A high frequency resonant method for the determination of the dynamic mechanical properties of solid polymers

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A resonant method for the determination of the dynamic properties of solid polymers is presented. A composite oscillator driven by a piezoelectric crystal, in longitudinal oscillations and at a frequency of the order of 50 kHz, is employed. The changes in the storage and loss moduli, the loss tangent and the attenuation coefficient for the material, as a function of temperature, can be obtained from the changes in the resonant frequency, the width of the resonance peak and the transference function of the composite oscillator. Finally, some data obtained in specimens of vulcanized rubber are presented, to illustrate the applicability of the method.

(Keywords: dynamic mechanical properties; composites; composite oscillator)

INTRODUCTION

The literature describes several methods for the measurement of the dynamic properties of solid polymers[1], which differ according to the frequencies employed. A torsion pendulum working either in free or forced vibrations is normally used at low frequencies (~ 1 Hz); for frequencies up to 10^3 Hz, free vibrations[2], non-resonant forced vibrations[3-6] and resonant forced vibration methods[7,8] are employed. At higher frequencies, above 10^4 Hz, a method of propagation of continuous waves has been used[9,10], where a piezoelectric crystal was employed as a driver to vibrate a polymeric material. Methods that propagate pulses in polymeric materials, at frequencies above 10^5 Hz[11,12] are also found in the literature. Ivey *et al.*[13], for example, have estimated tan δ and the glass transition temperature (T_g) in GR-S, butyl and Hevea rubbers by using a device that propagates pressure waves in the material. Finally, in a more recent work, Jang and Zhu[14] have obtained dynamic properties and T_g through the technique of mechanical impedance analysis.

It is the pupose of this paper to present a resonant technique for the measurement of the dynamic properties of polymeric materials, at high frequencies, by using a resonant method based on the principle of the composite oscillator developed by Quimby[15] and Read[16]. This device has been used in metals[17] but, to our knowledge, has not been employed to study the dynamic behaviour of polymeric solids, where special features appear due to the high damping presented by these materials. Consequently, the mechanical and electrical response of the composite oscillator will be studied in detail, to show how the dynamic behaviour of the material can be extracted from the measured response of the composite oscillator. Finally, some results obtained in specimens of vulcanized natural rubber will be presented, to illustrate the procedure and to show that reliable parameters are obtained for the material.

THEORY

The principle of the measuring device is based on the composite oscillator, shown in *Figure 1*. The composite oscillator involves the excitation of specimens by a piezoelectric crystal which is cut to resonate at a specific frequency, typically in the range 20–200 kHz for longitudinal vibration. The specimen is joined to the crystal with an appropriate bonding agent and it is cut with a length equal to a half wavelength at the specified resonant frequency (of the order of 50 kHz in our case). It is possible to apply to the composite oscillator the theory of longitudinal vibrations in a viscous medium[16]. The movement of each component of the system can be described by[15]:

$$\rho \frac{d^2u}{dt^2} = E' \frac{d^2u}{dx^2} + \frac{4}{3}(1+\sigma)\eta \frac{d^3u}{dx^2\,dt} \tag{1}$$

where ρ is the density of the material, u is the displacement, E' is the storage modulus, σ is Poisson's

