

## **FOURIER TRANSFORM MECHANICAL SPECTROSCOPY OF VISCOELASTIC MATERIALS WITH TRANSIENT STRUCTURE**

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### **Summary**

A new technique is presented to measure the frequency dependent complex modulus simultaneously at several frequencies instead of consecutively as in a frequency sweep. For this purpose, the strain in a dynamical mechanical experiment is prescribed as a superposition of several different modes (three in our case). The resulting stress is decomposed into sinusoidal components, each of them characterized by their frequency, amplitude, and phase shift with respect to the corresponding strain component. Phase shift and amplitude are expressible in a frequency dependent complex modulus. A single experiment gives, therefore, values for the complex modulus at a set of prescribed frequencies. The method was demonstrated on three stable viscoelastic fluids and was applied to determine the instant of sol-gel transition (gel point) of a crosslinking polymer.

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### **Introduction**

It is desirable to reduce the experimental time that is needed for rheological characterization of a polymer. This would prove extremely useful for characterization of polymers in general. However, it is particularly needed for samples with transient structure, because the measurement time has to be short compared to the time required for appreciable change in the

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sample. There are many possible mechanisms of transient structure such as changes in molecular structure (polymerization, degradation, or crosslinking), phase changes in a blend, change of microstructure in a multi-phase system, etc.

A general difficulty in the rheology of materials with transient structure is the occurrence of two competing time dependent mechanisms:

- 1) stress relaxation, i.e. the approach to an equilibrium state at rest, and
- 2) structural change in the material, i.e. the change of the equilibrium state with time, assuming that each transient structure can be characterized by an equilibrium state.

Stress relaxation in a viscoelastic material is described as a linear superposition of several relaxation processes of different characteristic times. The measurement of a relaxation process requires an experimental time in the order of the relaxation time of the process. The longer the relaxation time, the longer is the experimental time. However, the experimental time has to be short compared to the characteristic time of material change. Therefore, the longest relaxation time which can be measured is limited by the characteristic time of material change. For example, in a material with high rate of change of properties, we can only measure the short end of the relaxation time spectrum. Only if the stability criterion,

$$\frac{\lambda}{G} \frac{\partial G}{\partial t} \ll 1,$$

is valid, i.e. if the relative change of properties (using  $G$  symbolically for an arbitrary mechanical property) during the experiment is small compared to the longest relaxation time  $\lambda$ , can the entire relaxation spectrum be measured.

Presented here is a technique called *Fourier Transform Mechanical Spectroscopy* (FTMS) that effectively decouples the frequency dependence and time dependence of the fluid properties. This enables us to directly obtain the complex moduli,  $G'$  and  $G''$ , at several frequencies simultaneously as the system structure evolves with time. As an example, the gel point of a crosslinking polymer can be detected from dynamic mechanical behavior [1] since the critical gel (the polymer at the gel point) exhibits power-law relaxation, i.e. the loss-tangent  $\tan \delta$  is independent of frequency. The instant at which power-law relaxation dominates the sample can be detected with just one experiment using FTMS. Thus, we have a simple method to measure the instant of gelation.

It has to be emphasized that the method is based on the Boltzmann superposition principle and is not applicable outside the linear viscoelastic range. There, the stress response to the imposed strain is non-linear and the Boltzmann superposition is not valid any more.

### Working of method and procedure

In the experiment, the sample is subjected to an oscillatory strain as shown in Fig. 1,

$$\gamma = \sum_{i=1}^m \gamma(\omega_i) = \sum_{i=1}^m \gamma_i \sin \omega_i t$$

where  $m$  = number of frequency components

$\gamma_i$  = amplitude of the  $i$ th component

$\omega_i$  =  $i$ th frequency component (integer multiples of the fundamental frequency  $\omega_f$ )

