the steady-state fluorescence technique [1]. Pyranine was added as a fluoroprobe for monitoring the polymerization. It was observed that pyranine molecules bind to PAAm and SA chains upon the initiation of the polymerization. Fluorescence spectra from the bonded pyranines allowed us to monitor the sol–gel phase transition, and to test the universality of the sol–gel transition as a function of SA contents. Observations around the critical point showed that the gel fraction exponent and the weight average degree of polymerization exponent agreed with the percolation result for ($<0.25\%$ (w/v)) SA contents. However, classical results were produced at ($<2\%$ (w/v)) SA contents. In the second case, photon transmission techniques were used to study sol–gel and gel–sol transitions in K-carrageenan–water systems with carrageenan wt.% of 1.0, 2.0, 3.0 and 4.0 in the system [2]. The photon transmission intensity, I_{tr} , was monitored against temperature to determine critical phase transition temperatures and transition rates. It was observed that the sol–gel transition temperatures, T_{sg} , are much lower than the gel–sol, T_{gs} , transition temperatures based on the hysteresis of the sigmoidal phase transition loops. Here, T_{sg} and T_{gs} are the temperatures at which the first derivative of I_{tr} with respect to temperature reaches its maximum value. Sol–gel and gel–sol activation energies were also determined and it was found that a carrageenan-

water system required less energy for the gel–sol transition than for the sol–gel transition [2]. Here, for the calculation of activation energies, the well-known Arrhenius equation ($k = A\exp(-E/RT)$) was used by assuming the change in I_{tr} which ‘reflects’ the structural change in the system. The I_{tr} values were directly associated to the rate constant, k , during the gel–sol and sol–gel transitions. Then, the corresponding activation energies of the gel–sol and sol–gel transitions were produced from the slopes of the fits on the $\ln(I_{tr})$ versus T^{-1} graphs. The energy requirements to accomplish the transitions were interpreted by considering those activation energy values.

In the previous work, we modeled the gelation of (PAAm)–SA composite [1] by the Susceptible-Infected-Removed (SIR) and the Susceptible-Exposed-Infected-Removed (SEIR) models [3]. We have shown that low SA content polymerizations that display percolation type gelation properties obey SIR model, while high SA content polymerizations that agree with the classical theory obey the SEIR model [4]. In both cases, the irreversibility of the chemical gelation process is the key for representability of the phase transition on terms of the SIR and SEIR models. We had observed that the SIR and SEIR models were inadequate for modeling the gelation of K-carrageenan-water systems [2], which are typical examples of reversible, physical gelation processes. In the present work, we model these reversible physical gelation processes by a modification of the Susceptible-Infected-Susceptible (SIS) epidemic model, as discussed in Section 2.

In the case of the SIR and SEIR models, the dependent variables cannot be analytically expressed as a function of time, hence one has to use numerical methods to obtain time evolution curves. In [4], we determined the parameters of the models that match experimental results by minimizing the error between the numerical solution curves and the data. On the other hand, it is well known that the SIS model is equivalent to the generalized logistic equation and its solutions can be expressed in terms of the standard logistic growth curve [5]. Thus, data and the solution curves of the model can be compared directly by using regression software. However, the gelation data of [2] does not fit the standard logistic growth; but it fits the generalized logistic growth almost perfectly. Accordingly, in Section 3, we introduce a new parameter to obtain a modified SIS system whose solutions are generalized logistic growth curves. This result allows to interpret the chemical and physical gels in a common framework, in terms of epidemic models.

