복합유체의 퓨리어 변환 유변학에 관한 연구

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Fourier transform rheology under large amplitude oscillatory shear flow

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Introduction

There has been a growing interest in complex fluids, which include biological macromolecules, polyelectrolytes, surfactants, suspensions, emulsions, and so on [1]. These fluids are used in many fields of industry as food stuffs, personal care products, electronic and optical materials and for many biological applications. Complex fluids form complex microstructures depending on their thermal and deformation history conditions, which lead to diverse rheological properties. Recently, Hyun et al. [2] proposed that large amplitude oscillatory shear (LAOS) behavior is very sensitive to the interactions or the shear-induced formation of microstructures. Depending on the interactions between the microstructures, it is found that there exist at least four types of LAOS behavior: type I, strain thinning (G′, G" decreasing); type II, strain hardening (G′, G" increasing); type III, weak strain overshoot (G′ decreasing, G" increasing followed by decreasing); type IV, strong strain overshoot (G′, G" increasing followed by decreasing). However, as the strain amplitude is increased in an oscillatory shear flow, the stress is no longer sinusoidal and the validity of linear viscoelasticity fails [3]. But, the rheometer dose not recognize this change and generates moduli in the same way as in the linear case.

When the strain is large, the stress becomes non-sinusoidal and has higher harmonic components

$$\sigma(t) = \sum_{n=1,odd} \sigma_n \sin(n\omega_0 t + \delta_n)$$

where the magnitude σ_n and the phase angle δ_n depend on the strain amplitude and the frequency ω_0 [4]. The measured moduli at large strain neglect the higher harmonic contributions, and lose physical significance in a conventional sense. This non-linear response is analysed using the so-called " Fourier-transform rheology" method [5,6,7]

The purpose of this study is to understand LAOS test using FT-rheology for solutions of type III (xanthan gum solution and pluronic hard gel).

Experimental Methods

Materials and sample preparation. In this study, commercial grade $EO_{100}PO_{65}EO_{100}$, Pluronic F127(BASF), was used without further purification. Pluronic F127 was selected because it has the lowest gelation concentration and the simplest phase behavior of the Pluronic series. The nominal molecular weight of this copolymer is 12600 and weight fraction of PEO in the triblock copolymer is approximately 70%. This sample was dissolved in dust-free purified water. To make samples homogeneous and transparent, the solution was rotated at 100rpm for about 30min at 90℃. Xanthan Gum (XG) solution was also used. The XG sample used in this study is a commerical product (aldrich). The XG was dissolved in dust-free purified water for 1day at room temperature, and then the solution was rotated at 3000rpm for about 2h at 60 ℃. The XG concentration was 4wt%

Rheometry. Rheological measurements were carried out on a rheometer (RMS800, Rheometrics) using a parallel plate fixture with a diameter of 50mm and lower plate with a dam, and silicone oil was used to prevent water evaporation. Strain sweep test was carried out in the strain range from 1% to 1000% at a fixed frequency of 1rad/s. The raw data from the force transducer was digitized with a modern 16-bit analog to digital converter (ADC) operating at sampling rates up to 330 kHz for one channel. A 16 channel, 16bit PCI-ADC (PCI-6052E; National Instruments, Austin, USA) with a smapling rate up to 330 kHz was used. This ADC card was plugged into a stand-alone PC equipped with Labview 6.1 software (National Instruments).

Results and Discussion

Oversampling. When Fourier transform rheology is applied, the important thing is to obtain raw data without noise. The basic idea is to acquire the raw data at the highest possible acquisition rate as allowed by a modern analog to digital converter (ADC); the raw data is "oversampled" [8]. The sampling rate may exceed 50 kHz with this method. In a second step the raw data is truncated "on the fly" by means of a so-called "boxcar" average over, e.g., several hundreds or thousands of raw data points [9]. The application of the boxcar average to the raw data results in a new time domain data set with a strongly reduced number of data points.

