Journal of Thermal Analysis, Vol. 40 (1993) 1313-1320

MATHEMATICAL APPROACH FOR THE DYNAMIC TESTING TECHNIQUE

N. Nakamura, H. Katoh and Y. Teramoto

SEIKO INSTRUMENTS INC., SCIENTIFIC INSTRUMENTS DIVISION 36-1 TAKENOSHITA, OYAMA-CHO, SUNTO-GUN, SHIZUOKA, 410-13 JAPAN

In dealing with phenomena which show a linear response such as viscoelastic or dielectric properties, measurements are carried out by observing the relationship between the stimulus applied to the sample and the response from the sample. Since the Fourier analysis technique is effective in obtaining this relationship, two types of circuitries based on Fourier analysis have been created. Both DMA and dielectric measurement were used to evaluate these circuitries. Results were satisfactory, especially with respect to tanδ precision.

Keywords: DMA, dynamic testing technique, Fourier analysis technique

Introduction

Traditional thermal analysis techniques such as DTA, DSC, TG or TMA detect the signal as a direct current and output it as a real number.

In contrast a relatively new technique which uses an alternative current signal, i.e. DMA, is being used increasingly. In this method, a complex number or vector is often used for presenting the measurement result. This method is effective in analysing phenomena which respond linearly, and requires measurement of both amplitude and phase relationship between stimulus and response.

Circuitries based on Fourier analysis have been created for use as such a correlation analyser. The structure of the circuitries and results of their application in dynamic mechanical analysis (DMA) and dielectric measurement are described in the following sections.

Theory

When applying a sufficiently small external force (electric field) to the sample, the relationship between force (electric field) and displacement (electric displacement) obeys the following equation [1].

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

$$D(t) - D^{eq} = X^{\infty} \cdot F(t) + \int_{-\infty}^{t} \phi\,(t - t') \cdot F(t')\,\mathrm{d}t' \tag{1}$$

t, t': time; D : displacement (electric displacement); F: external force (electric field); X: compliance (capacitance); ϕ: time-dependent coefficient; D^{eq}: displacement at equilibrium; X^{∞}: X at $t = \infty$

Decomposition of the force and displacement to the superposition of the harmonic oscillators are given by the following Fourier transformations.

$$\hat{D}\,(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} [D\,(t) - D^{eq}\,] \cdot e^{i\omega t} \mathrm{d}t \tag{2}$$

$$\hat{F}\,(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(t) \cdot e^{i\omega t} \mathrm{d}t \tag{3}$$

Using these relationships, the following equation is derived from Eq. (1).

$$X(\omega) = \frac{\hat{D}(\omega)}{\hat{F}(\omega)} \tag{4}$$

where

$$X\,(\omega) = X^{\infty} + \int_{0}^{\infty} \phi(t) \cdot e^{i\omega t} \mathrm{d}t \tag{5}$$

Here, $X(\omega)$ signifies the complex compliance or the complex capacitance, depending on the associated force type (mechanical force or electric field).

For simplicity, it will be assumed that $F(t)$ is a function with a period of $2\pi/\omega0$. The following equation shows one example.

$$F(t) = F_o \sin\,(\omega_o\, t) \tag{6}$$

Since Eq. (1) is a linear equation in both $F(t)$ and $D(t)$, $D(t)$ also has a period of $2\pi/\omega0$ under this assumption. Equation (4) is then rewritten in the following simplified form by considering the orthogonality of each $\exp(i\omega t)$.

$$X(\omega_o) = \frac{\oint D(t) e^{i\omega_o t}\,\mathrm{d}t}{\oint F(t) e^{i\omega_o t} \mathrm{d}t} = \frac{\oint D(t) \cos\,(\omega_o t) \mathrm{d}t + i \oint D(t) \sin\,(\omega_o t)\,\mathrm{d}t}{\oint F(t) \cos\,(\omega_o t) \mathrm{d}t + i \oint F(t) \sin\,(\omega_o t)\,\mathrm{d}t} \tag{7}$$

Here $\oint$ denotes the periodical integration.