The determination of the gel point in phase transitions has been an intriguing problem because its location with respect to the inflection point of the sigmoidal transition curve depends on the nature of the gelation experiments. The gel point T_c is characterized by a drastic change in various physical properties and it is hard to measure without disturbing the transition process. In the experimental work that provides the basis of the results presented in [1], the gel points were determined by independent experiments. After modeling these gelation processes in terms of the SIR and SEIR systems of differential equations [6], we were challenged by finding a mathematical property that corresponds to the gel point. We observed that the derivatives of the sigmoidal curve that represent the Removed individuals of the SIR and SEIR models have an interesting property. The time instants t_i at which the i th derivative reaches its global extremum formed a seemingly convergent sequence. This limit point turned out to be in qualitative agreement with the location of the gel point as measured in [1] and the existence of such a limit point was proposed as a mathematical definition of the critical point of a phase transition [6]. Later on we proved that the existence of a critical point of a sigmoidal curve, in the sense above, was due to the wave packet behavior of the derivatives and it could be expressed in terms of the properties of the Fourier transform of its first derivative [7]. We have also computed the Fourier transform of the generalized logistic growth [8] and located its critical point. In Section 4, we use these results to locate the gel point in the sol–gel and gel–sol transitions, as the critical point of the generalized logistic growth curve that best fits the data.

2. Epidemic models and phase transitions

Compartmental epidemic models are based on the subdivision of the population into disjoint subgroups via their status with respect of the disease. Individuals that are prone to the disease are called

‘Susceptible’; the ones that carry the disease are called ‘Infected.’ If the disease has an incubation period, individuals in this latent stage are called ‘Exposed.’ Finally, those that are recovered from the disease and cannot be susceptible anymore are called ‘Removed.’ Depending on the characteristics of the disease, the passage between these compartments can be one-directional or reversible. Various interventions such as vaccinations, the effects of variable population size, insertion of new agents/individuals to the population can be incorporated to the basic models to obtain differential systems with a number of interesting global dynamics.

These compartmental models are used to represent not only epidemics in a society but also epidemics in animal populations, plant aggregations, spread of rumors, etc. The spread of an epidemic has also a resemblance to percolation phenomenon. Motivated by the description of the gelation as a percolation process, in the previous work [4] we modeled the (irreversible) gelation of SA by the SIR and SEIR models. In the present work we will model the reversible sol–gel, gel–sol passages for physical gels by the SIS.

2.1. The SIR, SEIR and SIS models

A detailed description of the SIR and SEIR models in the context of phase transitions is given in [4]. We recall that (S), (E), (I) and (R) stand for ‘Susceptible’, ‘Exposed’, ‘Infected’ and ‘Removed.’ Individuals that are prone to the disease are ‘Susceptible’ while the ones that can no more contact the disease are ‘Removed.’ ‘Infected’ individuals can communicate the disease to susceptible ones. ‘Exposed’ individuals are the ones that contacted the disease but cannot contaminate others yet. The existence of such an incubation period has the effect of slowing down the spread of the disease. In the SIS model, infected individuals do not gain immunity, hence they return to the population of the Susceptible individuals at the end of the infection period. The differential equations that govern these models are given below:

$$\text{SIR} : \quad dS/dt = -\beta S I, \quad dI/dt = \beta S I - \eta I, \quad dR/dt = \eta I, \quad (1)$$

$$\text{SEIR} : \quad dS/dt = -\beta S I, \quad dE/dt = \beta S I - \varepsilon E, \quad dI/dt = \varepsilon E - \eta I, \quad dR/dt = \eta I, \quad (2)$$

$$\text{SIS} : \quad dS/dt = -\beta S I + \eta I \quad dI/dt = \beta S I - \eta I, \quad (3)$$

The solution of the SIR and SIS systems for typical parameter values are given in Figure 1(a,b).