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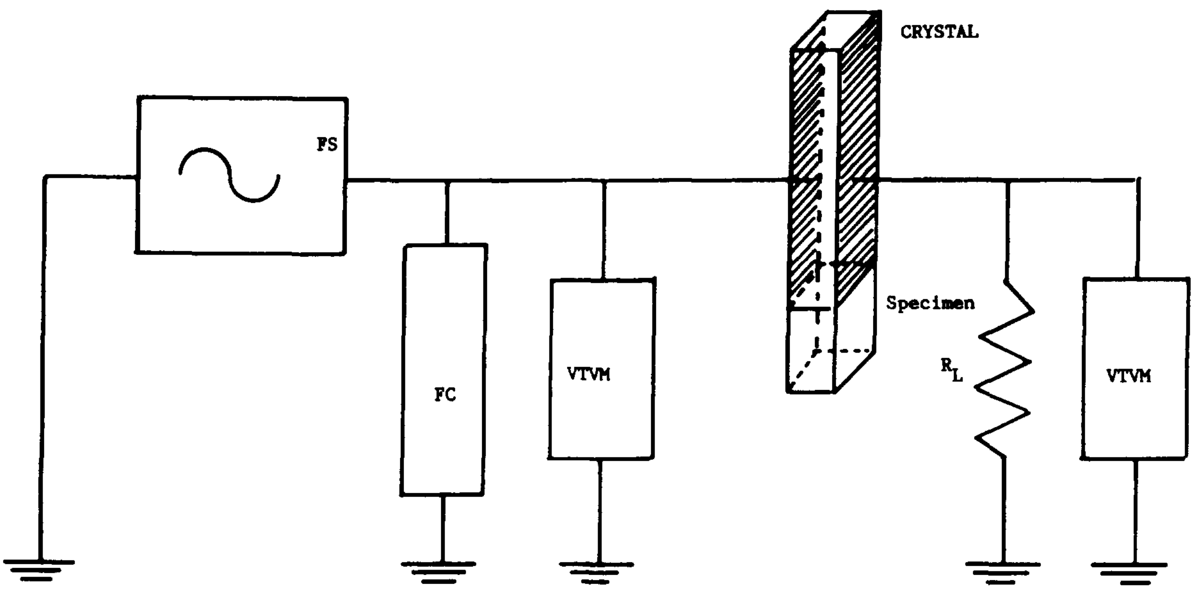

Figure 1 Schematic diagram of the composite oscillator: FS, frequency synthesizer; FC, frequency counter; VTVM, vacuum tube voltmeter; R_L, loading resistance

ratio, η is the viscosity, t is time and x is the variable associated with the displacement in the direction of propagation. The following boundary conditions apply: (1) there exists a physical displacement node at the centre of the piezoelectric crystal; (2) the condition of resonance in both components implies displacement maxima at both ends of the composite.

These two boundary conditions lead to a solution for equation (1) of the form

$$u_s = 2A_s \exp(i\omega t) \sinh[(\alpha_s + ik_s)x] \qquad (2)$$

where A_s is the maximum displacement, $\omega = 2\pi f$ with f the applied frequency, α_s is the acoustic attenuation coefficient which is proportional to η and $k_s = \omega/v_s$ where v_s is the phase velocity. The subscript s refers to the specimen. A similar equation would be obtained for the mechanical response of the crystal.

Substituting equation (2) into equation (1) leads to

$$E'_s = (2L_s f_s)^2 \rho_s \frac{(1 - r^2)}{(1 + r^2)^2} \qquad (3)$$

with

$$r = \alpha_s \lambda_s / 2\pi \qquad (4)$$

and

$$k_s = 2\pi/\lambda_s \qquad (5)$$

where L_s is the length of the specimen at resonance ($2L_s = \lambda_s$) and λ_s is the wavelength. If $r^2 \ll 1$, equation (3) reduces to the known expression:

$$E'_s = v_s^2 \rho_s = (2L_s f_s)^2 \rho_s \qquad (6)$$

Then, if the temperature dependence of f_s is known, equations (3) and (6) give the temperature dependence of E'_s. Finally, it can be shown that E'_s and $\tan \delta_s$ are related by:

$$2f_s L_s = (E'_s/\rho_s)^{1/2}\left(1 - \frac{\tan^2 \delta_s}{8}\right) \qquad (7)$$

In the case where the attenuation coefficient or the specimen are small, so that $\exp(\alpha_s x) \simeq 1$, equation (1) can be rewritten as

$$m\frac{d^2\varepsilon}{dt^2} + \eta'\frac{d\varepsilon}{dt} + E'_s\varepsilon = 0 \qquad (8)$$

where m is the mass, $\varepsilon = du/dx$ is the longitudinal strain and $\eta' = \frac{4}{3}(1 + \sigma)\eta$. It should be pointed out that equation (8) is analogous to the differential equation that describes the behaviour of the polymer through a Voigt model, including inertial effects[18]. The viscoelastic behaviour of the material, however, is generally not described by a single Voigt element but by several elements connected in series, relaxing independently.

