

Modelling diffusion of water solutes in food polysaccharide hydrogels

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Most of the mathematical models that have been used to describe the diffusion phenomena in gels do not take in account the elastodynamics of gel systems. A physical resistance to the macromolecule motion due to the free volume effects is supposed to take place, but a measure of this resistance is not completely defined. This work contributes to this subject by investigating diffusivities of glucose, a water solute of food interest, in relationship to various viscoelastic conditions of k-carragenan and agar hydrogels.

Mass transport of solutes was determined in gels according to the concentration-distance curve method. The glucose concentration profiles were drawn by means of polarimetric measurements on the fully melted gel after slicing.

Glucose diffuses faster in k-carragenan gels than in agar gels, no matter the gelling agent concentration. Accordingly, the relaxation spectrum of k-carragenan accounts for a faster relaxation of the network with respect to agar gel.

1. Introduction

The understanding of transport phenomena in food hydrogels is the basis for several industrial applications. As an example, biopolymeric gels are used as carriers and delivery devices. An attractive goal is to design gels in such a way that the entrapped active molecules are delivered by the material according to specific release sequences. The phenomenon is relevant to the development of tailor-made controlled release systems. On the side of gel structural and physico-chemical properties, the transport of macromolecules within polymeric gels depends: on the obstruction effects of the surrounding gel strands, on the molecular interactions between the gel and the solute, on the interactions between the solute molecules themselves and the interactions between the solute and the solvent. (Hermansson et al., 2006). A physical resistance to the diffusant motion due to these effects is supposed to take place, but a measure of this resistance is not completely defined. Elastodynamics of gelled systems could be an useful tool to be taken into consideration in mathematical modelling of diffusion in gels. In this work, a preliminary evaluation of the relationship between diffusion and relaxation phenomena taking place in polysaccharide soft networks is considered.

2. Materials and Methods

Polysaccharide gels with a final biopolymer concentration ranging from 0.4 to 2% (w/v) were obtained by dispersing agar powders (B&V, Milano, Italy) in deionized water and by dispersing *k*-Carrageenan powders (Cargill France SAS, Saint Germain, France) into 0.3% (w/v) KCl solution at room temperature under magnetic stirring until complete solubilisation. Glucose was bought from Sigma (Milano, Italy).

Mass transport of glucose was determined in agarose and *k*-carrageenan gels, according to the concentration-distance curve method (Boudhrioua et al., 2003). Two cylinders of gels of initial glucose concentrations $C_0 = 20\%$ w/w and $C_1 = 0.5\%$ w/w, respectively, were placed in contact end to end and stored at constant temperature (20°C) for 24, 120 and 312 hours respectively. Cylinders were then sliced and glucose content was determined on each solubilized slice by polarimetric detection using the JASCO DIP360 polarimeter (JASCO, Japan) equipped with a sodium lamp. Gel density, that was used for estimation of solute diffusivities, was measured with a pycnometer using toluene as the fluid medium.

Mechanical properties of gels were evaluated by means of the TA.XT. plus Texture Analyser (Stable Micro Systems, Godalming, U.K.). An uniaxial compression test was performed by using a parallel plates geometry. The deformation rate was 10 mm min⁻¹. In the stress relaxation test, a quasi-static uniaxial compression at constant deformation within the linearity of the material was applied at a strain rate of 2000 mm min⁻¹ and the stress as function of time was recorded over 3600 s.

The relaxation modulus function $E(t) = \sigma(t)/\varepsilon$, was fitted according to a generalised Maxwell model:

$$E(t) = E_{\infty} + \sum_{i=1}^K E_k (e^{-t/\lambda_k}) \quad (1)$$

where:

E_{∞} = the equilibrium elastic modulus (Pa) ;

E_k = the elastic modulus of the *i*-th Maxwell element (Pa) ;

λ_k = the relaxation time of the *i*-th Maxwell element (s).

