Food Research International 42 (2009) 130–136

Contents lists available at ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

Numerical computation of relaxation spectra from mechanical measurements in biopolymers

Vassilis Kontogiorgos [a,*], Bin Jiang [b], Stefan Kasapis [b]

[a] Department of Chemical and Biological Sciences, The University of Huddersfield, Queensgate HD1 3DH, UK
[b] Department of Chemistry, National University of Singapore, Block S3, Level 6, Science Drive 4, Singapore 117543, Singapore

ARTICLE INFO

Article history:
Received 1 September 2008
Accepted 9 September 2008

Keywords:
Regularization methods
Ill-posed problem
Stress relaxation
Relaxation spectrum
Gluten

ABSTRACT

In the present investigation, a computational methodology to treat relaxation spectra from mechanical data is developed. To calculate the spectral function that represents the relaxation process of the material, three different regularization algorithms were tested using MATLAB. Two algorithms employ Tikhonov's regularization whereas the third investigative tool is an implementation of the CONTIN algorithm. These efforts improved the ability to look at data hence allowing utilization of the L-curve criterion in order to locate the optimum regularization parameter for accurate data inversion. Algorithms were first evaluated with hypothetical data followed by experimental datasets of hydrated gluten as a model biopolymer system. Essentially, algorithms converge on a specific relaxation spectrum that unveils the molecular features of gluten structure. The methodology described is not limited to mechanical measurements but should be used with any type of exponential decay in studies of relaxation processes.

1. Introduction

The method of stress relaxation is widely used to test polymers as the data generated lead to numerous material functions including the relaxation spectrum of the system. The Maxwell mechanical analog can be used to interpret such stress relaxation data, which in its simplest form contains a Hookean spring and a Newtonian dashpot joined in series. As the number of the Maxwell elements increases approaching infinity, the stress function of the material is given by Ferry (1980):

$$\sigma(t) = \sigma_e + \int_0^{+\infty} \sigma(\tau) \exp\left(-\frac{t}{\tau}\right) d\tau \quad (1)$$

Expression (1) describes the gradual relaxation of stress, $\sigma(t)$, to the equilibrium stress (σ_e), with $\sigma(\tau)$ being the distribution function of the elements with relaxation time, τ. This is the time taken for the stress to decay to $1/e$ of its initial value. Complete material relaxation means that $\sigma_e = 0$ and the integral of the above expression can be written in terms of the generic form of the first-kind Fredholm equation:

$$g(s) = \int_a^b K(s,t) f(t) dt, \quad \alpha \leqslant s \leqslant \beta \quad (2)$$

where $K(s,t)$ is the kernel $\exp(-t/s)$ that describes the system, $g(s)$ is the measured signal, and $f(t)$ is the unknown integral solution. The goal of the analysis is to determine the spectral function $f(t)$ that represents the relaxation spectrum of the material.

Numerical solvation of this procedure is not a straightforward task since the Fredholm integral equation is a classical example of an ill-posed problem that requires a special mathematical treatment (Groetsch, 1984). An issue of concern is that arbitrarily small perturbations of the signal g may lead to large perturbations of the solution f or, in other words, the solution is extremely sensitive to experimental noise of the measurement (Hansen, 1992b). To overcome such a problem, regularization methods are employed, which allow incorporation of additional information about the sought solution. In the end, numerical algorithms find a regularized solution $\mathbf{x}_{reg}$ to a least squares problem (Groetsch, 1984; Provencher, 1982a, 1982b; Tikhonov & Arsenin, 1977).

In the formulation of such problems, a regularization parameter (λ) is involved that controls the trade-off between a small error in the solution (low λ values) and a smooth solution (large λ values). Clearly, the success of the regularization method depends on the appropriate choice of parameter λ. Several approaches are available to select a meaningful regularization parameter, with the L-curve method being the most popular (Hansen, 1992a). The L-curve is a plot for all valid regularization parameters of the semi-norm of the regularized solution *versus* the corresponding residual norm. In double logarithmic plots, the curve resembles the capital letter "L" and an essential feature is that the optimal regularization parameter corresponds to the corner of the L-curve (Hansen, 1992a).

Ill-posed problems in mechanical spectroscopy and numerical methods to solve them have been discussed in the literature

* Corresponding author. Tel.: +44 1484 472488.
E-mail address: v.kontogiorgos@hud.ac.uk (V. Kontogiorgos).

0963-9969/$ - see front matter Crown Copyright © 2008 Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodres.2008.09.005

(Brabec, Rögl, & Schausberger, 1997; Elster, Honerkamp, & Weese, 1991; Friedrich, Honerkamp, & Weese, 1996; Honerkamp, 1989; Honerkamp & Weese, 1993). They focus on the derivation of the relaxation spectrum from dynamic oscillatory data using mathematically robust algorithms, but the lack of suitable software to widely implement regularization methods has frustrated such efforts. Stress relaxation experimentation is a fundamental and direct approach in the elucidation of molecular dynamics of relaxation processes, yet application of regularization methods to such measurements on biopolymer systems are not documented in literature. The outcome of such an effort should be an improved understanding of the molecular processes involved in the relaxation of three-dimensional biopolymer structures.

Therefore, the objective of the present investigation is to present a comprehensive methodology for numerical computation of the relaxation spectrum from stress relaxation data using state of the art algorithms, and to evaluate the methodology in a model biopolymer system.