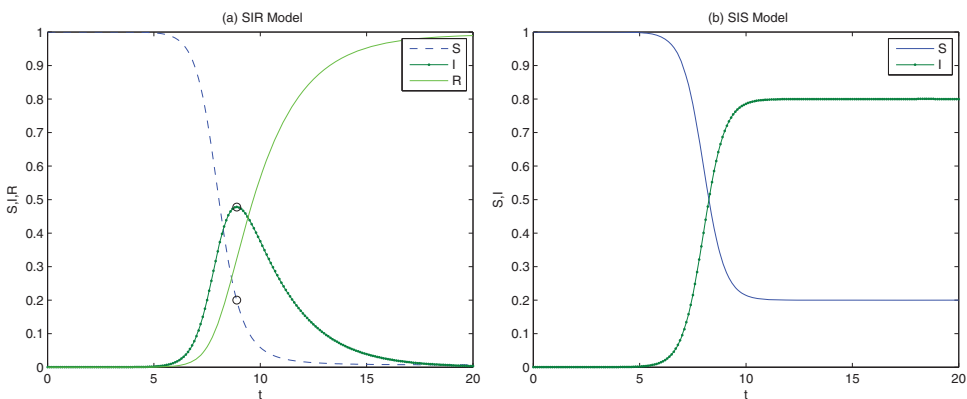


Figure 1. (a) Solutions of the SIR model with parameters $\beta = 2.5$, $\eta = 0.5$ and initial value $I(0) = 10^{-7}$. $S(t)$ is monotone decreasing, $R(t)$ is monotone increasing and $I(t)$ is a localized hump. $I(t)$ reaches its maximum when $dI/dt = 0$, hence $S = \eta/\beta = 0.2$. The final value of R , R_f is determined from the relation $R_f + \exp(-\beta/\eta R_f) = 1$. (b) Solutions of the SIS model with parameters $\beta = 2.5$, $\eta = 0.5$ and initial value $I(0) = 10^{-7}$. $S(t)$ is monotone decreasing and $I(t)$ is monotone increasing. The final values are determined from $dS/dt = dI/dt = 0$, hence $S = \eta/\beta = 0.2$. $I = 0$ is a stable equilibrium but $S = \eta/\beta = 0.2$ is an unstable equilibrium.

In the formation of chemical gels that are represented by the SIR and SEIR models the molecules are inactive in the gel state, hence the $R(t)$ curve represents the gel formation. The irreversibility of the chemical reaction corresponds to the permanent immunity at the end of the infection period. In the SEIR model, the existence of the compartment of Exposed individuals results in a slowdown of the spread of the epidemic. In [1], we have shown that the gelation of PAAm–SA follows the SIR and SEIR models, respectively, for low and high concentrations of SA, in accordance with slower reaction rates for high SA concentrations.

In the formation of gels by physical bonds as in the case of carrageenan–water samples, the sol–gel and gel–sol transitions are obtained by cooling and heating processes. In the experimental work, the heating and cooling rates are adjusted to be linear in time, hence one can think of the SIS system as evolving with respect to the temperature T .

The SIS system can be solved for I easily as follows. In Equation (3), since the right-hand side of the equations add up to zero, the sum of S and I is constant and by normalizing, we can take $S + I = 1$. Then replacing S by $1 - I$ in the derivative of I , we obtain

$$dI/dt = \beta SI - \eta I = \beta(1 - I)I - \eta I = \beta I[(1 - \eta/\beta) - I] \tag{4}$$

The right-hand side of this equation is exactly the logistic differential equation whose solution is the logistic growth curve. But as seen in [2], the sol–gel and gel–sol transitions both follow generalized logistic growth curves depending on a certain parameter c , rather than the standard logistic growth. We thus need to modify the SIS system and introduce a parameter so that the solution for $I(t)$ is the generalized logistic growth and we will justify this in terms of the gelation process. For this, we start with the relation $S + I^k = 1$, instead of $S + I = 1$. Then, Equation (4) is modified as

$$dI/dt = \beta SI - \eta I = \beta(1 - I^k)I - \eta I = \beta I [(1 - \eta/\beta) - I^k], \tag{5}$$

which is exactly the differential equation satisfied by the generalized logistic growth curve. Then, differentiating $S + I^k = 1$, we obtain the ‘Generalized SIS System’:

$$dS/dt = -k \beta I^k(S - \eta/\beta), \quad dI/dt = \beta I (S - \eta/\beta). \tag{6}$$

As a convenience in using regression software, we express this parametrization in terms of the SIS model. The generalized logistic growth model that we use for regression is given by

$$y - y_0 = a [1 + e^{-(x-x_0)/b}]^{-c} \tag{7}$$

and the corresponding differential equation has the form:

$$dy/dt = c/b (y - y_0) [1 - (y - y_0)^{1/c}/a^{1/c}]. \tag{8}$$

Comparing Equations (5) and (8), we can see that

$$I = y - y_0, \quad 1/c = k, \quad a^{1/c} = (1 - \eta/\beta), \quad c/(b a^{1/c}) = \beta. \tag{9}$$