The fitting was performed using the method developed by Kaschta for creep recovery test and adapted for stress relaxation experiments by Lefebvre (Lefebvre, 2006) with $N = 5$ logarithmically equidistant spacing of relaxation times λ_i (two per decade). The relaxation spectrum was obtained by reporting on a bi-logarithmic plot the value of E_k on the *y* axis and λ_k on the *x* axis for each *i*-th Maxwell element.

3. Results and Discussion

K-carrageenan gels show higher mechanical resistance (stress at break σ_{\max} ranging from 0.010 to 0.120 MPa) than agar gels (stress at break σ_{\max} ranging from 0.005 to 0.055 MPa), no matter the gelling biopolymer concentration (from 0.4 up to 2% (w/v)). The mechanical parameter σ_{\max} for both biopolymers follows roughly a scaling behaviour which is typical of physical gels.

The above evaluation of an overall mechanical index served the purpose of selecting an useful biopolymer concentration to give suitable gel to be used in glucose diffusion

experiment. As a result, agar and k-carrageenan gels at 1% w/v were chosen to evaluate glucose diffusivity.

The concentration-distance curve method was followed. It consists in measuring, at time t , the solute concentration profile within the sample as a function of distance during a one-dimensional unsteady state diffusive process.

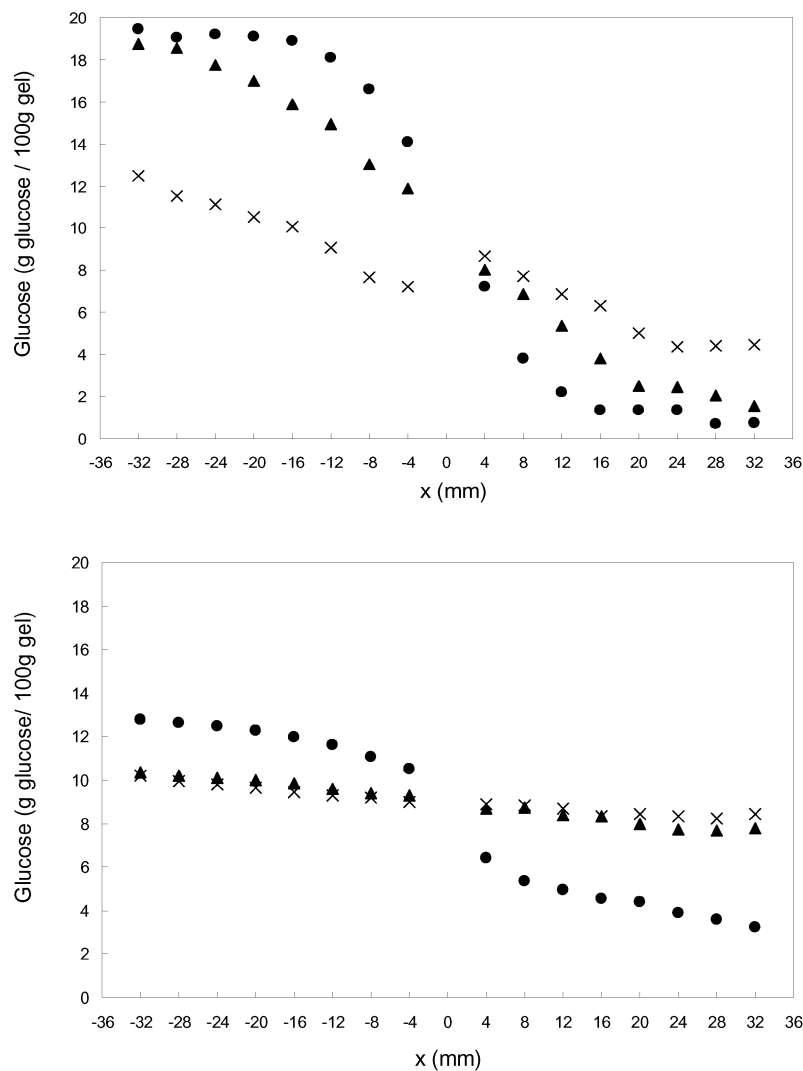


Figure 1: glucose profiles plotted in wet length in agar gels (upper picture) and in k-carrageenan gels (lower picture) after 24 (circle), 120 (triangle) and 312 (cross) hours at 20° C.

