**The Effect of Different Numerical Approaches on the Accuracy of Calculating Relaxation Spectra for Polysaccharides**

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**Abstract (max. 1000 characters)**

For polymeric materials, the relaxation spectrum contains complete information about the time-dependent part of the material response. The contribution of different numerical schemes, *i.e.*, different methods of reconstructing the dynamic relaxation modulus, to the accuracy of the approximation by calculating the corresponding relaxation spectra is investigated by analysing experimental data for four types of polysaccharides. It was found that there is no unique mathematical approach for the calculation of relaxation spectra that ensures a satisfactory approximation of the experimentally determined dynamic moduli for the selected types of polymeric materials. It is recommended to combine different numerical methods in parallel to achieve a reasonable approximation of the material functions.

**Keywords (max. 6):** polysaccharide, rheology, viscoelastic properties, relaxation spectrum, mathematical modelling

**1. Introduction**

When polymeric materials are exposed to mechanical loading during rheological testing, the changes in material structure manifest in their viscoelastic responses. Therefore, the rheological investigation of their material properties has become a widely used tool for obtaining information on the structural characteristics and behaviour under mechanical loading of very broad range of materials, *e.g.*, polymer melts, polymer solutions, blood, biological tissues, food gels, colloidal gels, emulsions, alumina suspensions, magnesium alloys, dispersions, asphalt, etc.

In line with the theory of viscoelasticity, the relaxation spectrum of polymers reflects molecular movements of macromolecules and thus can be interrelated with the molecular structure, *i.e.*, molecular mass and molecular weight distribution, branching and other aspects of molecular architecture. For example, Stadler1 used relaxation spectra to understand molecular processes, such as entanglement and reptation, in ring polymers. Many authors, *e.g.*, Thimm *et al.*2 and Friedrich *et al.*3 showed analytical relation between the relaxation time spectrum and the molecular weight distribution which greatly reduces the computational efforts to determine the molecular weight distribution from the relaxation time spectrum. Nobile and Cocchini4 introduced a generalized relationship between the molecular weight distribution and the relaxation time spectrum for sharp molecular weight distributions.

Polysaccharides are natural (bio)polymers, widely used in numerous applications due to their ability to form specific structures which manifest in diverse macroscopic behaviour and properties. They are polycarbohydrates composed of monosaccharide units bound together by glycosidic linkages to form long chain polymeric carbohydrate structures. Their functional properties depend not only on their chemical structure, but also on the microstructure which develops during processing.

Microbial polysaccharides xanthan, gellan, welan, and structural polysaccharide sodium carboxymethylcellulose have been extensively studied for several decades, *see, e.g.*, Lapasin *et al.*5 and Carmona *et al.*6 The rheological examination of these water-soluble polysaccharide systems have been used as a practical and efficient tool to investigate correlation between structural and mechanical characteristics of the systems, *see, e.g.*, Lim *et al.*7 and Song *et al.*8 By using empirical approach researchers analyse different rheological responses to study the influence of different parameters, *i.e.*, pH, temperature, polymers concentration, additive content, mechanical loading, on the structure evolution in polysaccharide systems such as gelation, crosslinking, formation of entangled polymer networks, crystalline aggregates, etc.9,10

Many papers discuss a linear viscoelastic behaviour of polysaccharides xanthan, gellan, welan, and Na CMC in terms of frequency dependence of elastic (storage) and viscous (loss) dynamic moduli, but only few of them report on the relaxation spectra of these materials.

***Relaxation spectra of polysaccharides***

The relaxation spectra of polymeric materials can only be calculated from the experimental data, for example frequency dependence of dynamic functions, creep or relaxation functions. In last decades, many different mathematical approaches have been developed to model mechanical behaviour of numerous polymeric materials, and to determine either their discrete or continuous spectra. In fact, the spectra calculated by using different mathematical models and corresponding numerical approaches for the same polymeric material may differ significantly which naturally leads to the question about uniqueness of the spectra calculations.

