

FOURIER-TRANSFORM-RHEOLOGY ON LINEAR POLYSTYRENE MELTS

T. NEIDHÖFER, M. WILHELM, H.W. SPIESS

Max-Planck-Institut für Polymerforschung
Postfach 3148, 55021 Mainz, Germany

e-mail: neidht@mpip-mainz.mpg.de

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ABSTRACT:

Large amplitude oscillatory shear (LAOS) was applied to a linear polymer melt in order to study the mechanical harmonic generation in the nonlinear regime. In the nonlinear regime mechanical harmonics at $3\omega_1$, $5\omega_1$, etc. are generated under oscillatory shear with a shear frequency ω_1 . These higher harmonics can be analysed with respect to frequencies, amplitudes and phase if the time data of the torque is Fourier transformed. This experimental method (FT-Rheology) permits therefore to quantify the mechanical nonlinearities if sinusoidal shear rates are applied.

This article describes the basic idea of this experimental method as well as the application to different anionically polymerized polystyrene melts. The dependence of the nonlinear, rheological properties with respect to the molecular weight M_n , the applied strain γ_0 , the frequency ω_1 and the temperature was investigated. In addition to simple nonlinear theories we could also observe even harmonics at $2\omega_1$, $4\omega_1$, etc. in the FT-rheology spectra. The appearance of even harmonics was correlated with the appearance of a more complex nonlinear behaviour.

ZUSAMMENFASSUNG:

Polymere Schmelzen wurden mit großen Amplituden unter oszillatorischer Anregung im nichtlinearen Bereich untersucht. Im nichtlinearen Bereich werden durch die oszillatorische Verscherung mechanische Obertöne bei $3\omega_1$, $5\omega_1$, etc. bezüglich der Anregungsfrequenz ω_1 generiert. Diese mechanischen Obertöne können bezüglich ihrer Frequenz, Amplitude und Phase mit Hilfe einer Fouriertransformation analysiert werden. Die sogenannte FT-Rheologie erlaubt es somit Nichtlinearitäten bei einer oszillatorischen Anregungen zu quantifizieren.

Dieser Artikel beschreibt die Grundidee dieser experimentellen Methode sowie die Anwendung auf verschiedene anionisch polymerisierte Polystyrol Schmelzen. Die Abhängigkeit der nichtlinearen Eigenschaften als Funktion vom Molekulargewicht, Dehnamplitude γ_0 , der angelegten Frequenz ω_1 sowie der Temperatur wurden untersucht. Neben den theoretisch erwarteten ungeraden Obertönen konnten auch gerade mechanische Obertöne bei $2\omega_1$, $4\omega_1$ etc. in den FT-Rheologie Spektren detektiert werden. Diese Obertöne wurden mit komplizierteren nichtlinearen Verhalten wie beispielsweise dem Auftreten von Wandgleiten oder dem Einsetzen von Scherbanden in Verbindung gebracht.

RÉSUMÉ:

Afin d'étudier l'apparition d'harmoniques mécaniques en régime non linéaire, un cisaillement oscillatoire de large amplitude (LAOS) à été appliqué sur un système constitué de polystyrène linéaire. L'objectif fondamental de la rhéologie par transformée de Fourier consiste en la mesure des harmoniques mécaniques d'ordre supérieur – $3\omega_1$, $5\omega_1$, etc. – générées en régime non linéaire sous cisaillement oscillatoire. De telles harmoniques peuvent être mesurées avec une grande précision en fonction de la fréquence ω_1 et de la contrainte γ_0 appliquée. La FT-Rhéologie permet ainsi de mettre facilement en évidence et de décrire des comportements non linéaires lors de l'application de taux de cisaillement variant en fonction du temps.

Cet article décrit les concepts de base de la rhéologie par transformée de Fourier. La méthode expérimentale y est appliquée à l'étude rhéologique de polystyrènes linéaires à l'état fondu en régime non linéaire et sous cisaillement oscillatoire ceci afin de quantifier les phénomènes mécaniques non linéaire sous jacent. Le polystyrène utilisé a été obtenu par polymérisation anionique. La dépendance de ses propriétés rhéologiques non linéaires en fonction de la masse moléculaire, de l'amplitude de la contrainte, de la fréquence de cisaillement et de la température a été analysée par FT-Rhéologie. En complément aux simples théories non linéaires, nous avons pu observer sur les spectres de FT-Rhéologie des harmoniques paires à $2\omega_1$, $4\omega_1$, etc. Ce phénomène a été corrélé à l'apparition d'un comportement « stick-slip ».