In Fig. 1a the torque response as a function of time is shown for a data set with oversampling number. Oversampling number (N) means that the data is oversampled for N data points and afterwards reduced to a single data point. Fig. 1b shows FFT results. As a result, torque transducer sensitivity increases with increasing oversampling number and the results of Fourier transform analysis decrease noise with increasing oversampling number.

Time sweep test. We obtain many cycles of torque data. Thus time sweep was carried out at a fixed freqeucy 1rad/s with changing strain. Fig. 2 shows time sweep results of XG 4% at different strain, and torque data as a function of time. Fig. 3 shows time sweep results of F127 20% solution at hard gel region (28℃), and torque data as a function of time at different strain. Both XG 4% solution and F127 20% solution at hard gel region show LAOS III type (G′ decreasing, G" increasing followed by decreasing). However, torque(stress) curve shows different shape at non-linear region. The origin of these difference is different shear-induced structure. In case of F127 20% solution, the microstructure shows cubic array of micelles at hard gel region. When large strain is imposed, layer are slid with the flow direction.

In case of XG 4% solution, the small side chain form weakly structured materials.

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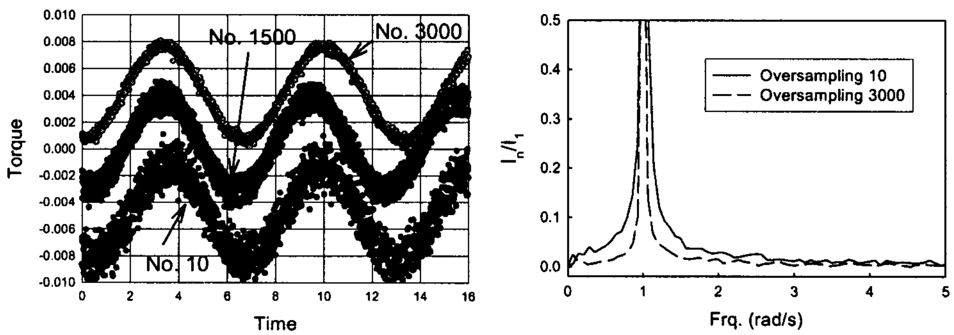
References

[1] R. G. Larson, The Structure and Rheology of complex fluids, Oxford University Press, Oxford, 1999 (Chapter 1).
[2] K. Hyun, S. H. Kim, K. H. Ahn, S. J. Lee, Large amplitude oscillatory shear as a way to classify the complex fluids, accepted to J. Non-Newtonian Fluid Mech. (2002).
[3] J. M. Dealy, K. F. Wisbrun, Melt Rheology and Its Role in Plastics Processing Theory and Applications, Van Norstand Reinhold, New York, 1990, Chapter 5, pp. 219-225.
[4] A. J. Giacomin, J. M. Dealy, Large-amplitude oscillatory sher, in: A.A. Collyer (Ed.), Techniques in Rhelogical Measurment, Chapman & Hall, London, 1993, Chapter 4, pp. 99-121.
[5] M. Wilhelm, D. Maring. H. W. Spiess, Fourier-transform rheology, Rheol Acta, 37(1998) 399.
[6] M. Wilhelm, P. Reinheimer, M. Ortseifer, High sensitivity Fourier-transform rheology, Rheol Acta, 38(1999) 349.
[7] M. Wilhelm, Fourier-transform rheology, Macromol. Mater. Eng., 287(2002) 83.
[8] D. V. Dusschoten, M. Wilhelm, Increased torque transducer sensitivity via oversampling, Rheol Acta, 40(2001) 395.
[9] D. A. Skoog, J. J. Leary, Principles of instrumental analysis, Saunders College Publishing, Fort Worth.



(a) (b)

Fig. 1. (a) The torque as function of time for XG 4% at fixed strain 3%, (b) FFT results at different oversampling.