The parameter c is crucial in determining the shape of the generalized logistic growth curve. In Section 4, we will see that the parameter x_0 is exactly the gel point. For $c > 1$, the gel point is before the inflection point, while for $c < 1$ it is after the inflection point. From Equation (7), one can see that the final value of I is a . In epidemic models, the strength of the epidemic is expressed in terms of the so-called Basic Reproduction Number, $R_0 = \beta/\eta$ and $1/\eta$ is interpreted as the mean duration

of the epidemic. In the next section, these values will be presented together with the parameters of the best fitting generalized logistic growth curves.

3. Curve fitting to experimental results

The sol–gel and gel–sol transition curves (as smoothed in [2]) are given in Figure 2.

We use regression analysis to find parameters a , b , c , x_0 , y_0 , of the generalized logistic growth given by Equation (7), in Tables 1 and 2. All values are obtained with standard errors less than 0.001. The values of R_0 and $1/\eta$ are computed using Equation (9).

4. The gel point

In the previous work [4, 6] we observed that the experimentally determined gel point in the gelation of PAAm–SA coincide with our mathematical description of the critical point of a sigmoidal curve, as a point of accumulation of the absolute extrema of its derivatives. In the current case also, the points T_i where the absolute values of the derivatives reach their extreme values accumulate at certain points. We present these in Figures 3(a–d) and 4(a–d) for gel–sol and sol–gel transitions, respectively. In these figures, the first 20 derivatives of the generalized logistic growth curve corresponding to sol–gel transitions with parameter values given in Tables 1 and 2 are normalized and plotted. One can see that the extreme values agglomerate near the values x_0 given in these tables.

The graphs above indicate that the points where the derivatives of the sigmoidal curves reach their absolute extrema form a convergent sequence. This was proved in fact in subsequent work [7], where we showed that this critical point is determined in terms of the phase of the Fourier transform of the first derivative of the sigmoidal curve. We have computed the Fourier transform of the generalized logistic growth curve in [8] and proved that the origin is its critical point. It follows that if the sigmoid is obtained by a horizontal shift, as in the cases above, the values x_0 correspond to critical point, or the gel point. The critical points for each of the gel–sol and sol–gel transitions are given below.

In these figures that represent the heating process, we can see that except for the last sample, the gel point occurs after the peak of the first derivative but its location is close to this maximum. Thus, during the heating process the gel–sol transition occurs relatively late, with respect to the peak of the first derivative.

On the other hand, for sol–gel transition corresponding to the cooling process, the gel point is located at the right of the peak of the first derivative. But it should be noted that as this is a cooling process, the sol–gel transition occurs early in time, well before the peak of the first derivative.

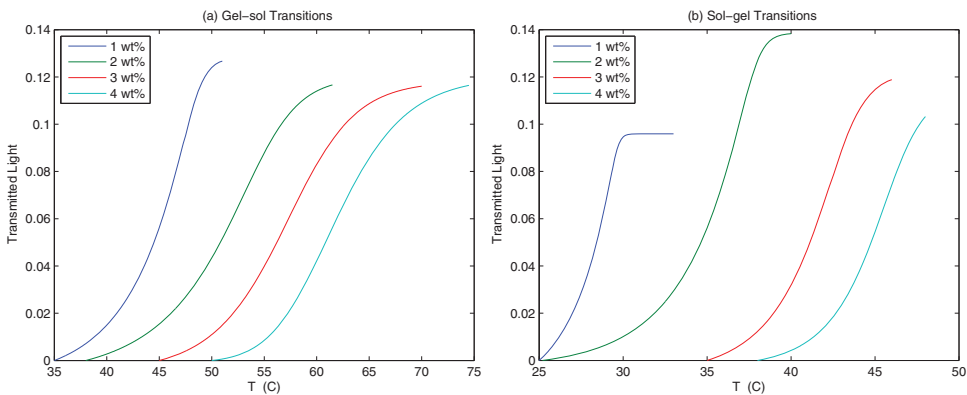


Figure 2. (a) Gel–sol transition for 1.0, 2.0, 3.0 and 4.0 wt.% carrageenan samples from left to right. (b) Sol–gel transition for 1.0, 2.0, 3.0 and 4.0 wt.% carrageenan samples from left to right.