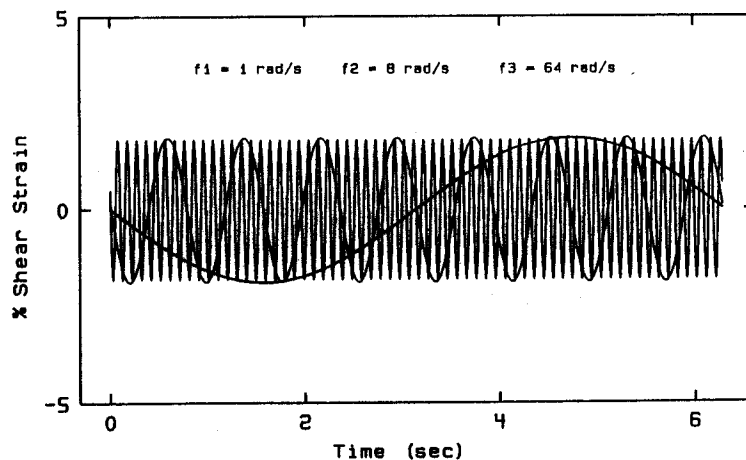
and the resulting stress is measured. The prescribed experimental parameters are the strain amplitudes and the fundamental frequency  $\omega_f$ . The sum of strain amplitudes has to be below a critical value  $\gamma_c$ , the linear viscoelastic range of the material

$$\sum_{i=1}^m \gamma_i \leq \gamma_c.$$

The frequencies chosen are harmonics of the fundamental frequency, i.e. they are integer multiples of a fundamental frequency  $\omega_f$ .

$$\omega_1 = m_1 \omega_f \quad \omega_2 = m_2 \omega_f \quad \omega_3 = m_3 \omega_f$$

A typical choice of the integer coefficients is:  $m_1 = 1$ ,  $m_2 = 8$  and  $m_3 = 64$



Decomposed strain signal showing equal amplitudes of all three frequencies

Fig. 1. Sinusoidal shear strain signals generated by the computer at three different frequencies, 1 rad/s, 8 rad/s and 64 rad/s. The three waveforms have equal amplitudes.

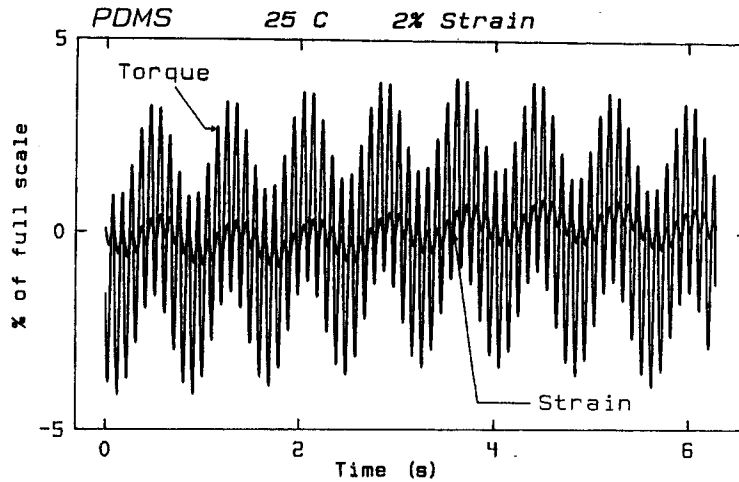


Fig. 2. Complex strain signal obtained by superposition of the three waveforms shown in Fig. 1, and the resulting torque on the material as measured.

(fundamental frequency, 8th harmonic and 64th harmonic). This can be seen as the complex waveform in Fig 2.

A discrete Fourier transform is performed on the resulting stress data to obtain the individual stress values for each frequency component (Fig. 3) as:

$$\tau = \sum_{i=1}^m \tau(\omega_i) = \sum_{i=1}^m (A_i \sin \omega_i t + B_i \cos \omega_i t)$$

where  $A_i$  and  $B_i$  are the Fourier coefficients.

(See Oppenheim and Schaffer [2] for a theoretical discussion of digital signal processing and Ramirez [3] for a detailed practical discussion of Fourier transforms).