The electrical equivalent of a piezoelectric crystal is a series RLC circuit[19], which is valid also for a small polymeric specimen since on identifying the inductance L with the mass, the resistance R with η' and the current I with ε, the equation for Voigt's model, equation (8), converts to the differential equation for a series RLC circuit. Then, if the polymer is represented by several elements connected in series, the electrical equivalent will be a set of series RLC circuits, which will be equivalent to a unique RLC circuit where $L = \sum_i L_i$, $R = \sum_i R_i$ and $l/C = \sum_i l/C_i$.

In summary, the electrical equivalent of the composite oscillator of *Figure 1* is the electrical circuit shown in *Figure 2*, where the subscripts c and s refer to the crystal and the specimen, respectively. The capacities C_o and C_p represent the influence of the mounting device on the crystal and the connecting leads, respectively. Moreover, Z_L represents the impedance of the measuring system and V_i and V_o are the input and output voltages, respectively.

The measured transference function, that is, the ratio V_o/V_i, is given by:

$$V_o/V_i = Z_L\left(\frac{1}{Z^2} + \omega^2 C_t^2\right)^{1/2} \qquad (9)$$

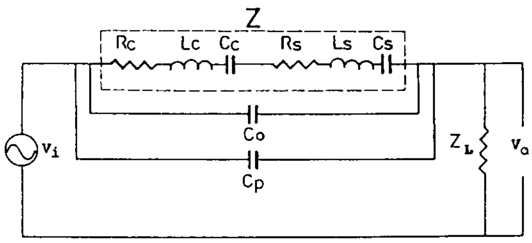

Figure 2 Equivalent electrical circuit for the composite oscillator in *Figure 1*. V_i and V_o represent the input and output voltages, respectively, Z is the impedance of the composite, and C_o and C_p represent the capacitances of the mounting device for the crystal and the connecting leads, respectively

where Z is the impedance of the composite oscillator and

$$C_t = C_o + C_p \qquad (10)$$

Finally, on taking into account the electrical equivalent of the composite oscillator it can be shown that at resonance[20]:

$$m_t f_t \tan\delta_t = m_s f_s \tan\delta_s + m_c f_c \tan\delta_c \qquad (11)$$

and

$$m_t f_t^2 = m_s f_s^2 + m_c f_c^2 \qquad (12)$$

EXPERIMENTAL

The composite oscillator was located in a vacuum chamber which allowed measurements in vacuum or inert atmosphere[21]. The vacuum chamber was immersed in a Dewar that contained the refrigerating medium (liquid nitrogen or dry ice and alcohol). The temperature of the composite was easily changed by a small electric furnace located in the vacuum chamber. The temperature was sensed with two thermocouples near the ends of the specimen and stabilized within ±1 K. Argon transfer gas was added to the system from a valve placed between the mechanical pump and the vacuum chamber.

The resonant frequency and the damping of the crystal were measured, as a function of temperature, before attaching the specimen. Once $\tan\delta_c$ and f_c are known, f_s and $\tan\delta_s$ can be determined from the measured f_t and $\tan\delta_t$ values, by using equations (11) and (12). The output of the system, for a given input voltage from the oscillator, is sensed with a vacuum tube voltmeter through the loading resistance R_L (*Figure 1*). The resonant frequency of the composite, f_t, is the frequency that gives maximum output on R_L at each temperature and $\tan\delta_t$ is given by:

$$\tan\delta_t = \Delta f/f_t \qquad (13)$$

where Δf is the difference between frequencies at -3 dB from the output of the system at resonance.

The specimens were prepared from natural rubber with 65 parts of carbon black and 5 parts of sulphur, per hundred parts of rubber, and vulcanized at 428 K up to different curing levels (80, 100 and 140%). The lengths of the specimens were adjusted, at room temperature, in such a way that the resonant frequency of the composite did not differ >10% from the resonant frequency of the crystal.

Measurements of the transference function and $\tan\delta_t$ were performed at room temperature and the resonant frequency of the composite was measured on heating, between 193 K and 323 K, in steps of 5 K. Finally, all measurements were made at very low strain amplitudes (of the order of 10^{-7}).