Glucose profiles within the gel cylinder were obtained, as it is shown in figure 1, where glucose concentration was plotted versus wet length x for agar and k-carrageenan gels, at 20° C and for different aging times, i.e. 24, 120 and 312 hours.

Diffusivity was calculated from experimental data using numerical or analytical solutions of Fick's laws of diffusion.

From concentration-distance curves, a variable diffusivity, $D(X_i)$ was evaluated at a specific concentration X_i obtained at time t using the following equation (Crank, 1975):

$$D(X_i) = -2 \frac{\partial \eta}{\partial X_i} \Big|_{X=X_i} \int_{X_0}^{X_i} \eta \partial X_i \quad (2)$$

where $\eta = x/(2t^{0.5})$ is the Boltzman variable (Crank, 1975).

Gel shrinkage can also be taken into account by using Lagrangian coordinates related to dry matter (ξ, t) that were used instead Eulerian ones (x, t). In particular, ξ is the solid abscissa and $\Delta \xi$ is the anhydrous thickness: $\Delta \xi_i = \Delta x_i / (1 + \varepsilon X_i)$, where ε is the coefficient of retraction of the material ($\varepsilon = \rho^* / \rho_0$, density of anhydrous gel divided for density of water). This coefficient assumes that the change in volume corresponds to the amount of the moisture lost by material.

In that case, Eq. (2) becomes:

$$D(X_i) = -2 \frac{\partial \eta}{\partial X_i} \Big|_{X=X_i} \int_{X_0}^{X_i} \eta_i \partial X_i \times (1 + \varepsilon X_i)^2 \quad (3)$$

with $\eta_i = \xi_i / (2t^{0.5})$

Numerical methods were adopted to solve Eq. (3), as described by Boudhrioua, (Boudhrioua et al., 2003).

The diffusion coefficient of glucose in k-carrageenan gels was one order of magnitude higher than in agar gels. It varied from 10^{-9} to $10^{-8} \text{ m}^2\text{s}^{-1}$ in agar gels and from 10^{-8} to $10^{-7} \text{ m}^2\text{s}^{-1}$ in k-carrageenan gels, as function of diffusion times.

In order to reduce the effect of time on diffusion, diffusant concentration is plotted the *versus* the Boltzman variable ($\eta = x/(2t^{0.5})$). Over 312 hours aging, glucose diffusion profile falls on a single master curve for agar gels, while k-carrageenan based system behaves in a different way (figure 2).

Results let then to presume that time dependence of diffusion phenomena could be a function of structural properties of the gel matrix. Polymer chains dynamic approach can provide explanation for faster diffusion of glucose in k-carrageenan gels. The analysis of the discrete relaxation spectra, that were drawn as described in the material and methods section, lets to conclude that k-carrageenan gels relax faster than agar gels: a pronounced difference exists in network stiffness at local level for lower relaxation times (between 1 and 10 s). Chain mobility at local level, that was evaluated in the short relaxation time windows, differs between agar and k-carrageenan gels in terms of about one order of magnitude. The differences of chains stiffness and relaxation rates between the two gels explain the difference in glucose transport within the polymer matrix. In the framework of the free volume theory, both the relaxation rate and the stiffness of the chains represent a dynamic obstacle to diffusant molecules movements in disordered soft materials, such as physical gels under study. These rheological observation, in conclusion, quantitatively confirm the differences in glucose diffusion coefficients, which is roughly on the same order of magnitude.