In the last decades, numerous publications have been devoted to development of the methodologies for spectra calculation, *see, e.g.*, Honerkamp and Weese,11 Baumgaertel and Winter,12 Emri and Tschoegl,13 Malkin,14 Shtrauss and Kalpinsh,15 Bae and Cho,16 and references therein. For calculation of the relaxation spectra of polysaccharides xanthan, gellan, welan, and Na CMC different models and mathematical approaches have been applied, that has been presented by numerous authors, for example Zupančič and Žumer,17 Florjančič *et al.*,18 Quintana *et al.*,19 Moraes *et al.*,20 Lorenzo *et al.*,21 Lapasin *et al.*,22 and many others. Some authors used commercial software for spectra analysis, *e.g.*, Berta *et al.*23 compared continuous relaxation time spectra of a xanthan aqueous solution, calculated by applying the IRIS® software and the TRIOS® software. Jaishankar and McKinley24 used a fractional K-BKZ constitutive mathematical model for describing the nonlinear rheology of multiscale complex fluids such as water-soluble polysaccharide xanthan.

In the theory of linear viscoelasticity, the relaxation spectrum contains complete information on the time-dependent part of the material response.25 The spectrum itself is not accessible by direct experiment, rather it can be calculated exactly from experimental data as an approximation to the unknown 'true' continuous spectrum by numerical differentiation or by the use of finite difference calculus. Another approach is based on the representation of the experimental response by discrete models leading to distributions of line spectra.

There are two main reasons for the interest in the continuous spectra. They generally present the details of the time-dependent behaviour of a given material more clearly than the discrete line spectra do. In addition, a continuous spectrum is unique, while the appearance of a line spectrum depends on the somewhat arbitrary choice of the density and the location of the lines along the relaxation time coordinate. Therefore, a discrete relaxation spectrum is not unique. ~~One might consider that simply connecting the end points of a line spectrum by a continuous line,~~ *~~e.g.~~*~~, using cubic spline function would directly yield a continuous from a discrete spectrum. However, such an envelope over the endpoints cannot furnish a valid continuous spectrum.~~ Poudel and Shanbhag26 investigated strategies to improve the quality and interpretability of the extracted discrete spectrum for viscoelastic liquids and solids and found out that the number of modes has a significant effect on the height and location of the discrete relaxation spectrum lines.

Therefore, it is important to investigate the contribution of different numerical schemes, *i.e.*, different methodologies for approximating dynamic material functions such as relaxation modulus, to accuracy of the approximation by means of calculating the appropriate relaxation spectra. In the paper, three different approaches for the calculation of the relaxation spectra from frequency dependencies of dynamic functions, experimentally determined in oscillatory shear conditions, are explored. The experimental data on dynamic moduli for four water-based polysaccharide systems of xanthan, gellan, welan, and sodium carboxymethylcellulose were analysed.

**2. Experimental**

**2. 1. Materials**

The materials, used in our research, are listed in Table 1. Gellan, welan and xanthan are microbial extracellular polysaccharides produced by different species of bacteria in aerobic fermentation process, while sodium carboxymethylcellulose (Na CMC) is water-soluble cellulose derivative.

Table 1. List of tested materials.

|  |  |  |
| --- | --- | --- |
| Material | Type | Producer |
| gellan | KELCOGEL | CP Kelco |
| welan | K1C376 | CP Kelco |
| xanthan | KELTROL | CP Kelco |
| Na CMC | BLANOSE 7HF Cellulose gum | Aqualon |

For all four materials, no stability problems occurred during the storage period and the measurements.

**2. 2. Sample preparation**

The samples were prepared by dissolving powdered polymers in distilled water by mechanical stirring. Welan, xanthan and Na CMC are soluble in water at ambient temperature, while gellan requires temperature above 90 °C. The aqueous gellan solutions undergo thermally induced sol – gel transition; at higher temperatures exhibit sol behaviour, and after cooling the gelation appears.