The phase relationship between stress and strain components is given by

$$\tan \delta(\omega_i) = B_i/A_i$$

The complex moduli,  $G'$  and  $G''$ , are found by the standard expressions

$$G'(\omega_i) = K\tau(\omega_i) \cos \delta(\omega_i)/\gamma(\omega_i) \text{ and}$$

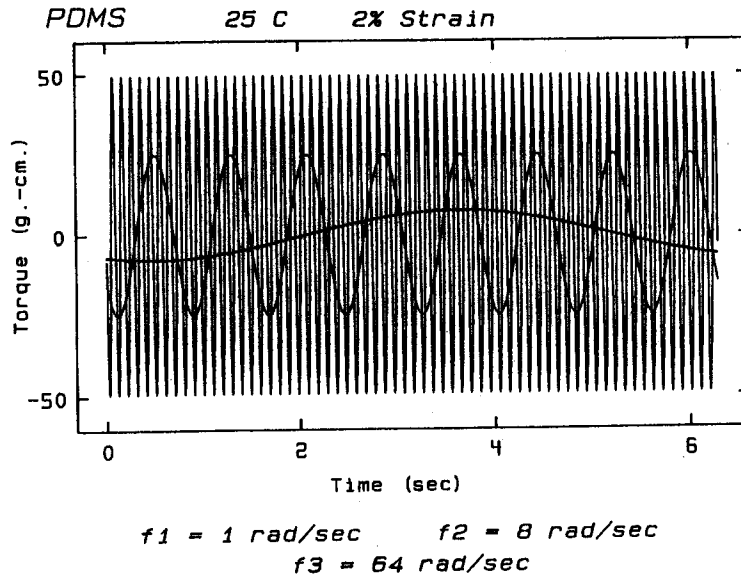
$$G''(\omega_i) = K\tau(\omega_i) \sin \delta(\omega_i)/\gamma(\omega_i),$$

where the quantity  $K$  is a geometric scaling constant of the rheometer.

The minimum time for the experiment is given by one period of the fundamental frequency as

$$t_e \geq 2\pi/\omega_f$$

though in practice, the material is allowed to reach a quasi steady state after



*Decomposed torque signal showing relative amplitudes*

Fig. 3. The complex torque signal is decomposed into three components corresponding to the three frequencies chosen initially. The amplitudes are seen to increase with the frequencies.

several cycles before taking the measurement. The strain amplitudes are adjusted such that the stress amplitudes are about the same for each frequency.

If there were no practical constraints, the frequency dependent modulus could be obtained by using an arbitrary transient strain and by a Fourier transform of the stress response. An example of such a procedure has been given by Marin et al. [4] using experimental data of stress growth and stress relaxation after cessation of flow. However, the strain is limited in a linear viscoelastic experiment ( $\gamma < \gamma_c$ ), and the resulting stress is small. If this small stress is then decomposed into a spectrum of many modes, the contribution of each mode is too small to be detectable with sufficient accuracy. For our experiment which is restricted to a small number of modes (three, for instance), the stress contribution of each mode is sufficiently large. Additionally, there is an independent choice of strain amplitude for each of the (three) modes. In this way, we can adjust the strain amplitudes in such a way that the sensitivity is about equal for all (three) modes.

#### **Experimental set-up**

An 8088-based STD bus microcomputer is used to control and gather data from the experiment. The waveform is computed and stored in main

memory of the computer. The wavetable is sampled and used as the strain command input of a Rheometrics Dynamic Spectrometer model 7700. The rheometer's strain and torque outputs are sampled and stored in memory.