KEY WORDS: Fourier-transform rheology; LAOS; oscillatory shear; polystyrene melt; nonlinear shear

Figure 5c (left): Scheme for extreme cases of the torque response in the time domain and the correlation FT-rheology spectra which is normalized to the ground frequency, ν_1 . In the time domain T_1 expresses the periodicity. A rectangular step function in the time domain yields only odd harmonics in the Fourier spectra. A saw tooth figure contains both even and odd harmonic of the fundamental frequency, $\nu_1 = 1/T_1$.

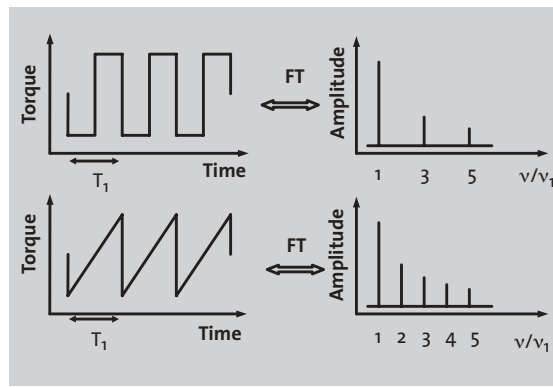
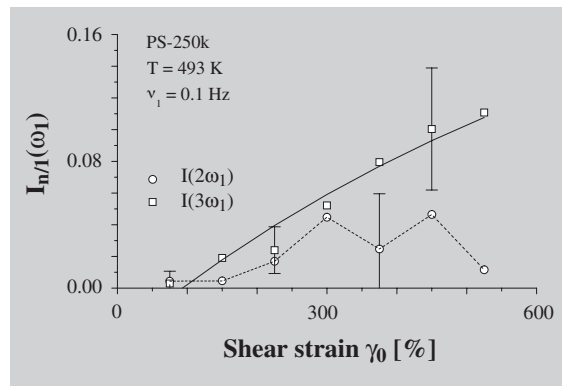


Figure 5d (right): Relative intensity of the third harmonics $I_{n/3}(\omega_1)$ as a function of the strain amplitude γ_0 for PS-250k at $T = 493$ K and $\nu_1 = 0.1$ Hz.



together with the FT-rheology spectra. In general, an experimental spectra should lie in between these two extreme cases if the theoretical constraints are met. A quantitative measure for the degree of wall slip or shear bands could therefore be the relative intensity of the second harmonic $I_{2/1}(\omega_1)$ at the specific experimental conditions.

Experimentally we received relative intensities of the second harmonic up to $I_{2/1}(\omega_1) \approx 10\%$. Fig. 5.b displays also the FT-rheology spectra corresponding to the displayed time data. Both the second and the fourth harmonic are clearly visible. The relative peak intensity of the second harmonic in Fig. 5.a can be quantified as $I_{2/1}(\omega_1) \approx 9\%$, thus being nearly as high as the relative peak intensity of the third harmonic.

The appearance of even harmonics under LAOS conditions, however, is not fully understood at this time and it is not clear whether their appearance will be more useful for the understanding of the rheological behaviour of polymers or as control of sample preparation and rheometer-performance. We found that the even harmonics depend strongly on the previous sample handling in a complex way. They vary over a wide range for different measurements under similar conditions, meaning that the reproducibility for the even harmonics is in general much less than for the odd harmonics. As shown in Fig. 5.d, in the beginning the second harmonic $I(2\omega_1)$ and the third harmonic $I(3\omega_1)$ can be similar while for higher strain amplitudes the second harmonic decays. In order to prevent wall slip we used rough surfaces but still even harmonics occurred in the spectra. We therefore favor an inner slip similar to shear bands or edge fracture. The literature describes also stick-slip motion as a function of the material used for the measurement tools [20]. Research along those lines is currently being carried out in our laboratory.

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