Experimental

Two types of discrete Fourier transformation circuitry were created as a direct application of Eq. (7). One is a digital processing type [2, 3] which covers the frequency range 0.01 to 100 Hz and the other is an analog type with a range of 10 Hz to 100 kHz. The former was incorporated in the Seiko Instruments DMS 110, dual cantilever type DMA [4], and the latter was incorporated in the Seiko Instruments DES 100 dielectric analyser to evaluate the performance of these circuitries.

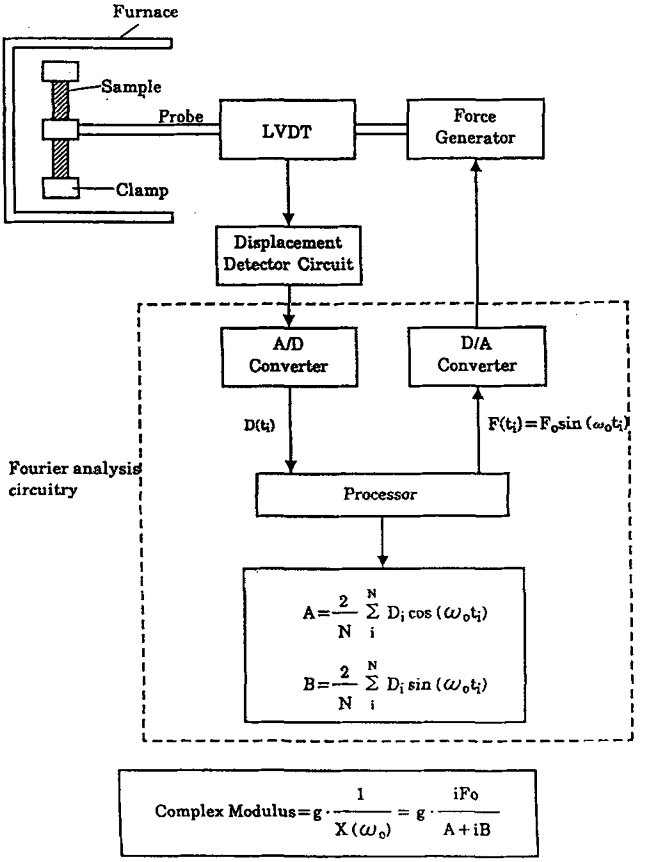
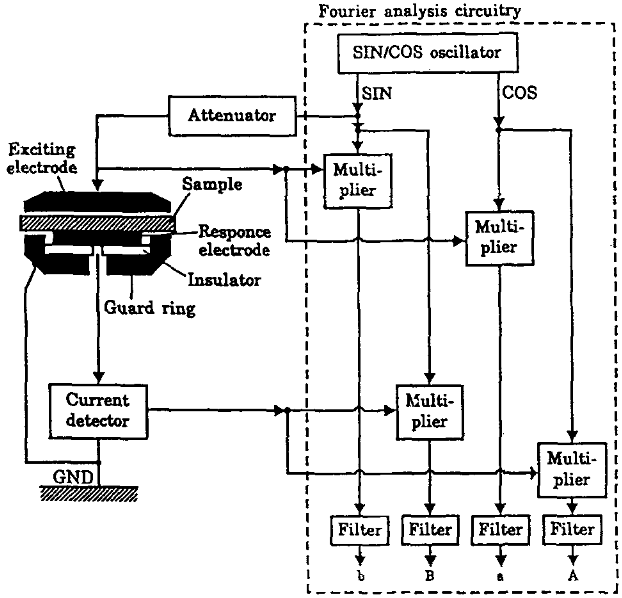


Fig. 1 Schematic diagram of the DMS 110 with FT circuitry

Figure 1 shows a schematic diagram of the DMS 110. When the sinusoidal force produced by processor, D/A converter, and force generator is applied to the sample, it deforms sinusoidally. The deformation is then detected by the LVDT as the displacement of the probe and this signal is sent to the processor through the

A/D converter. The Fourier analysis calculation for the deformation signal is carried out in the processor. The complex modulus is then obtained as shown in Fig. 1, where g denotes the coefficient depending on the sample geometry.