Water-based systems of welan, xanthan and Na CMC were prepared at ambient temperature, having the same overall polymer concentration of 1 wt. %. Gellan powder at the same polymer concentration of 1 wt. % was dissolved in distilled water at 96 °C by mechanical stirring. When gellan solution was cooled the gelation appeared at temperature about 29 °C.

All samples were stored for two days in a refrigerator at 4 °C in covered glass beakers to prevent the evaporation of water and to ensure a complete wetting of the polymers, before the rheological tests were carried out.

**2. 3. Testing methodology**

The viscoelastic properties of water-based polysaccharide systems were measured by using a controlled stress rheometer HAAKE RS 150,18 equipped with a cone and plate sensor (measuring) system, having diameter of 60 mm and the cone angle of 4 °. The rheological tests were performed under oscillatory shear conditions at 20 ± 0.3 °C. Each measurement was repeated several times in order to achieve proper repeatability of experimental results.

Welan, xanthan, and Na CMC samples, tempered for 10 min at room temperature and manually stirred to assure homogeneous substance before testing, were poured onto sensor system from glass beaker. After applying the sample to the measuring system, the sample was left to rest for few minutes before testing to be evenly tempered to 20 °C throughout the measuring system.

Gellan sample had to be heated in water bath to 50 °C and manually stirred to become homogenous, because it was still not fluid-like to be applied to the sensor system. Still warm it was poured onto sensor system and then left to cool down to 20 °C, which was testing temperature for all examined samples.

**2. 3. 1. Determination of the linear viscoelastic response of tested materials**

It is required for frequency tests to be performed in a linear viscoelastic range, where shear storage (elastic) modulus and shear loss (viscous) modulus are independent on maximum amplitude of shear strain.17 Above the limit of a linear viscoelastic response, both dynamic shear moduli and characteristically change with increasing shear strain amplitude. In a non-linear viscoelastic range, a response of periodic oscillation is no longer sinusoidal and values of measured rheological quantities change with shear strain amplitude. The transition from a linear to a non-linear viscoelastic range is determined by the critical amplitude of shear strain and the critical shear stress, which depend on the mechanical properties of the sample under investigation.

Therefore, the amplitude tests were performed first to determine the limit of the linear viscoelastic response. In the amplitude test, the shear storage modulus and the shear loss modulus were monitored as a function of the shear strain amplitude at constant oscillation frequency. For all samples under investigation the amplitude tests were performed at constant oscillation frequency ω of 1 Hz.

**2. 3. 2. Frequency test**

In the frequency test, the dependence of shear storage modulus and shear loss modulus is measured as a function of oscillation frequency . It is a non-destructive method which is performed in the range of linear viscoelastic response to keep the internal structure of the sample non destructed.18 Therefore, it is important to choose appropriate sensor system, to run experiment at shear strain which is required for linear viscoelastic response and to select appropriate frequency range for the experiments. For all investigated samples a constant shear strain amplitude of 0.03 was chosen to measure dynamic shear storage modulus and dynamic shear loss modulus as functions of oscillation frequency in a range from 0.01 to 100 rad/s.

**3. Mathematical treatment for calculating relaxation spectra**

Below, three conceptually different mathematical approaches for calculating relaxation spectra from experimental data on storage and loss moduli are presented in short, *i.e.*, (i) generalized Maxwell model, (ii) interconversion between material functions and (iii) Honerkamp & Weese method using the commercial software. To the best of our knowledge, there is no mathematically consistent comparative analysis of the existing mathematical models for spectra calculations, commonly used in practical applications, until now.

**3.1. Generalized Maxwell model**

Discrete relaxation spectra for the examined polysaccharide systems were calculated using generalized Maxwell model with five Maxwell elements, based on experimentally determined discrete data of dynamic moduli, and , as functions of oscillation frequency, :

, . (1)

where are characteristic relaxation times and corresponding relaxation strengths. First, it is required to select a set of relaxation times, evenly spaced on a log scale, *i.e.*, one per decade, and then the fitting procedure to determine the relaxation strengths, , using the least-squares regularization method that minimizes the sum of squared relative deviations between the calculated values and the experimental data, has to be run. The resulted complete set of (, ) is called the spectrum of the relaxation times, *i.e.*, a discrete relaxation spectrum.