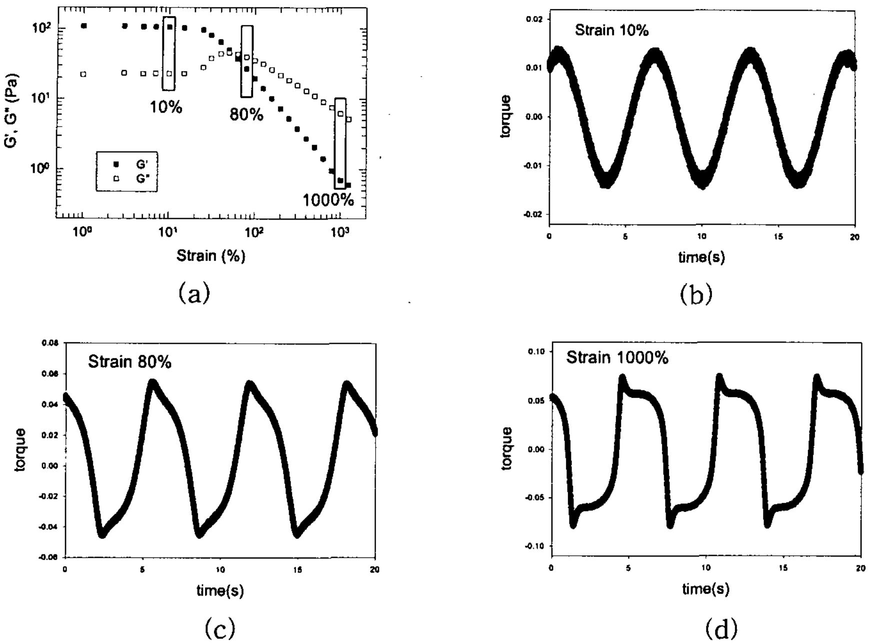


Fig. 2. (a) Results of time sweep at 1rad/s for XG 4% solution. Torque data as function of time, (b) strain 10%, (c) strain 80%, (d) strain 1000%.

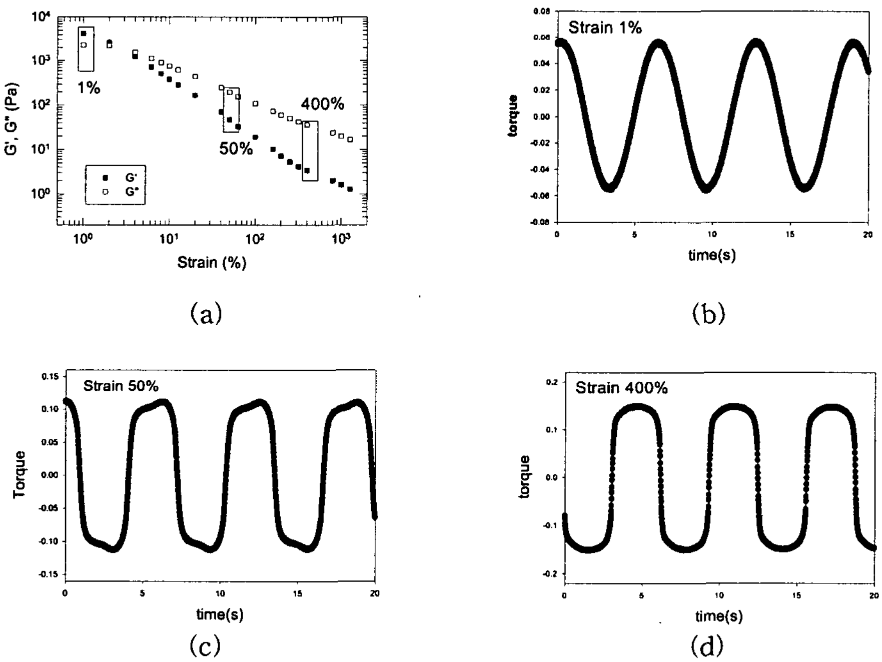


Fig. 3. (a) Results of time sweep at 1rad/s for F127 20% solution at hard gel region (28℃). Torque data as function of time, (b) strain 1%, (c) strain 50%, (d) strain 400%.