$$A = \frac{\pi}{\omega_0} \int I(t) \cos(\omega_0 t)\, dt \qquad a = \frac{\pi}{\omega_0} \int V(t) \cos(\omega_0 t)\, dt$$

$$B = \frac{\pi}{\omega_0} \int I(t) \sin(\omega_0 t)\, dt \qquad b = \frac{\pi}{\omega_0} \int V(t) \sin(\omega_0 t)\, dt$$

$$\text{Complex dielectric constant} = g \cdot X(\omega_0) = \frac{g}{i\omega\varepsilon_0} \; \frac{A+iB}{a+ib}$$

Fig. 2 Schematic diagram of the DES 100 with FT circuitry

A schematic diagram of the DES 100 is shown in Fig. 2. The sine wave function output from the SIN/COS oscillator is sent to the exciting electrode through the attenuator. The charge displacement induced in the sample is then detected as the displacement current between the response electrode and the earth. Both input voltage and the output current are multiplied by the synchronized sine and cosine waves, respectively. The complex dielectric constant is then expressed as shown in Fig. 2, where g also denotes the geometric coefficient.

PMMA was used for both measurements. In the DMA experiment, a comparison between this Fourier analysis circuitry (which detects peaks and zero-intercepts) was made using two sample geometries at 1 Hz. In the dielectric measurement, the precision of permittivity and loss tangent were investigated at room temperature using PMMA with approximately 0.2 mm thickness. The precision was determined using an average of five data. Finally, the β'-transition was measured using both instruments at a heating rate of 3 deg·min^{-1}.

Results and discussion

Table 1 shows a performance comparison of two DMS 110 modules, one with conventional circuitry, the other with digital processing circuitry. A PMMA sample with 20 mm effective length and 10 mm width was used in both cases.

Table 1 Comparison of signal precision

Sample thickness		Conventional	FT circuitry
1.5mm	Modulus precision	0.19%	0.06%
	tan δ precision	0.00038	0.00007
3 mm	Modulus precision	Could not be	0.16%
	tan δ precision	measured	0.00019

Table 2 Signal precision with the DES100

	10 Hz	100 Hz	1 kHz	10 kHz	100 kHz
Permittivity precision / %	0.013	0.013	0.013	0.013	0.013
tan δ precision (x10^{-5})	2.9	1.9	0.9	1.2	1.5

These results show that use of this method significantly reduces the noise level, especially in the case of the tanδ signal. This is because the Fourier analysis circuitry works not only as the amplitude and phase detector but also as an ideal monochromatic filter. This function as an ideal filter is more important in measuring the dielectric constant (where the capacitance is actually measured by detecting the displacement current rather than charge) because it is proportional not only to the electrical field but to the frequency used. Therefore, a contribution from the higher harmonic noise inevitably contained in the sinusoidal electric field always tends to be emphasized, thus reducing measurement precision.

The DES 100 with the analog circuitry had the following capability at room temperature (Table 2).

PMMA was measured to check the capability of both apparatus when the temperature is scanned. Figures 3 and 4 show DMA results at 1 Hz and dielectric measurements at 10, 100, 1 k, and 100 kHz. In addition to the α and β-transition, which associates the relaxation of micro-Brownian motion of the main chain and the rotational motion of the ester side group, a small transition is observed in a