**3. 2. Interconversion between material functions**

The material functions in frequency- and time-domain are interrelated in a close form via the corresponding relaxation (or retardation) spectrum. The time-dependent relaxation modulus can be obtained from the relaxation spectrum, *i.e.*, from the set of (, ), using the relation

. (2)

Calculation of the relaxation and retardation spectra, and correspondingly determination of the material functions, requires an inverse solution of the Fredholm integral equation of the first or second kind, which is an ill-posed problem. Therefore, numerous approximate methods for the interconversion between frequency- and time-dependent material functions have been developed in the past. Then time-domain response, *i.e.*, the relaxation modulus can be predicted from the experimental data of dynamic moduli and .

Ninomiya and Ferry~~26~~27 developed an algorithm for calculating that comprises contributions from the real and the imaginary parts of the dynamic modulus, *i.e.*,

. (3)

It should be noted that the relaxation spectrum (, ) used in Eq. (2) is identical to that used in Eq. (1). Thus, for the purpose of comparative analysis of all three methods for spectra calculations, we first reconstructed the relaxation modulus from experimentally determind dynamic moduli and using the approximate formula, *i.e*., Eq. (3). In the next step we calculated the spectrum using the least-squares minimization method that incorporates Levenberg–Marquardt algorithm.

**3. 3. Honerkamp & Weese method using the commercial software**

The third approach, used for calculating relaxation spectra for all four selected polysaccharides with the aim of comparative analysis of three mathematical models or methodologies, is based on the earlier developed Honerkamp & Weese method~~27~~28 exploiting an efficient, open-source, multi-platform computer program ReSpect to infer the continuous and discrete relaxation spectra from dynamic moduli measurements.~~28~~29, 30

This approach employs the numerical calculations that include nonlinear Tikhonov regularization and the Levenberg-Marquardt method to extract the continuous relaxation spectrum that is an essential part of the mathematical representation of the dynamic moduli and in the form

, . (4)

To obtain the discrete relaxation spectrum presented in the Eq. (1), a novel algorithm that exploits the continuous spectrum to position the modes was introduced. It uses a simple criterion which balances accuracy and conditioning of the resulting least-squares problem to determine a parsimonious number of modes.

In this commercial software, an intermediate approach was used, *e.g.*, a potentially parsimonious choice for the number and location of the relaxation time was enabled. However, the user was allowed to incrementally overlay the simple strategy of equally spaced discrete values of relaxation times on the parsimonious choice. According to the developed methodology, first the continuous spectrum has to be computed using the Levenberg- Marquardt algorithm, and then the resulting linear least squares problem is solved to obtain the discrete spectrum.

**4. Results and discussion**

The frequency dependent shear storage modulus and shear loss modulus for all four investigated materials, *i.e.*, three microbial extracellular polysaccharides welan, gellan and xanthan, and water-soluble cellulose derivative sodium carboxymethylcellulose, are experimentally determined accordingly to the procedure reported in Section 2, and presented in Fig. 1.

 

(b)

(a)

 

(d)

(c)

**Fig. 1.** The frequency dependence of the storage modulus and the loss modulus for 1 wt. % water-based systems of (a) welan, (b) gellan, (c) xanthan and (d) Na CMC.

From the diagrams of dynamic moduli for polysaccharides welan, gellan and xanthan, it is clearly seen that both dynamic moduli show relatively slight variation, *e.g.*, monotonic change (increase) of the moduli is within one decade or less over three decades of oscillation frequency range. Moreover, storage moduli predominate over the loss moduli for all those three polysaccharides. Such rheological behaviour is typical for weak gel structures, having elastic properties more pronounced than viscous. On the other hand, rheological behaviour of the material Na CMC is different. Namely, it exhibits significantly bigger change of the dynamic moduli over the same oscillation frequency range as for the rest three materials, and in a contrast to welan, gellan and xanthan, its loss modulus predominates over the storage modulus. More pronounced viscous character in the whole frequency range examined is typical viscoelastic response for solutions.