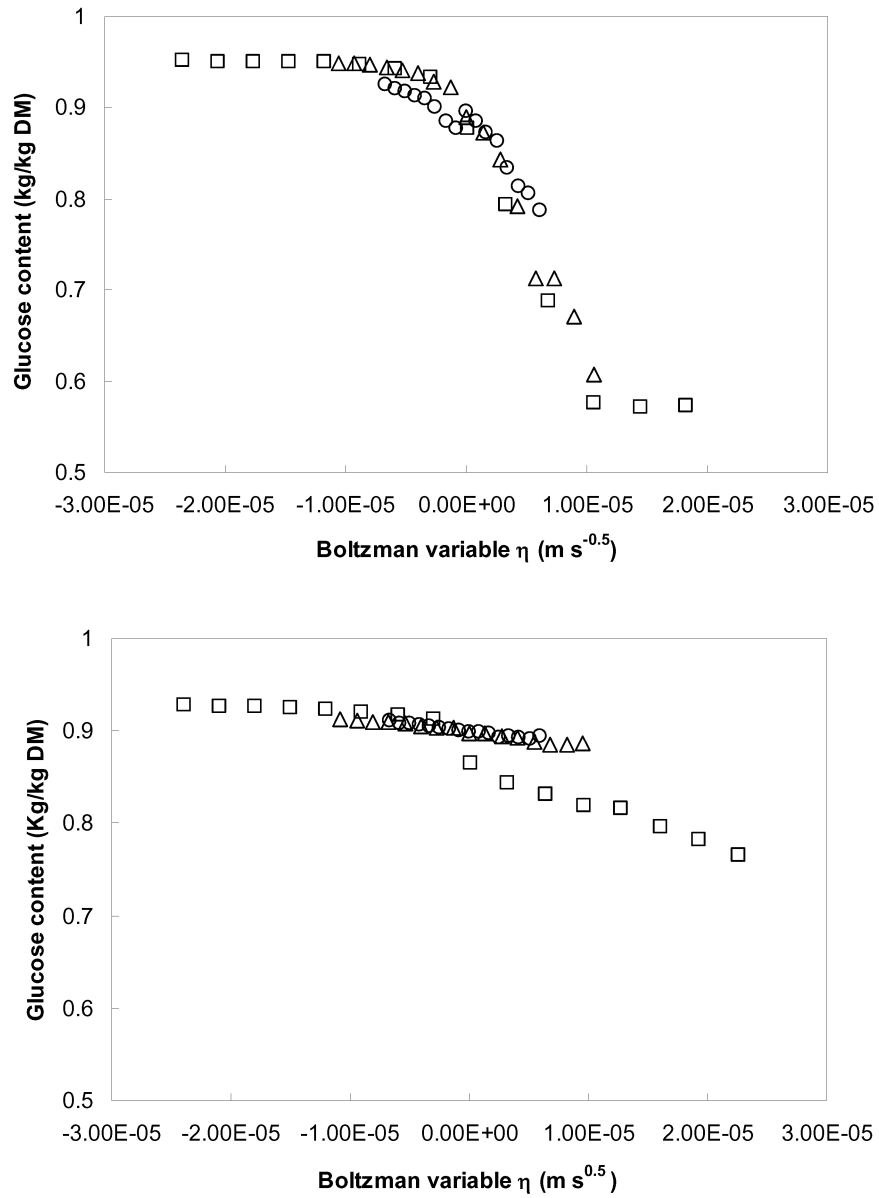


Fig 2: glucose content profile plotted versus Boltzman variable in agar gels (upper figure) and k-carrageenan gels (lower figure) after 24 (square), 120 (triangle) and 312 (circle) hours at 20° C.

4. Conclusions

It was shown that the mass transport of glucose within agar and k-carrageenan physical gels is related to variations of intrinsic material functions that were here extrapolated for discrete relaxation spectra of the materials.

Diffusion of glucose in these polysaccharide gels of different rheological properties met the free volume theory, according to which polymer dynamics represent an obstacle to diffusant molecules movements in disordered soft materials. Results that were obtained represent a basic contribution in view of the design of food gels in such a way that the active molecules are delivered by the material according to specific release sequences. This material property is needed in the development of tailor-made controlled release systems.

5. References

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