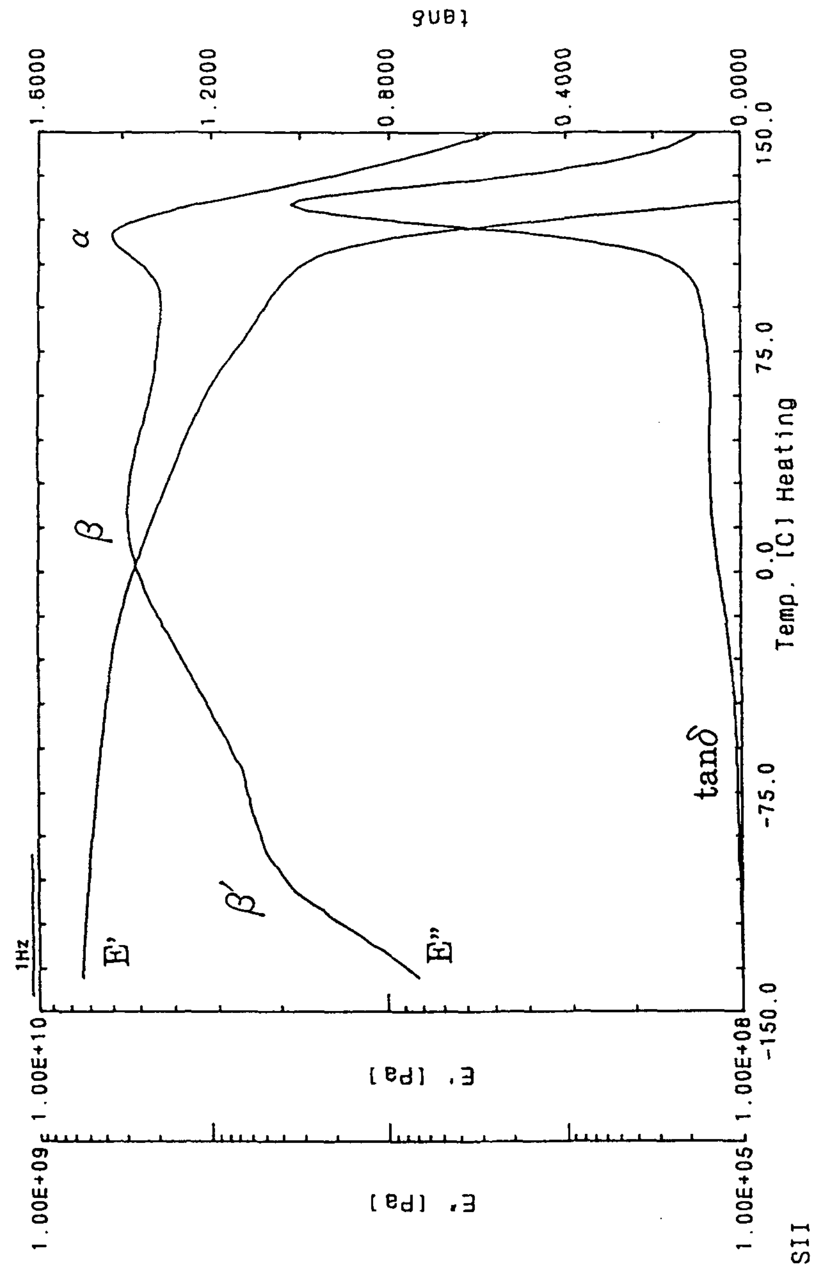


Fig. 3 PMMA data using the DMS 110

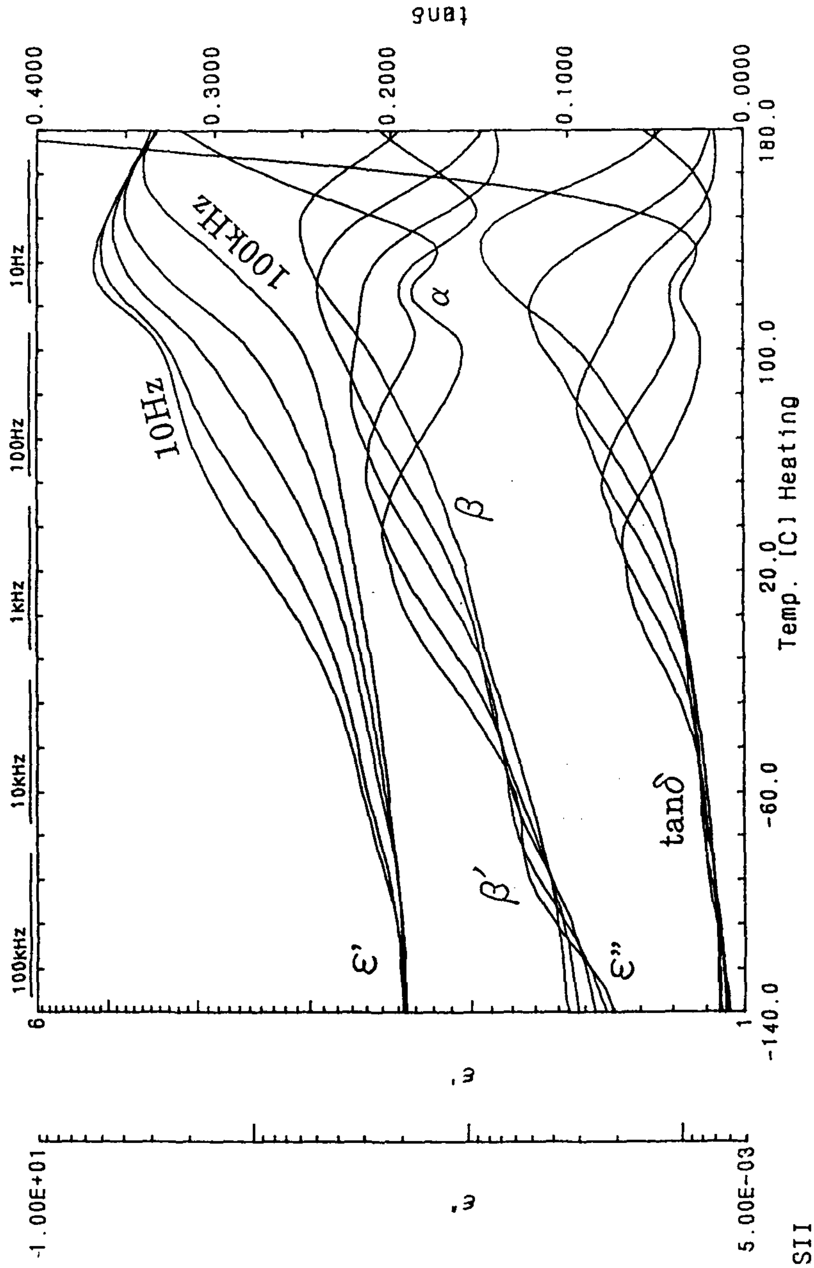


Fig. 4 PMMA data using the DES 100

lower temperature region in each case. This is considered to be the β'-transition which corresponds to a side chain relaxation affected by the low-molecular-weight content in the sample [5].

Conclusions

Both digital and analog circuitries based on a discrete Fourier transformation have been created for use in dynamic TA testing. These circuitries work simultaneously as both amplitude and phase detector and as an idealized band pass filter.

The digital circuitry has a frequency range of 0.01 to 100 Hz and improves the capability of the DMA apparatus. In comparison with measurements using conventional circuitry, the tanδ precision in DMA was improved more than five times and the measurable high modulus range was enhanced by one decade because of the improvement of the low-strain amplitude detection limit (0.5 μm).

The analog circuitry covers the range 10 Hz to 100 kHz. Using this circuitry in the dielectric measurement apparatus, tanδ precision was confirmed to be better than 0.00005 (using an average of five data points).