The computer is interfaced to the rheometer via 12-bit digital to analog (DAC) and analog to digital (ADC) converters. The resolution of a DAC (or ADC) is defined as

$$R = \frac{V_{p-p}}{2^r - 1}$$

where  $V_{p-p}$  = peak to peak full scale voltage range

$r$  = number of bits in the converter

The RDS 7700 uses a  $-10$  V to  $+10$  V full scale range on all inputs and outputs. Therefore, the resolution of our DAC (and ADC) is

$$R = 20 \text{ V} / (2^{12} - 1) = 4.88 \text{ mV}.$$

For strain amplitudes less than full scale, an attenuation amplifier can be used to improve the resolution. An amplifier with a gain of 0.01 used with the above set-up gives a resolution of  $(0.01 \times 4.88) \text{ mV} = 48.8 \text{ } \mu\text{V}$ .

The frequency resolution of the system is determined by the sampling rate of the computer and the size of the wavetable. According to the Shannon sampling theorem [5], the highest measurable frequency can be no higher than one half the sampling rate.

$$\omega_h = \omega_s / 2$$

Once the sampling rate is set, the lowest measurable frequency will depend on the size of the wavetable as:

$$\omega_1 = \omega_s / N$$

where  $N$  = number of entries in the wavetable.

The real limit on the highest measurable frequency,  $\omega_h$ , is dictated by the ability of the motor in the rheometer to respond accurately to the input signals, and by sample inertia, which is negligible for most high polymers. The output (command) strain signal is always measured and compared to the input strain. This is to check for losses in the line, motor response differences as a function of the frequency, etc.

### Application to polymeric liquids

Comparison of the rheological data obtained by the FTMS method and the data directly from the RDS 7700 demonstrate the accuracy of this method. This can be seen from the  $G' - G''$  data for stable, non-reacting polydimethylsiloxane (PDMS), Polyethylene (PE), and Polystyrene (PS) in

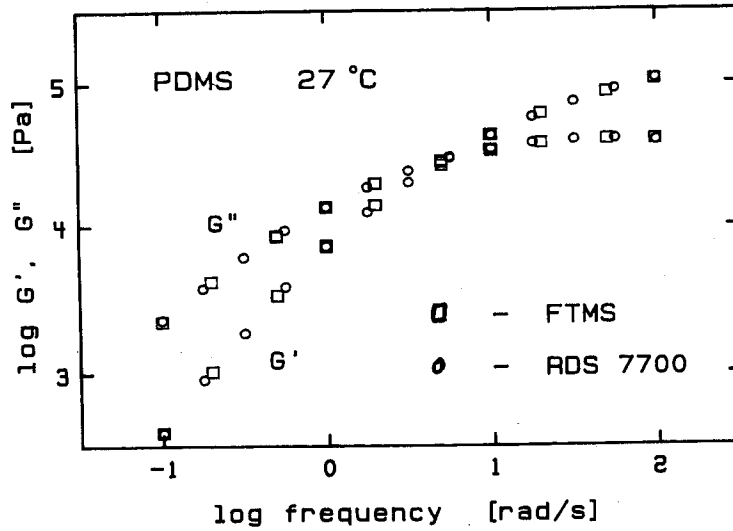


Fig. 4. Complex moduli,  $G'$  and  $G''$ , of stable, non-reacting polydimethylsiloxane (PDMS) as measured by the rheometer directly and by FTMS.  $T = 27^\circ\text{C}$ . The geometry used was cone and plate.

Fig. 4, 5 and 6 respectively. For each material, the FTMS data was obtained from five sweeps, each at three frequencies. Some overlap of data occurred between sweeps as a check on reproducibility. The agreement between the