Table 1. Gel–sol transition for 1.0, 2.0, 3.0 and 4.0 wt.% carrageenan samples.

wt.%	1.0	2.0	3.0	4.0
<i>a</i>	0.1364	0.1266	0.1230	0.1211
<i>b</i>	0.8117	2.3052	3.0932	3.8862
<i>c</i>	0.1648	0.3911	0.7519	2.2331
x_0	48.6621	55.2244	58.2233	57.9312
y_0	−0.0085	−0.0068	−0.0049	−0.0010
$R_0 - 1$	$5.6 \cdot 10^{-6}$	$5.1 \cdot 10^{-3}$	$6.6 \cdot 10^{-2}$	$6.6 \cdot 10^{-1}$
$1/\eta$	$2.8 \cdot 10^{-5}$	$3.0 \cdot 10^{-2}$	$2.7 \cdot 10^{-1}$	$1.1 \cdot 10^0$

Table 2. Sol–gel transition for 1.0, 2.0, 3.0 and 4.0 wt.% carrageenan samples.

wt.%	1.0	2.0	3.0	4.0
<i>a</i>	0.1106	0.1417	0.1275	0.1169
<i>b</i>	0.1870	0.4817	0.9684	1.0977
<i>c</i>	0.0809	0.1447	0.3569	0.4827
x_0	29.6652	37.9045	43.2535	46.3316
y_0	−0.0147	−0.0031	−0.0061	−0.0030
$R_0 - 1$	$1.5 \cdot 10^{-12}$	$1.4 \cdot 10^{-6}$	$3.1 \cdot 10^{-3}$	$1.2 \cdot 10^{-2}$
$1/\eta$	$3.5 \cdot 10^{-12}$	$4.5 \cdot 10^{-6}$	$8.5 \cdot 10^{-3}$	$2.7 \cdot 10^{-2}$

Here, the transition curves in Figures 5 and 6 can be explained by assuming that, during cooling, double helices were formed through the association of carrageenan molecules and then these double helices aggregated to form ordered assemblies to create a three-dimensional network. During gelation, the carrageenan-water system decomposed into two separate phases with different network

