망상구조의 대변형 거동에 대한 FFT 해석

김승하, 심훈구, 안경현, 이승종
서울대학교 응용화학부

Fourier transformation analysis of LAOS behavior of network models

Seung Ha Kim, Hoon Goo Sim, Kyung Hyun Ahn, Seung Jong Lee
School of Chemical Engineering, Seoul National University

Introduction

Recently, interests in complex fluids are growing. Complex fluids are used in many fields of industry like foods, personal care products and biological applications. Elucidation of the relationship between the microstructures of complex fluids and its physical properties is very important for its application. Up to date, microstructures of complex fluids are generally characterized by the rheological properties obtained from the small amplitude oscillatory shear (SAOS) flow, in which the microstructures are slightly deformed from its equilibrium configuration, so called linear viscoelasticity. In this regime, the stress response to the sinusoidal strain is also sinusoidal curve, and decomposed into storage modulus and loss modulus. As the strain amplitude increases, the stress response begin to deviate from the sinusoidal shape and the nonlinear regime begin, where the complex fluids usually undergoes in practical application. Under the Large amplitude Oscillatory Shear(LAOS) flow, the microstructure will be destroyed and reconstructed repeatedly. The rheological properties obtained in this regime by commercial rheometry lose its physical meanings. More precise information in this regime can be derived by a spectral analysis by a Fourier Transformation(FT). Fourier Transformation of the stress response decompose its higher harmonics into frequency domain. We calculate the stress response under the LAOS for three network models; Marrucci model, Liu model and modified Lodge model. Fast Fourier Transformation(FFT) results show the differences between the network models.

Theory

Marrucci model

The equation for the distribution of active chains

$$\frac{\partial \psi}{\partial t} = -\frac{\partial}{\partial R} \cdot (\psi k \cdot R) - \beta(R)\psi + \alpha(R)\phi \tag{1}$$

The equation for the distribution of pendent chains

$$\frac{\partial \phi}{\partial t} = -\frac{\partial}{\partial R} \cdot \left(-D\frac{\partial \phi}{\partial R} + \phi\frac{D}{kT}F(R) + \phi k \cdot R\right) - \alpha(R)\phi + \beta(R)\psi \tag{2}$$

The stretching force

$$F(R) = -\frac{3kT}{Nb^2}\frac{R}{1 - R^2/(Nb)^2} \tag{3}$$

The rate coefficients

$$\alpha(R) = \alpha_0 + \alpha_1\frac{R}{R_0} \tag{4}$$

$$\beta(R) = \frac{\beta_0}{1 - R^2/(Nb)^2} \tag{5}$$

Liu model

for simple shear

$$\frac{d\sigma_{i,xy}}{dt} = G_i\gamma + \frac{\sigma_{i,xy}}{x_i} - \frac{\sigma_{i,xy}}{\lambda_i} \tag{6}$$

The kinetic equation

$$\frac{dx_i}{dt} = k_1\frac{1-x}{\lambda_i} - k_2 x\left(\frac{1}{2}|\gamma|\right) \tag{7}$$

The relaxation time & modulus

$$G_i = G_{0i}\, x_i \tag{8}$$

$$\lambda_i = \lambda_{0i}\, x_i^{1.4} \tag{9}$$

Modified Lodge model

Constitutive equation

$$\tau_i + \lambda_i(t)\, \tau_{i(1)} = k_B T\, \hat{L}_i^{eq}(t)\, \lambda_i^{eq}(t)\gamma + k_B T[\hat{L}_i(t)\, \lambda_i(t) - \hat{L}_i^{eq}(t)\, \lambda_i^{eq}(t)]\delta \tag{12}$$

The creation & loss rates

$$\hat{L}_i(t) = \hat{L}_{i0}\, f(t) \tag{13}$$

$$\lambda_i(t) = \lambda_{i0}/g(t) \tag{14}$$

The creation & loss terms

$$f(t) = \exp(a|\tau_{12}|) \tag{15}$$

$$g(t) = \exp(b|\tau_{12}|) \tag{16}$$

Results

Some examples of FT analysis for Marrucci and Liu model are given below.