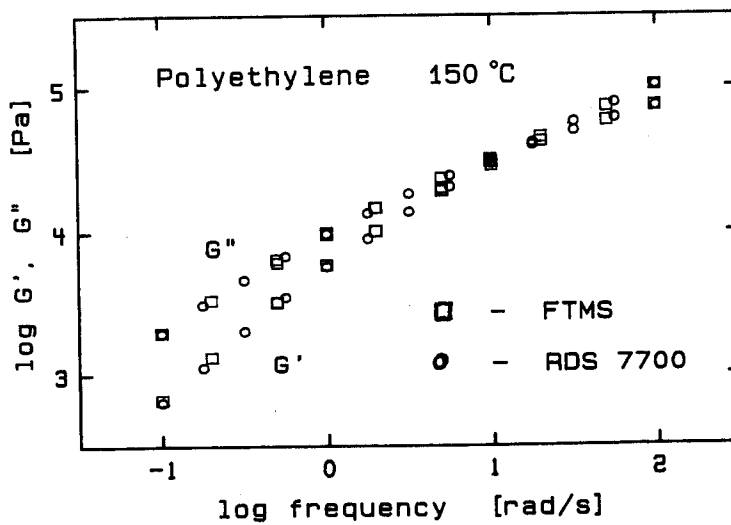


Fig. 5. Comparison of the  $G'$ ,  $G''$  data obtained from the rheometer and from FTMS for polyethylene (LDPE Dupont Alathon 20) at  $150^\circ\text{C}$ . The geometry used was cone and plate.

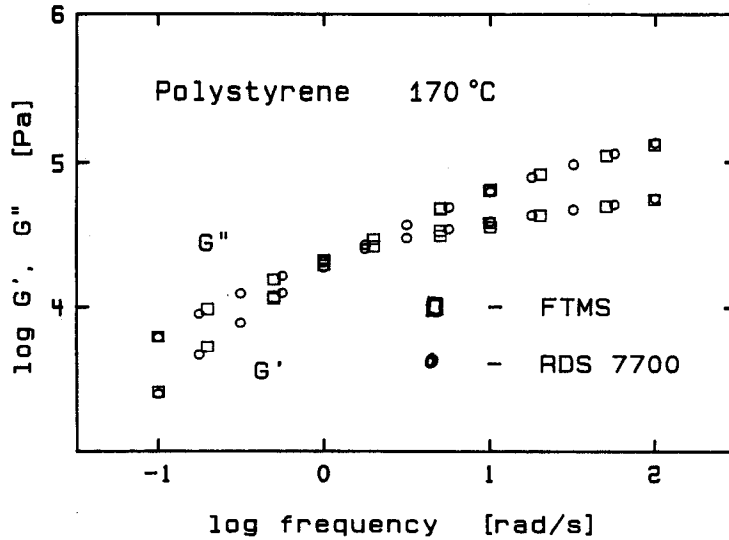


Fig. 6. Comparison of the  $G'$ ,  $G''$  data obtained from the rheometer and from FTMS for polystyrene (Dow 666) at  $170^\circ\text{C}$ . The geometry used was cone and plate.

two sets of data is found to be well within acceptable limits (about  $\pm 5\%$ ). The torque amplitudes have been adjusted to be about the same at each frequency and the total strain is kept well within linear viscoelastic limits.

#### Application to reacting system

The storage modulus ( $G'$ ) and the loss modulus ( $G''$ ) of the crosslinking polydimethylsiloxane (PDMS) system in an oscillatory shear experiment depend on both the reaction time and the frequency of deformation of the sample. A power law relaxation behavior indicates the instant of gelation (gel point) as found by Winter and Chambon [6] and Chambon and Winter [6]. At the gel point, the loss tangent  $\tan \delta (= G''/G')$  is independent of frequency, i.e. the  $\tan \delta$  curves cross at one point, the gel point. An important result is that this single experiment gives the value of the relaxation exponent ' $n$ ' in the *Gel Equation* [6,7]

$$\tau(t) = S \int_{-\infty}^t (t-t')^{-n} \dot{\gamma}(t') dt', \quad 0 < n < 1$$

which describes the linear viscoelastic behavior at the gel point. The relaxation exponent ' $n$ ' is obtained from the value of  $\tan \delta$  at the gel point using the relation