2. Materials and methods

2.1. Sample preparation

Samples of hydrated gluten (40% w/w protein solids, 60% w/w deionized water) from Sigma–Aldrich, St. Louis, MO, USA were prepared as described previously (Kontogiorgos, Goff, & Kasapis, 2007), wrapped thoroughly with a plastic membrane and left to hydrate at 4 °C for 30 min.

2.2. Stress relaxation measurements

Stress relaxation measurements were performed with the advanced rheometric expansion system (ARES, TA Instruments, New Castle, DE, USA), which is a controlled strain rheometer. ARES is equipped with a mechanical chiller for temperature regulation (Polycold Gas Chiller, Polycold Systems International, CA, USA) and controlled using the operational software accompanying the instrument (TA Orchestrator).

Experimental protocol of the present investigation includes the following steps:

(i) At the end of the hydration period, samples were loaded onto the preheated platen of the rheometer (20 °C) employing a parallel plate geometry of 40 mm diameter and 2 mm gap. Preliminary time sweeps in dynamic oscillation on shear, which were carried out at 1 rad/s and 3% strain, showed that the elastic (storage modulus; G') and viscous (loss modulus; G'') components of the network reached a "pseudo-equilibrium" plateau within 10 min. Therefore, samples were left to relax for 10 min prior to measurement.
(ii) Strain sweeps in dynamic oscillation on shear were carried out at 20 °C to identify the linear viscoelastic region (LVR) of the sample under test conditions and an angular frequency of 1 rad/s.
(iii) Stress relaxation tests were carried out using 3% instantaneous strain at 20 °C. Samples relaxed for 20 s, 30 min, 1 h, 5 h and 10 h following application of the instantaneous strain. Modulus data ($G'(t)$) were collected in a logarithmic mode with respect to the timescale of observation.

A thin layer of low viscosity silicone oil (dimethylpolysiloxane, Sigma–Aldrich, St. Louis, MO, USA) was applied to minimize moisture loss during the course of stress relaxation testing. Mechanical measurements were performed in triplicate, and representative figures that depict accurately the behavior of the material are illustrated.

2.3. Numerical computation

Numerical computation was performed in MATLAB (v7.0 R14 Service Pack 2, The Mathworks Inc., MA, USA) using three different scripts. The algorithms are available online and, in the present work, they will be denoted as Hansen (1994, 2002), Wendlandt (2005), Wendlandt, van Beek, Suter, and Meier (2005) and Marino (2007) following the names of the authors. The first two algorithms use Tikhonov's regularization with different approaches in their structure, whereas the third routine is a MATLAB implementation of the CONTIN algorithm (Provencher, 1982a, 1982b). Detailed instructions of operation are provided together with the scripts by the authors. From Hansen's package, the scripts *csvd.m*, *l_curve.m* and *tikhonov.m* were used, whereas from Wendlandt and Marino packages we employed the routines *NLCSmoothReg.m* and *rilt.m*, respectively.

3. Results and discussion

3.1. Hypothetical exponential decay

In order to confirm the utility of the proposed algorithms, we worked initially with hypothetical data. In particular, we created an exponential decay of the function $f(t) = \exp(-t/1)$ with linear equidistantly separated points and explored the effect of regularization parameter (λ) and decay (partially decayed or completely decayed transient) on the solution. The first step in the numerical computation to solve Eq. (2) is to discretize the problem resulting in a system of linear equations so as

$$A\mathbf{x} = \mathbf{b}, \quad A \in \boldsymbol{R}^{n\mathbf{x}m}, \ \mathbf{x} \in \boldsymbol{R}^{n}, \ \mathbf{b} \in \boldsymbol{R}^{m} \tag{3}$$

where matrix A is a discrete representation of kernel $K(s,t)$ from Eq. (2), $\mathbf{b}$ is a discrete vector that represents $g(s)$, and $\mathbf{x}$ is the solution vector that describes the desired solution $f(t)$. Vector $\mathbf{b}$ corresponds to the measured signal of the stress relaxation modulus. To discretize kernel $K(s,t) = \exp(-t/s)$ we developed the MATLAB routine *discr*, which is given in the appendix of this work. The script produces the matrix, *A*, and the space, *sp*, where the relaxation time ranges using a simple quadrature. This is an essential complement to Hansen and Wendlandt algorithms because they do not provide such a discretization routine. It must be noted that the quadrature based discretization protocol is also used in Marino's algorithm hence the current discretization procedure does not introduce a source of variation in the computation. Therefore, the relaxation spectra obtained with the various algorithms can be compared on the basis of the common algorithmic structure.

Following the creation of matrix *A* and space *sp*, and prior to proceeding with the main computations of the case study, it is essential to optimize the regularization parameter. This was performed with the routine *lcurve*, which is provided in Hansen's package, with the view to utilizing the outcome of optimization in subsequent algorithms. Fig. 1 shows a typical L-curve obtained for the hypothetical dataset of the partially decayed exponential function. The routine *lcurve* varies the regularization parameter until a compromise is achieved between the minimization of the residual and solution norms. The vertical part of the curve corresponds to data where the solution norm is very sensitive to changes in the regularization parameter because the error in measurements dominates the regularized solution $\mathbf{x}_\lambda$. The horizontal part corresponds to solutions where the residual norm is the most sensitive to the regularization parameter because $\mathbf{x}_\lambda$ is now dominated by the regularization error (Hansen, 1992a).