Modelling the continuous relaxation time spectrum of aquous xanthan solutions using two commercial softwares

Citation for the original published paper (version of record):
Lopez-Sanchez, P., Moser, J., Berta, M. et al (2018). Modelling the continuous relaxation time spectrum of aquous xanthan solutions using two
commercial softwares. Annual Transactions - The Nordic Rheology Society, 26: 183-186

Modelling the continuous relaxation time spectrum of aqueous xanthan solutions using two commercial softwares

Marco Berta[1], Josefine Moser[1], Patricia Lopez-Sanchez[1], and Mats Stading[1,2]

[1]RISE Bioscience and Materials, 40229 Gothenburg, Sweden
[2]Chalmers University of Technology, Department of Materials and Manufacturing Technology, 41296 Gothenburg, Sweden

ABSTRACT

The continuous relaxation time spectrum was modelled from the mechanical spectrum of a xanthan aqueous solution both using the TA Instruments TRIOS® software, and with the rheology software IRIS®[1]. Two types of calculation were applied to obtain the relaxation modes since the software bundles used in this study base the calculation upon two different algorithms, named "parsimonious" as it models continuous relaxation spectra using a minimum number of modes to obtain continuous relaxation times[2], and a nonlinear regularization method that provides a larger spectrum with several modes[3]. The results were overall comparable but slightly different for long relaxation times.

INTRODUCTION

Xanthan gum is a non-gelling biopolymer that in aqueous media displays a ordered rigid chain conformation[4-5]. The stability of xanthan aqueous solutions to temperature and pH determines its great acceptance in industry as thickener[6-7]. It displays strong temperature dependence and for a given temperature the viscosity increases sharply with concentration, making it also a model system for biopolymer solutions rheological properties. For this reason the dynamic mechanical properties of xanthan have been investigated extensively[5, 8-15]. Modelling the continuous relaxation spectrum from the mechanical spectrum of xanthan solutions can be of interest for theoretical rheology since it would allow finding stress-vs.-deformation relationships from oscillatory data without measuring them directly with creep tests. In practice, these are calculated using rheological models to obtain a continuous relaxation spectrum. Several have been proposed by theoreticians, and some have been adopted as part of rheology software packages. In this work, a mechanical spectrum obtained from a xanthan solution has been fitted using two widespread rheology software bundles to obtain continuous relaxation times and the results are compared. While a complete screening of different algorithms would require a more extensive work, and investigations have been carried out for simpler synthetic polymer systems[16-18], this study attempts to test the application of some of the most common to a model biopolymer solution.

EXPERIMENTAL

Solutions were prepared by dissolving in water Xanthan gum, purchased from Sigma Aldrich (MO, USA). The concentration was 0.25 wt% of xanthan powder in deionized water. The rheological properties of the xanthan solutions were measured at several temperatures temperature in the range 5-25 ºC, using an Ares-G2 (TA instruments, Waters LLC, USA) strain controlled rotational rheometer equipped with a cone-plate geometry having a 40 mm diameter. A layer of paraffin oil was used to prevent evaporation. Oscillatory frequency sweeps were carried out with a constant strain range of 2-5% within the solution linear viscoelastic region. The model has been applied to mechanical spectra obtained at several temperatures in order to obtain, by time temperature superposition, a wider spectrum to be modelled than that allowed by the experimental limits of the rheometer. The temperature range was 5 - 25 ºC. Data were analysed both using the TA Instruments TRIOS® software, supplied with the rheometer and the software IRIS®.

RESULTS AND DISCUSSION

An example of mastercurve with reference temperature of 25 ºC obtained by time-temperature superposition is shown in Fig.1.