It is anticipated that the methodology used in this paper can also be applied in other types of measurement such as AC calorimetry and magnetic susceptibility.

References

1 N. Hashizume, Basis of modern physics, Iwanami, Tokyo 1978, p..297.
2 S. Koyasu, H. Katoh, Y. Ichimura, N. Nakamura and Y. Teramoto, Proc. of 27th Conference of the Society of Calorimetry and Thermal Analysis, Japan 1991. p. 132.
3 W. Sichina, American Laboratory, 1 (1992) 44.
4 N. Matsumori, J. Penn, N. Nakamura and Y. Teramoto, Proc. of 18th NATAS, San Diego 1989, p. 758.
5 Y. Wada, Physical properties of polymeric solids, Baifukan, Japan, 1971.

Zusammenfassung — Bei der Arbeit mit Erscheinungen, die wie z.B. viskoelastische oder dielektrische Eigenschaften eine lineare Reaktion zeigen, wurden Messungen durch Beobachtung der Beziehung zwischen der auf die Probe angewendeten Aktion und der von der Probe gezeigten Reaktion durchgeführt. Da die Fourier-Analyse eine effektive Technik zur Ermittlung dieser Beziehung ist, wurden auf der Grundlage der Fourier-Analyse zwei Typen von Schemen geschaffen. Sowohl DMA als auch dielektrische Messungen wurden zur Entwicklung dieser Schemen verwendet. Die Resultate waren zufriedenstellend, insbesondere mit Hinblick auf die Genauigkeit von tanδ.