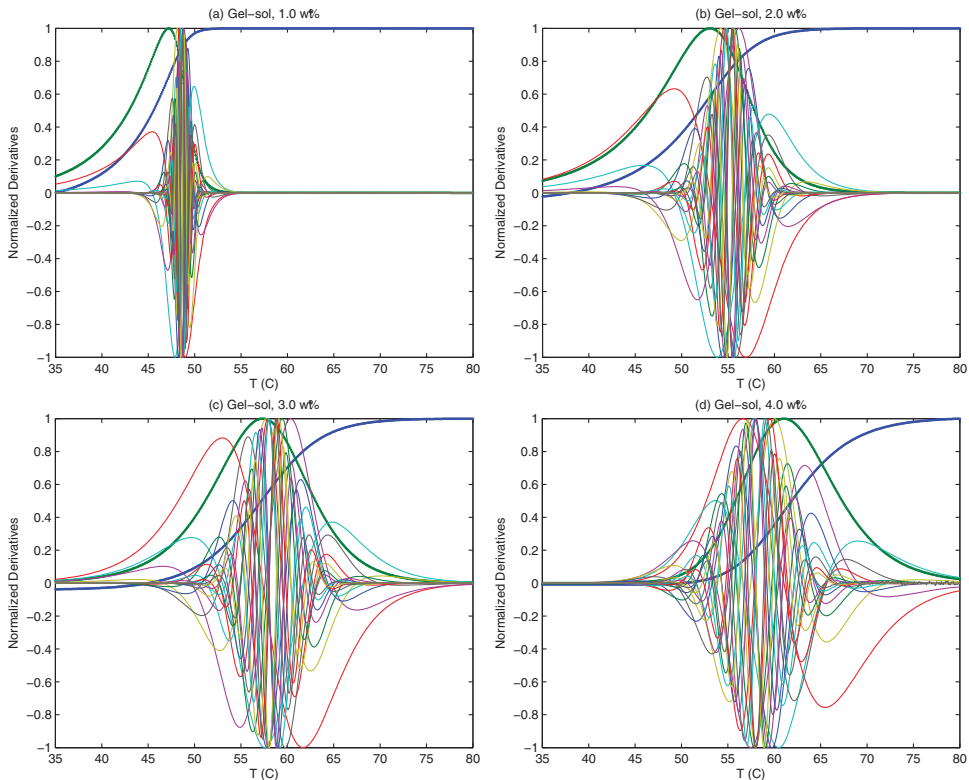


Figure 3. (a)–(d). Normalized derivatives of the generalized logistic growth corresponding to the gel–sol transition with 1.0–4.0 wt.% carrageenan sample. First 20 derivatives are normalized and plotted. The points where the derivatives reach their absolute extreme values accumulate close to the points x_0 , as given in Table 1, i.e. near $T = 48, 55, 58$ and 57 , respectively.

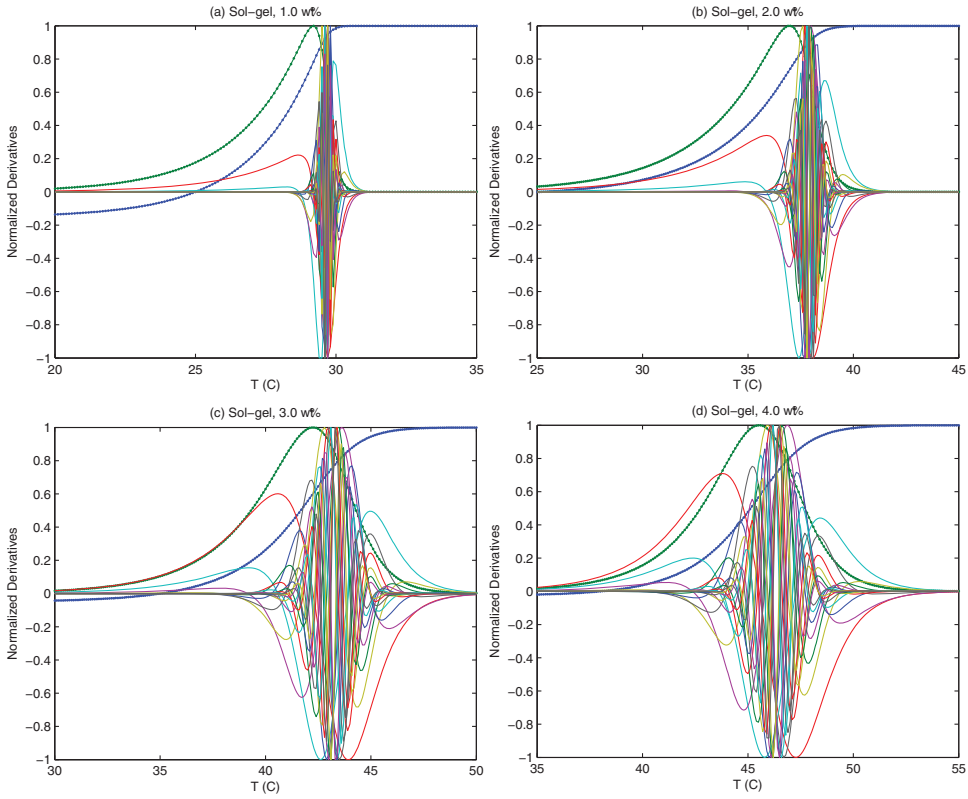


Figure 4. (a)–(d). Normalized derivatives of the generalized logistic growth corresponding to the sol–gel transition with 1.0–4.0 wt.% carrageenan sample. First 20 derivatives are normalized and plotted. The points where the derivatives reach their absolute extreme values accumulate close to the points x_0 , as given in Table 2, i.e. near $T = 29, 37, 43$ and 46 , respectively.