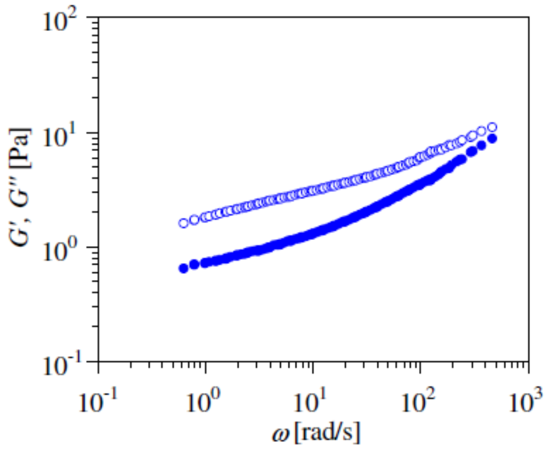

Figure 1. Mastercurve obtained by time–temperature superposition of the frequency dependence of the storage (empty circles) and of the loss (full circles) modulus Data were obtained from mechanical spectra of an aqueous solution with 0.25%wt xanthan concentration. Reference temperature, 25 ºC.

Theoretical modeling was applied to the mastercurve and continuous relaxation spectra H(t)[3] was calculated. It is important to stress that generally the calculation of a relaxation spectrum from experimental oscillatory rheology data is an ill-posed problem, since it is subjected to random error in the data, especially at low frequency[17]. Modeling data obtained from a mastercurve provides additional noise in the data since the theory of time-temperature superposition is based on the assumption that all relaxation times of the material have the same temperature dependence, but this is fairly accurate only over certain ranges of frequency that depend on the material. Near the ends of these ranges, where data obtained at different temperatures overlap, discrepancies can appear and conversely affect the accuracy of the relaxation spectrum calculation. The software IRIS® uses the parsimonious model[17] Developed by Baumgärtel and Winter[2]. The TRIOS® software uses a similar algorithm[3], based on a Tihonov regularization[19] with nonlinear regression developed by Honercamp and Weese[3, 18], that produces a continuous relaxation spectrum with more data points over a larger frequency range. The results are shown in Fig. 2.

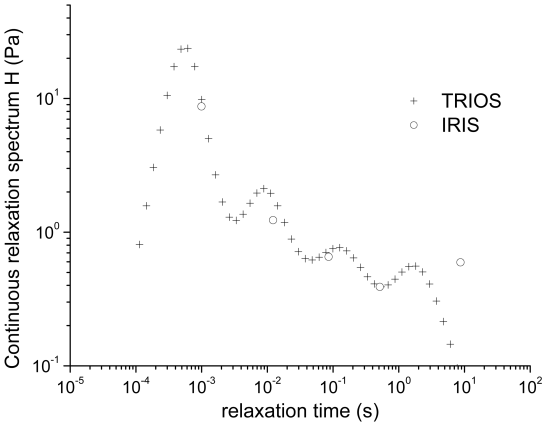

Figure 2. Continuous relaxation spectra obtained with two IRIS (open symbols) and TRIOS (crosses) software. Data corresponds to those presented in Fig. 1.

The two data sets plotted in Fig. 2 are practically coincident, with a discrepancy that occurs at high relaxation time, corresponding to low frequencies which are harder to model since, as stated earlier, more prone to error. A similar divergence was reported for propylene random copolymers by Malkin and Masalova[16].

CONCLUSIONS

Both algorithms showed consistent results for the calculation of continuous relaxation spectra from a model biopolymer solution. Small discrepancies occurred only for long relaxation times corresponding to very low frequencies since those are subjected to higher experimental error.

REFERENCES

1. Jensen, H.K. and Hansen, O. (1993), "Simulation of Viscoelastic Flow", *J. Non-Newtonian Fluid Mech.,* **42**, 293-308.

2. Barnes, H.A., Hutton, J.F., and Walters, K. (1989), "An Introduction to Rheology", Elsevier, Amsterdam, pp. 115-139.

1. Winter, H. H. (1997), "Analysis of dynamic mechanical data: inversion into a relaxation time spectrum and consistency check", *Journal of Non-Newtonian Fluid Mechanics,* **68**, 225-239.

