Modeling and fundamental aspects of structural relaxation in high-solid hydrocolloid systems

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ABSTRACT

The structural relaxation properties of high-solid gelling polysaccharides, gelatin and whey protein with small-molecule co-solute have been reviewed focusing on the glass transition region and glassy state of the mechanical master curve. Compliance with the principle of thermorheological simplicity is established allowing horizontal superposition of viscoelastic functions in the form of small-deformation stress relaxation or dynamic oscillation modulus. Numerical calculations *via* the Tikhonov regularization yield smooth stress relaxation spectra over a broad timescale that encompasses the isothermal process of vitrification in these systems. Next, the molecular coupling theory addressed the polymer chain dynamics of the local segmental motions that determine the glass transition temperature (T_g) of condensed matrices. Thus a more complete picture of the physics of intermolecular interactions in the short-time region of the glass dispersion has emerged. It allows estimation of the relaxation time for local segmental motions at T_g, and the extent of cooperativity between adjacent chemical moieties governing kinetics of viscoelastic relaxation in hydrocolloid based systems at the glass transition region.

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1. Introduction

Hydrocolloid chains have a large number of motions at different length scales due to the plethora of monomers that result in numerous degrees of freedom. For instance, the rapid local groups or segmental motions observed at the vicinity of the glass transition region of concentrated preparations contrast vividly with the slow movements due to the reptation of the entire chain along its contour in the elastomeric plateau response leading to the molecular flow region of the viscoelastic master curve (Rubinstein & Semenov, 2001).

Molecular motion is of the outmost importance for the physical properties of hydrocolloids, including viscoelasticity, diffusion and glass transition, which are controlled by chain dynamics. Macromolecular motion, also termed structural relaxation, is accompanied by changes in chain conformation leading to a reduction in chain stiffness, hence mechanical network strength, and if allowed to proceed over a prolonged timescale of observation to eventual molecular flow. It usually takes place over long times as different length-scale components relax at characteristic times, τ. Timescales of various molecular motions can be plotted on a relaxation spectrum that describe chain dynamics. As a result, relationships between molecular structure and physical properties are drawn to optimize techno-functionality.

Physicochemical techniques (e.g., NMR relaxation, light scattering, calorimetry etc.) probe molecular motions at different length scales. Rheological tests, which are the interest in this treatise, focus on motions occurring between 0.00628 and 628 rad/s although this range can be extended with appropriate (horizontal only) superposition of data obtained at different temperatures. In the following sections, we shall discuss approaches to calculate the relaxation spectrum from rheological data underlined by prevalent schools of thought.

2. Calculation methods of relaxation spectra

Relaxation spectra cannot be measured directly but instead calculated from rheological data, most commonly dynamic, creep or stress relaxation, performed in the linear viscoelastic response of the material. Mechanical perturbations (e.g., stress) displace chains from their equilibrium positions but they attempt to return to a thermodynamic stable state *via* an array of molecular motions known as relaxations. The objective of calculating relaxation

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spectra is to identify characteristic relaxation times (τ) with which polymeric chain-populations of known molecular weight and fine structure relax to equilibrium. Correct identification of the characteristic times is important, as it gives information on mechanical features at desired temperatures of operation or storage that links to molecular architecture.

The process of extracting relaxation spectra is, mathematically speaking, an inverse problem defined as the process of first obtaining the rheological responses (e.g., relaxation modulus) and afterwards linking them to molecular motion. Fredholm integrals of the first-kind are used to generalize the response of various viscoelastic functions:

$$g(x) = \int_0^a K(x,\tau)H(\tau)\mathrm{d}\tau, 0 \leq s \leq a \qquad (1)$$

where, $g(x)$ is the measured signal and x is either t or ω for $G(t)$, $G'(\omega)$, $G''(\omega)$, and $H(\tau)$ is the unknown solution that represents the continuous relaxation spectrum of the material.

Depending on rheological measurement, the kernel $K(x, \tau)$ is either $e^{-t/\tau}$, $(\omega^2\tau^2/(1 + \omega^2\tau^2)$ or $\omega\tau/(1 + \omega^2\tau^2)$ for $G(t)$, $G'(\omega)$, $G''(\omega)$, respectively. Numerical calculation of $H(\tau)$ from Equation (1) results in ill-conditioned algebraic systems of equations, which means that small perturbations in the measured signal $g(x)$ results in large deviations in the solution $H(\tau)$ (i.e., relaxation spectrum). If the ill-posed nature of the problem is overcome then the relaxation spectrum can be calculated with accuracy and provide structural information for the material under investigation. Early attempts to calculate the relaxation spectrum have been met with numerical difficulties and the non-uniqueness of the solution (Ferry, 1980). To resolve such problems, various algorithms that perform numerical calculations have been proposed over the years. The major issue at hand is whether the resulting spectrum is a characteristic feature of the material or an artifact of the algorithm. The desired properties of the algorithms have been outlined in the literature (Winter, 1997) but an important characteristic of the calculation process is the ability of several algorithms to return similar relaxation spectra (McDougall, Orbey, & Dealy, 2014).