The corresponding relaxation moduli for all four investigated materials are reconstructed from the dynamic moduli and using the methodology developed for interconversion between material functions in frequency- and time-domain, and presented in Fig. 2 (see the graph on the left). The accuracy of prediction of the relaxation moduli, obtained as a difference between the approximated values of the relaxation moduli calculated accordingly to Eq. (3) and the values calculated accordingly to Eq. (2), *i.e.*, reconstructed from spectrum, may be estimated from the graph on the right in Fig. 2.



**Fig. 2.** The relaxation moduli (left) and the relative errors of moduli reconstruction (right) for all four investigated materials.

From the diagram of relative errors of relaxation moduli reconstruction, one may conclude that the interconversion methodology works successfully for all examined materials except sodium carboxymethylcellulose, for which deviations are bigger than 10 % at longer times, *e.g.*, at the range above 1 s. We can assume, that the apparent discrepancy between the experimental data and the corresponding approximation for Na CMC is due to a significant change in the dynamic moduli (about 3 decades within frequency range, see Fig. 1d) which is much deeper increasing than for the other three materials.

The corresponding relaxation spectra for all four materials, calculated using three methodologies described in Section 3, are shown in Fig. 3.

 

(b)

(a)

 

(d)

(c)

**Fig. 3.** The relaxation spectra for 1 wt. % water-based systems of (a) welan, (b) gellan, (c) xanthan and (d) Na CMC.

Similar difference, as for dynamic moduli itself, is observed in spectra change for the group of microbial extracellular polysaccharides (welan, gellan and xanthan) and for water-soluble cellulose derivative, *i.e.*, sodium carboxymethylcellulose (Na CMC) as well. Namely, the decrease of relaxation strength within the same range of relaxation times is much deeper for Na CMC rather than for the rest of three materials. In addition, we observe the difference in spectra for all four examined materials resulting from the application of three used methodologies for their calculating.

We also considered the findings of the work of Davies and Anderssen31 related to the sampling of the storage and loss moduli over the frequency range and its influence on the determining the relaxation spectrum. The authors emphasised that the relaxation spectrum is determined on a shorter interval of relaxation times than the reciprocal frequency range. In order to assess the reliability of the calculated relaxation spectra, we performed error analysis using experimental data on moduli and their reconstructed values based on the calculated relaxation spectra.

To demonstrate the deviations of the approximated functions for shear storage moduli, , and shear loss moduli, , obtained by their reconstruction with the help of Eq. (1) on one hand, and using the relaxation spectra presented in Fig. 3 on the other hand, from the corresponding experimentally determined moduli, the relative errors calculated as differences between both material properties, *i.e.*, experimentally obtained and mathematically reconstructed, as functions of frequency, have been calculated and are shown in Figs. 4 – 7. Each diagram involves three curves for the relative errors of the approximations obtained by applying three different methodologies described in details in Section 3.

 

**Fig. 4.** The relative errors for reconstructed storage moduli (left) and loss moduli (right) as functions of frequency for welan.

 

**Fig. 5.** The relative errors for reconstructed storage moduli (left) and loss moduli (right) as functions of frequency for gellan.

 

**Fig. 6.** The relative errors for reconstructed storage moduli (left) and loss moduli (right) as functions of frequency for xanthan.

 

**Fig. 7.** The relative errors for reconstructed storage moduli (left) and loss moduli (right) as functions of frequency for Na CMC.

The diagrams vividly show that the accuracy of prediction of the dynamic moduli for all four materials depends on the methodology of calculating relaxation spectra applied.

Two of three approaches, *i.e.*, the computation of the relaxation spectra using generalized Maxwell model and the commercial software ReSpect based on Honerkamp & Weese method, demonstrated more or less similar results on the accuracy of prediction of experimentally obtained material functions. In most cases, the errors of approximation did not exceed 10 %. However, it is clearly seen in Fig. 5 that for gellan the error increased to 15 %, and even up to 20 % for certain frequencies.