2. Baumgaertel, M. and Winter, H. H. (1992), "Interrelation between continuous and discrete relaxation time spectra", *Journal of Non-Newtonian Fluid Mechanics,* **44**, 15-36.

3. Honerkamp, J. and Weese, J. (1993), "A nonlinear regularization method for the calculation of relaxation spectra", *Rheologica Acta,* **32**, 65-73.

4. E., P., C., V., J., M. and A., W. P. (2001), "A rheological study of the order–disorder conformational transition of xanthan gum", *Biopolymers,* **59**, 339-346.

5. Choppe, E., Puaud, F., Nicolai, T. and Benyahia, L. (2010), "Rheology of xanthan solutions as a function of temperature, concentration and ionic strength", *Carbohydrate Polymers,* **82**, 1228-1235.

6. Ahmed, J. and Ramaswamy, H. S. (2004), "Effect of high-hydrostatic pressure and concentration on rheological characteristics of xanthan gum", *Food Hydrocolloids,* **18**, 367-373.

7. Marcotte, M., Taherian Hoshahili, A. R. and Ramaswamy, H. S. (2001), "Rheological properties of selected hydrocolloids as a function of concentration and temperature", *Food Research International,* **34**, 695-703.

8. Whitcomb, P. J. and Macosko, C. W. (1978), "Rheology of Xanthan Gum", *Journal of Rheology,* **22**, 493-505.

9. Rochefort, W. E. and Middleman, S. (1987), "Rheology of Xanthan Gum: Salt, Temperature, and Strain Effects in Oscillatory and Steady Shear Experiments", *Journal of Rheology,* **31**, 337-369.

10. Milas, M., Rinaudo, M., Knipper, M. and Schuppiser, J. L. (1990), "Flow and viscoelastic properties of xanthan gum solutions", *Macromolecules,* **23**, 2506-2511.

11. Renou, F., Petibon, O., Malhiac, C. and Grisel, M. (2013), "Effect of xanthan structure on its interaction with locust bean gum: toward prediction of rheological properties", *Food Hydrocolloids,* **32**, 331-340.

12. Cuvelier, G. and Launay, B. (1986), "Concentration regimes in xanthan gum solutions deduced from flow and viscoelastic properties", *Carbohydrate Polymers,* **6**, 321-333.

13. Song, K.-W., Kuk, H.-Y. and Chang, G.-S. (2006), "Rheology of concentrated xanthan gum solutions: Oscillatory shear flow behavior", *Korea-Australia Rheology Journal,* **18**, 67-81.

14. Wyatt, N. B. and Liberatore, M. W. (2009), "Rheology and viscosity scaling of the polyelectrolyte xanthan gum", *Journal of Applied Polymer Science,* **114***,* 4076-4084.

15. Lim, T., Uhl, J. T. and Prud'homme, R. K. (1984), "Rheology of Self-Associating Concentrated Xanthan Solutions", *Journal of Rheology,* **28***,* 367-379.

16. Malkin, A. Y. and Masalova, I. (2001), "From dynamic modulus via different relaxation spectra to relaxation and creep functions", *Rheologica acta,* **40***,* 261-271.

17. McDougall, I., Orbey, N. and Dealy, J. M. (2014), "Inferring meaningful relaxation spectra from experimental data", *Journal of Rheology,* **58***,* 779-797.

18. Hatzikiriakos, S. G., Kapnistos, M., Vlassopoulos, D., Chevillard, C., Winter, H. H. and Roovers, J. (2000), "Relaxation time spectra of star polymers", *Rheologica acta,* **39***,* 38-43.

19. Calvetti, D., Morigi, S., Reichel, L. and Sgallari, F. (2000), "Tikhonov regularization and the L-curve for large discrete ill-posed problems", *Journal of Computational and Applied Mathematics,* **123***,* 423-446.