Various mathematical approaches have been proposed to calculate the relaxation spectra of polymeric materials over the years (Baumgaertel & Winter, 1989; Elster & Honerkamp, 1991; Jensen, 2002; Provencher, 1982; Stadler & Bailly, 2009), and more recently (Bae & Cho, 2015; Ciocci Brazzano, Pellizza, Matteo, & Sorichetti, 2016; Soo Cho & Woo Park, 2013). In practice, very few are used, as most are either proprietary information to the researchers who developed them or a suitable computer program is not available. To overcome these hurdles, regularization methods, attempting to calculate a smooth solution, are commonly employed in the calculation of relaxation spectra. They incorporate ancillary information about the attributes of the sought solution (e.g., non-negativity) and facilitate the calculation of a meaningful spectrum (Elster, Honerkamp, & Weese, 1991).

In order to determine a relevant approximation of $H(\tau)$, the initial system of linear equations describing the relaxation process is replaced with a set of equations that is less sensitive to noise. Solution of the latter system of equations results in the best possible approximation of $H(\tau)$, with the entire process being referred to as regularization. An established methodology to numerically calculate the relaxation spectrum is through the Tikhonov regularization (Tikhonov, Goncharsky, Stepanov, & Yagola, 1995). In common least squares problems (e.g., linear regression for construction of a calibration curve), the approach is to minimize the sum of squares of errors and arrive at the best approximate solution (i.e., linear curve fitting). In ill-posed

problems, the Tikhonov regularization favours and achieves a desirable solution by including a regularization term in the minimization process.

Utility of the regularization term is controlled by the regularization parameter, λ, which plays a central role in successful calculations to yield the final relaxation spectrum. In regularized calculations, the solution is dominated by two types of errors: the regularization error caused by the numerical calculation and the perturbation error being inherent to measurement (e.g, $G'(\omega)$ or $G(t)$). Choice of λ away from the optimum being either smaller, with the perturbation error dominating the solution, or greater, with the regularization error dominating the solution, result in either noisy spectra with a meaningless number of peaks or over-smoothed solutions that lack information. For a fixed set of data, there is an optimal λ that balances the two types of errors yielding the best $H(\tau)$ approximation. A common method to find the optimum λ is with the aid of the L-curve criterion that addresses in the calculation the two types of errors (Hansen, 1992; Rezghi & Hosseini, 2009).

Once the spectrum has been calculated, it is important to assess the range of relaxation times that result in meaningful properties for the hydrocolloid system under investigation. It is common practice to determine the relaxation spectrum within a reciprocal frequency range of $\omega^{-1}_{max} < \omega^{-1} < \omega^{-1}_{min}$ for measurements that have been carried out at the corresponding frequency range of $\omega_{min} < \omega < \omega_{max}$. However, this practice is incorrect due to various experimental limitations associated with the rheological measurement (Davies & Anderssen, 1997). The interval on which the relaxation spectrum should be determined is $e^{\pi/2}\omega^{-1}_{max} < \omega^{-1} < e^{\pi/2}\omega^{-1}_{min}$, i.e. shorter than $\omega^{-1}_{max} < \omega < \omega^{-1}_{min}$ by 1.36 decades (Davies & Anderssen, 1997).

A software platform that is readily available to the experimentalist for numerical calculations of relaxation spectra is MATLAB. There are several MATLAB algorithms that employ the Tikhonov regularization to estimate parameters with the L-curve criterion leading to relaxation spectra derivation (Hansen, 2002; Kontogiorgos, 2010; Kontogiorgos, Jiang, & Kasapis, 2009; Wendlandt, 2005). In the following section, we utilize the most recent version of the program ReSpect v 2.0, which is available with a standalone graphic user interface in MATLAB (Takeh & Shanbhag, 2013) to revisit the relaxation spectra of high-solid hydrocolloid samples from dynamic data in shear.

3. Structural relaxation spectra of high-solid hydrocolloid systems

A common approach to increase the experimental timeframe of observation is by constructing the master curve of viscoelasticity at a reference temperature within the glass transition region. This process results in a plot that depicts the effect of molecular motions on the viscoelastic functions for several decades, i.e. beyond the operational frequency range achieved with current instrumentation (typically $0.628 < \omega < 628$ rad/sec). In the present work, we have re-analysed the relaxation spectra of selected high-solid polysaccharides, proteins and their mixed systems in an effort to identify relaxation phenomena.

All systems have been prepared using high levels of co-solute (glucose syrup, sucrose or mixtures thereof) and industrially relevant amounts of κ-carrageenan, gellan (Kasapis & Sworn, 2000), pectin at pH 3.0 or 7.0 (Alba, Kasapis, & Kontogiorgos, 2015), gelatin or gelatin/carrageenan mixtures (Kasapis & Al-Marhoobi, 2005), and whey protein (unpublished data). Calculations were performed using the Tikhonov regularization to extract the continuous relaxation spectrum from ω, $G'(\omega)$ and $G''(\omega)$ datasets. The strict criterion for the range of relaxation times was imposed (i.e., $e^{\pi/}$