concentrations, which created concentration fluctuations. In other words, the double helix aggregates formed a separate phase by excluding water from their domains. As a result, the contrast difference between carrageenan–water phases scatters light, by reducing the transmitted light intensity, I_{tr} . On reheating, the double helix aggregates disassemble and then the double helices decompose, which results in the destruction of the gel structure. Now, the carrageenan–water system becomes homogeneous and the transmitted light intensity, I_{tr} , increases. On the other hand, it is also observed that T_{sg} values are much lower than the T_{gs} values for all carrageenan samples. During reheating, the gel does not liquefy at T_{sg} , causing hysteresis which can be explained as follows; in order to break up the double helix aggregates and double helices during heating, the system needs lower energy than it needs for gel formation. The energy term here refers to the activation energy of the associated or disassociated carrageenan chains, which is mentioned in the Introduction section. The temperature has to be then lowered to reform the double helices and the corresponding aggregates during cooling [5]. It is understood that the sol–gel transitions require much higher energy than the gel–sol transitions. That is because, to form double helix aggregates more energy is needed than to destroy itself, i.e. much less energy is needed for gel–sol transition (liquefaction) process.

The relation between gel point, T_c and T_{sg} and T_{gs} can be understood from Figures 5 and 6, where at T_c the percolation cluster starts appear. In Figure 5 during gel–sol transition, percolation cluster appears quite late, i.e. at higher temperature ($T_c > T_{gs}$) due to low energy requirement for cluster formation from double helices. However, in Figure 6 during sol–gel transition upon cooling, percolation cluster is formed early ($T_c > T_{sg}$) due to high energy needs for double helix aggregates to form percolation cluster.

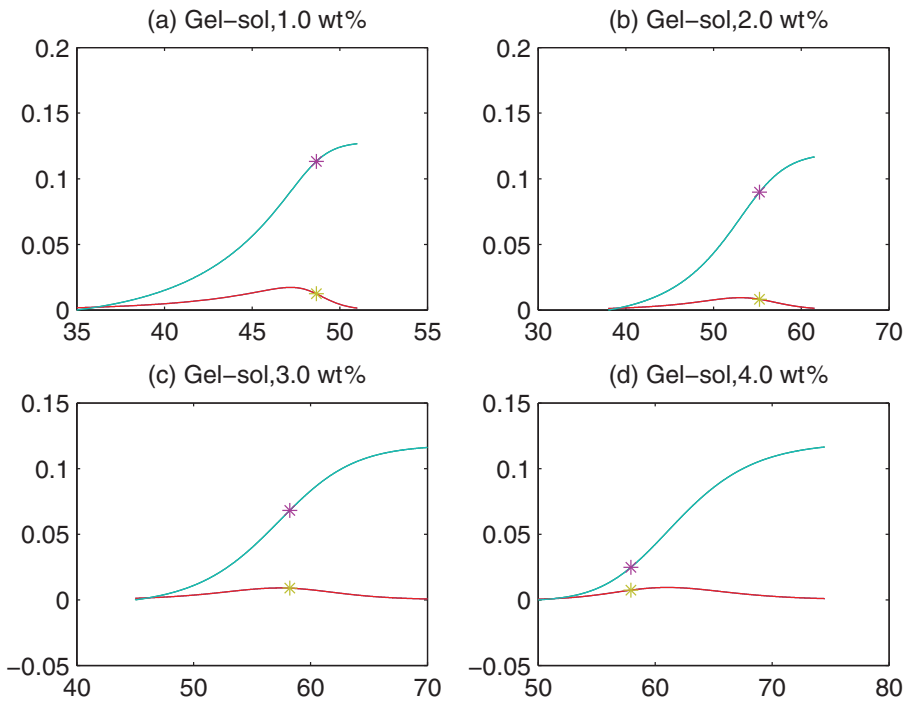


Figure 5. (a)–(d). Gel points, T_c for the gel–sol transition (during heating T_{gs}) for 1.0, 2.0, 3.0 and 4.0 wt.% carrageenan samples. Horizontal axis is temperature (degree Celsius). Sigmoidal curves and localized pulses represent, respectively, the transmitted light intensity and its first derivative.