$$\tan \delta(\omega_i) = \tan(n\pi/2)$$



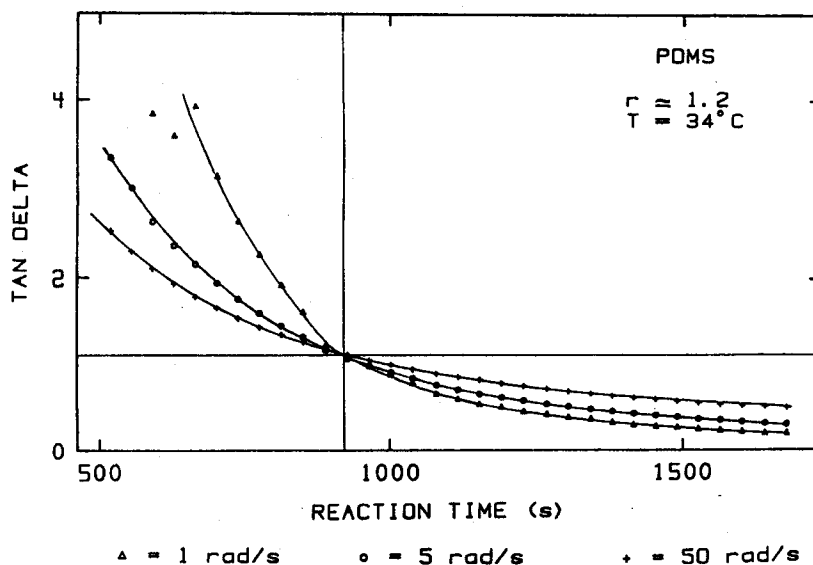


Fig. 7. The loss tangent  $\tan \delta$  measured simultaneously at three different frequencies in a small amplitude oscillatory shear experiment on a crosslinking PDMS system. At the gel point,  $\tan \delta$  is independent of frequency and the curves pass through a single point. Here, parallel plate geometry was used.

In this case again, the total strain has to be kept well within linear viscoelastic limits and the stress is kept low to avoid any chance of breaking the delicate network in its intermediate stages.

Preliminary experiments using FTMS with three frequencies have been performed successfully and the data are shown in Fig. 7. This technique not only enables accurate measurement of the time to gel, but also gives complete characterization of the polymer at the gel point.

### Conclusions

Experiments show that the proposed method is able to measure the dynamic mechanical behavior of polymeric materials. The data from the FTMS method agree well with conventional measurements on stable polymer melts. The experimental time is reduced through the FTMS procedure.

The major advantage of the proposed method compared to earlier applications of the Fourier transformation of mechanical measurements lies in its accuracy. This improved accuracy is based on the fact that we do not probe the entire relaxation spectrum but only a small number of relaxation modes. For each mode, we can select the strain amplitude which gives the highest signal to noise ratio. The sum of strain amplitudes is kept below the critical strain to remain in the linear viscoelastic range. A material with a large

critical strain allows the measurement of many relaxation modes simultaneously, while a more sensitive material might limit the number of modes to two or three.

FTMS has its specific merits for materials with transient structure. The experimental time  $t_e = 2\pi/\omega_f$  is determined by the fundamental frequency. Higher relaxation modes do not require additional time since they are measured simultaneously. The lowest fundamental frequency possible is given by the stability criterion,

$$\frac{2\pi}{\omega_{f,\min}} \frac{1}{G} \frac{\partial G}{\partial t} \ll 1$$

where  $G$  stands symbolically for a mechanical equilibrium property of the changing sample. Sample changes are negligible if the stability criterion is valid for the rheological experiment. Lower fundamental frequencies would give meaningless experimental results since stress relaxation and structural change interfere in some unknown way. The longest measurable relaxation time  $\lambda$  is in the order of  $2\pi/\omega_{f,\min}$ . Longer relaxation times of the changing sample are not accessible.

FTMS is especially useful for determining the instant of gelation in crosslinking polymers. At the gel point, these materials were found to exhibit power-law relaxation, i.e. their loss tangent  $\tan \delta = G''/G'$  is constant over a wide range of frequency. FTMS allows measurement of  $G''/G'$  simultaneously at several frequencies. The gel point of a crosslinking polymer is therefore found when  $G''/G'$  becomes independent of frequency. This was demonstrated on a crosslinking PDMS sample.

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