At the same time, the numerical analysis showed that the computation of the relaxation spectra using interconversion between material functions demonstrated much lower capabilities in case of three materials, *i.e.*, welan, xanthan and Na CMC, *see, e.g.*, diagrams in Fig. 4, on the right, Fig. 6, on the right, and Fig. 7, on the left. Relative errors for reconstructing loss moduli of welan and xanthan, and the storage modulus of Na CMC are extremely high.

The effect of the calculus scheme on the accuracy of calculating relaxation spectra for polysaccharides, and consequently on the quality of approximation of the dynamic moduli is even more vividly demonstrated via diagrams containing the experimental data of storage and loss moduli of wellan and their appropriate approximations with the help of all three approaches described in Section 3, as shown in Fig. 8.

 

**Fig. 8.** The experimental data on the storage moduli (left) and the loss moduli (right) for wellan and their corresponding approximations.

It is necessary to point out that the value of relative errors for approximation of the dynamic relaxation moduli is not the only criteria for a goodness of the selected mathematical approach. Regardless the fact that applying generalized Maxwell model and the commercial software ReSpect for calculating relaxation spectra we obtain relatively small errors of approximation, in some cases the reconstructed dynamic moduli from the calculated spectra do not satisfy general necessary conditions required by the theory of viscoelasticity.

Indeed, in the case of welan the reconstructed curves of storage and loss moduli using the relaxation spectrum calculated with the help of generalized Maxwell model and presented in Fig. 3a, are non-monotonic, see Fig. 8, whereas accordingly to the theory of viscoelasticity the material functions for all polymeric materials must be smooth and monotonic. Similar is valid for the reconstructed curves of storage and loss moduli using relaxation spectrum calculated with the help of interconversion between material functions.

Note as well that the error curves presented in Figs. 4 - 7 are non-monotonic within the whole frequency range under investigation. The reason for that could be experimental errors in discrete values of storage and loss moduli determined in the oscillatory shear conditions. It is known that the determination of the discrete relaxation spectra from the point of view of a mathematical problem statement is an ill-posed problem, and consequently may cause significant errors in the predicted data of the dynamic moduli even if the experimental data errors are relatively small.

One may observe that the best methodology for reconstructing material functions curves is Honerkamp & Weese method with combination of calculating continuous and discrete spectra. It is known from practical application of the theory of viscoelasticity that for accurate spectra calculation in order to provide more exact approximation of relaxation curves, it is required to obtain experimental data for the “complete” curve, *i.e.*, including the whole frequency range from the glassy state to the rubbery state. In this regard, truncation errors, *i.e.*, the absence of information outside of the experimentally obtained dynamic moduli, play an important role. The truncation errors always occur because we never have experimental information extending from to .

**5. Conclusions**

Three different numerical methodologies for calculating relaxation spectra of water-based polysaccharide systems were compared. The experimental data of frequency dependent shear storage modulus and shear loss modulus for three different microbial extracellular polysaccharides, *i.e.*, gellan, welan and xanthan, and one water-soluble cellulose derivative, *i.e.*, sodium carboxymethylcellulose (Na CMC), were used for the numerical analysis.

All three numerical approaches demonstrated significant differences in the resulted calculated spectra for each of the materials. Moreover, error analysis for reconstructing storage and loss moduli as functions of frequency showed that the contribution from all three applied numerical approaches to approximation accuracy differ for the studied materials. Therefore, we may conclude that there is no any unique mathematical approach for calculating relaxation spectra for polysaccharides that ensure satisfactory approximation of the experimentally determined dynamic moduli for any polymeric material.

The results showed that the application of Honerkamp & Weese method with combination of calculating continuous and discrete spectra demonstrated significantly better prediction of polymer dynamic response in the sense of better accuracy in approximation of the dynamic moduli.

Based on the systematically performed numerical analysis, for practical purposes, one may recommend applying combination of different numerical schemes in parallel, *i.e.*, different methodologies, for calculating relaxation spectra with the aim of proper approximation of dynamic material functions such as relaxation modulus.

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