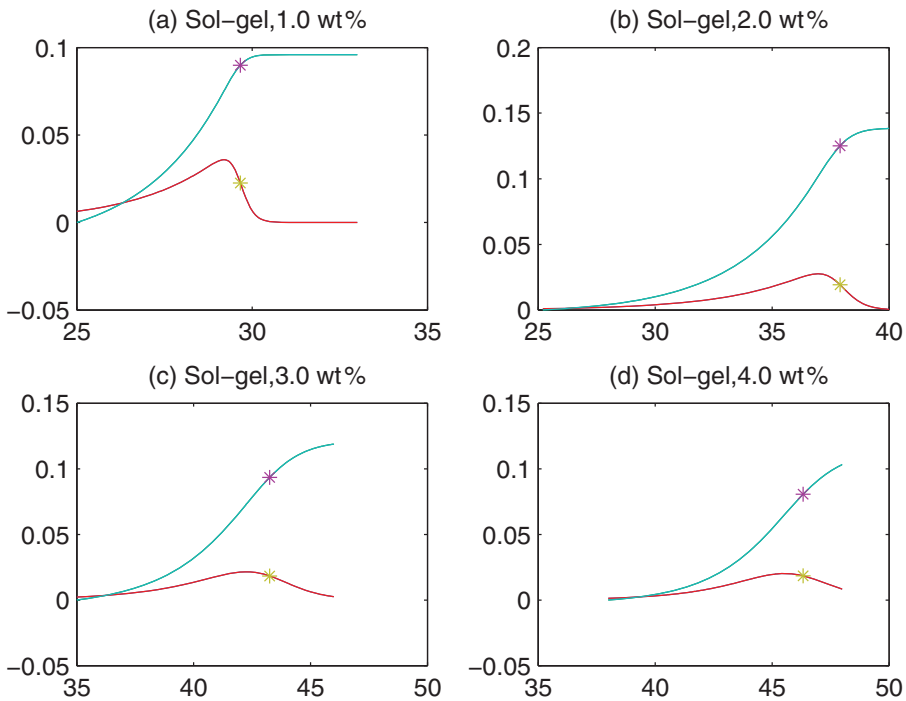


Figure 6. (a)–(d). Gel points, T_c for the sol–gel transition (during cooling T_{sg}) for 1.0, 2.0, 3.0 and 4.0 wt.% carrageenan samples. Horizontal axis is temperature (degree Celsius). Sigmoidal curves and localized pulses represent, respectively, the transmitted light intensity and its first derivative.

Conclusion

This work presents the study on carrageenan gels, which are characterized by reversible sol–gel and gel–sol transitions under cooling and heating processes, presenting hysteresis on the sigmoidal phase transition loops. Here on the heating process, it can be seen that except for the last sample, the gel point occurs after the peak of the first derivative, its location is close to this maximum, i.e. during gel–sol process the transition occurs relatively late, with respect to the peak of the first derivative. However, during sol–gel transition which corresponds to the cooling process, the gel point is located at the right of the peak of the first derivative, which indicates that the sol–gel transition occurs early in time, well before the peak of the first derivative. All these behaviors can be explained as follows. During gel–sol transition, percolation cluster appears quite late, i.e. at higher temperature ($T_c > T_{gs}$) due to low energy requirement for cluster formation from double helices. However, during sol–gel transition upon cooling, percolation cluster is formed early ($T_c > T_{sg}$) due to high energy needs for double helix aggregates to form percolation cluster.

Disclosure statement

No potential conflict of interest was reported by the authors.

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