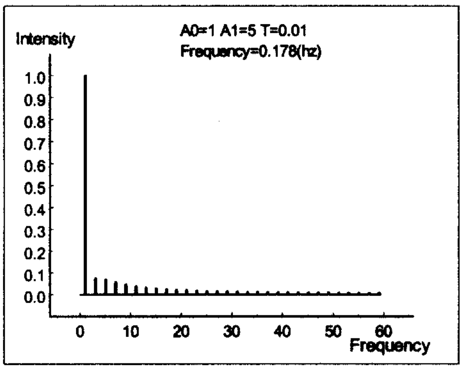

Fig 1) $\lambda\gamma$=5.62, Marrucci model (G′ & G″ overshoot)

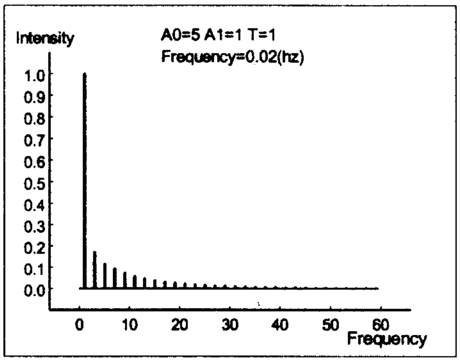

Fig 2) $\lambda\gamma$=100, Marrucci model (G′ overshoot & G″ decrease and increase)

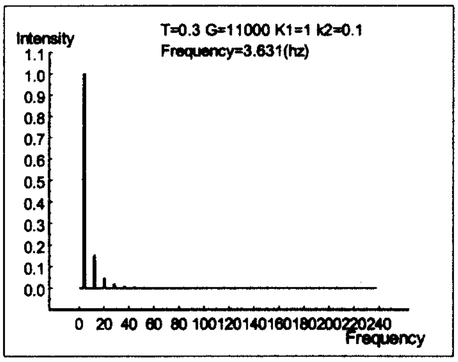

Fig 3) $\lambda\gamma$=5.62, Liu model (shear thinning)

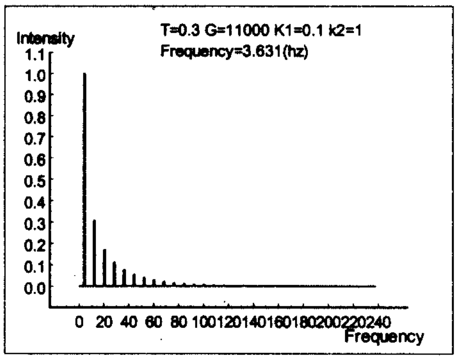

Fig 4) $\lambda\gamma$=23.82, Liu model (weak overshoot)

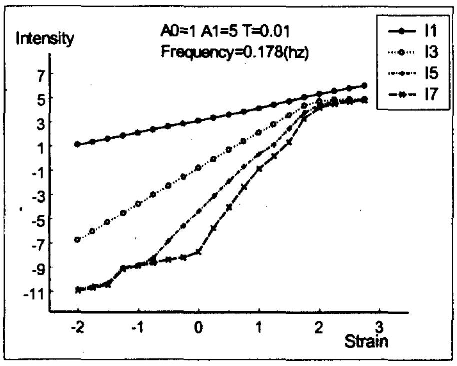

Fig 5) Intensity of higher harmonics for Marrucci model

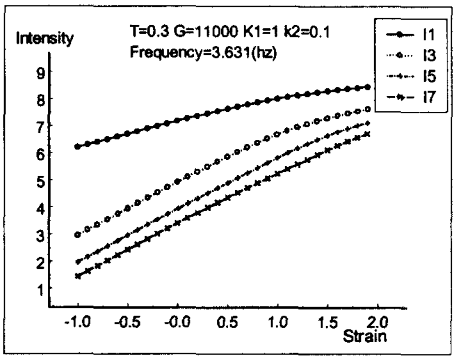

Fig 6) Intensity of higher harmonics for Liu model

Conclusions

In the FT analysis the intensity of higher harmonics is closely related to the microstructure of the complex fluids and the higher harmonics have a similar pattern to the properties in the nonlinear region. In most network model the intensity of higher harmonics is in proportion to the square of strain but in Marrucci model it has a different pattern from other network model.

References

[1] R. Byron Bird, Dynamics of polymeric liquids, volume 2, 353-391
[2] A. Vaccaro, and G. Marrucci, A model for the nonlinear rheology of associating polymers, J. Non-Newtonian Fluid Mech., 92(2000) 261-273
[3] Joseph A. Yosick, A. Jeffrey Giacomin, and Paula Moldenaers, A kinetic network model for nonlinear flow behavior of molten plastics in both shear and extension, J. Non-Newtonian Fluid Mech., 70(1997) 103-123
[4] Kyung Hyun Ahn, and Kunihiro Osaki, Mechanism of shear thickening investigated by a network model, J. Non-Newtonian Fluid Mech., 56(1995) 267-288
[5] Manfred Wilhelm, Pierre Reinheimer, Martin Ortseifer, Thorsfen Neidhofer, and Hans-Wolfgang Spiess, The crossover between linear and non-linear mechanical behaviour in polymer solutions as detected by Fourier-transform rheology, Rheology Acta, 39(2000) 241-246

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