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Linear Viscoelastic Model for Different Flows Based on Control Theory

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Abstract:
Traditional Maxwell-type models have limitations when applied to the flows of real polymers containing macromolecules and complex microstructures. The main weakness of Maxwell models is the use of relaxation-time spectra that conducts to ill-posed problems in integral functions, and shear-induced relaxation spectrum transformations may lead to non-linearity. In contrast, control theory, which has apparently not been applied in rheology so far, enables modelling without knowledge of relaxation times. This study used viscoelastic constitutive equations derived from control theory and a new polymer fingerprint, which we call the rheologically effective distribution (RED). The study shows that a relaxation-time scheme is not essential to describe viscoelasticity, and applying the RED to computational modelling provides many theoretical and practical benefits, including giving higher accuracy. The proposed model is versatile and presents viscoelastic formulas for shear viscosity and other types of flow. Furthermore, the new model provides explanations for the empirical Cox-Merz rule and a power law behavior, the origin of which is frequently disputed in rheology.

Key words:
Viscoelasticity, shear and dynamic viscosity, control theory, rheologically effective distribution (RED), empirical rules

1 INTRODUCTION

Viscoelasticity is most commonly described using the generalized Maxwell model (also called the Maxwell-Wiechert model, first reported in 1889), which consists of a parallel arrangement of spring-and-dashpot elements and the stress of the relaxation modulus to include the relaxation-time concept. Numerous significant works have used this phenomenological theory of linear viscoelastic behaviour as a starting point [1–4]. The generalized Maxwell model is a presentation of the relaxation modulus within the linear viscoelastic behaviour of a molten polymer. It is mathematically valid, but it cannot be used to model higher strains or polymer flows over wider ranges of the shear rate and temperature. Even though the original model was limited to describing the relaxation modulus only at small strains in the linear viscoelastic region, the relaxation-time schema has been widened and used to model several types of flow and calculate data in various practical engineering and industrial polymerization applications, such as in detecting the molecular-weight distribution (MWD). While the Maxwell principle is a good educational tool to explain simple viscoelastic events, recently developed computation programs use a new function, the rheologically effective distribution (RED) that represents a more accurate and versatile indicator related to the polymer structure and MWD.

The starting point of the linear model is control theory, which is widely used in various technology applications. However, according to our best knowledge, control theory has not been used previously in rheology. Two variations of the model are presented: (1) an analytical model that is strictly based on fundamental principles and (2) a modified version that represents a more practical characteristic model. The viscoelastic data of flows are partitioned in two RED components related to the MWD as a source for further information outputs. One of the first ideas for partitioning viscoelasticity involved applying oscillatory shear rheometers to obtain storage and loss moduli. Bersted [5] suggested separating viscosity flow curves into Newtonian and non-Newtonian components, based on molecule sizes to obtain the MWD. This method involved cutting off

cy of 10^{-6} 1/s, where the analytical model shows a η^*_o value that is too high. Pure control theory includes all size chains of the MWD and the effects of the complete RED at very low frequencies are too strong, while the modified characteristic model derived using control theory produces a more realistic fit. The quality of the fit between the observed η^*_{obs} and predicted η^*_{fit} viscosity values was quantified using a modified least-square procedure that yielded the percentage root-mean-square error (% RMSE). Least-square procedures are widely used in numerical computations, and the differences obtained in the present study are shown in Figure 5b. The used viscosity LDPE data are curved and difficult to fit to some models, which is why the %RMSE values of other models are more than twofold higher than normal. The characteristic and analytical models actually included the form of data for the RED function, which partly explains why the observed error is small. Moreover, the characteristic viscosity fits might still be accurate when extrapolated outside of the measurement range over a wide scale of 10^{-6} 1/s < ω <10^6 1/s since they are computed from the true MWD/RED.

5 CONCLUSIONS

This study successfully derived viscoelastic constitutive equations from control theory purely from a phenomenological standpoint, even though the model was originally developed for detecting the MWD. Microlevel structures and long-chain branches from viscoelastic measurements are discussed elsewhere in a similar way in terms of the temperature dependencies of polymers [11]. We have demonstrated that applying control theory to polymer viscoelasticity offers an alternative to the relaxation-time schema, which until now has been considered fundamental and exclusive in rheology and viscoelasticity. Comparisons with the generalized Maxwell model show that the developed model has a different theoretic background and procedure. The linear relation to the RED was first developed from viscosity measurements, and then accurate fits to *G'* and *G''* moduli were obtained. Formulas for the relaxation modulus, shear viscosity and dynamic viscosity were generated, and the results show that the shear viscosity is not a simple viscometric function, instead having similar characteristics to viscoelasticity, as for the dynamic viscosity. This therefore expands the usage of the term linear viscoelasticity, defined normally by time-strain separability, by including time-rate separability to different types of flows [14]. The empirical power-law model and Cox-Merz rule receive an explanation by our model. The Cox-Merz rule holds more often by controlled probability and is manipulated by the same MWD. While the applied method offers more realistic and accurate models for rheology and polymer science, further efforts are needed to increase its use and acceptance within the rheology community. Also, the reasons for differences between modelled *G'* and dynamic measurements at low frequencies need to be clarified.

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