RESULTS

Figure 3 shows the variation of the resonant frequency of the composite with temperature, for the rubber specimen cured up to 140%. An abrupt change of frequency is observed near 240 K and since the frequency of the crystal does not show important changes in the temperature region covered by *Figure 3*, the temperature dependence of f_t reflects mainly the changes produced in the mechanical response of the elastomer. As will be shown later, the attenuation coefficient for the material is of the order of 0.63, so that $r^2 = 0.04 \ll 1$ and Young's storage modulus is given by equation (6). Then, equations (6) and (12) can be used to determine E_s' from the measured f_t against temperature curve. The storage modulus against temperature data obtained in this way are shown in *Figure 4* (subscript s has been omitted). Here also a

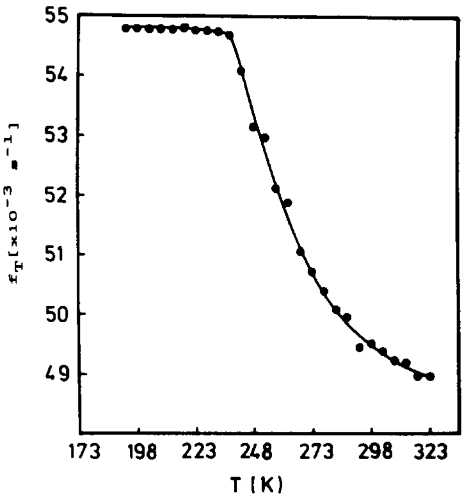

Figure 3 Resonant frequency against temperature for the composite with a specimen of vulcanized rubber cured up to 140%

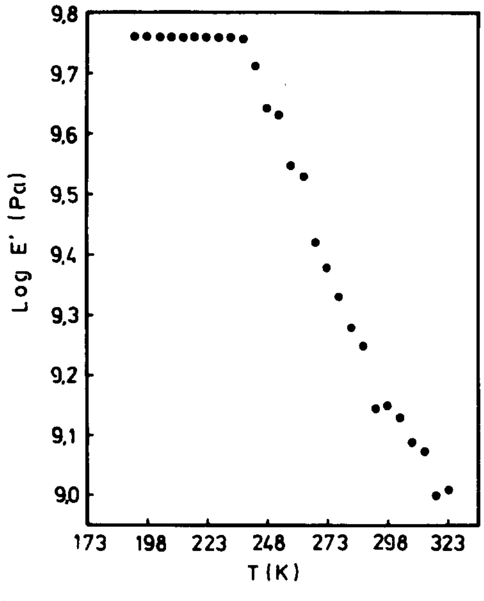

Figure 4 Young's storage modulus against temperature for the vulcanized rubber specimen cured up to 140%

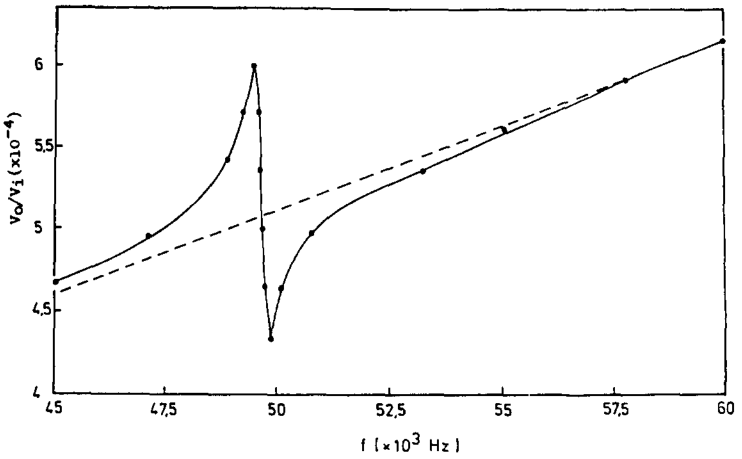

Figure 5 Transference function against frequency (solid curve), at 298 K, for the rubber specimen cured up to 140%. The broken line represents the contributions of C_o and C_p from *Figure 2*

large drop in the modulus is observed near 240 K. If an attempt is made to measure tan δ_t by using equation (13), to extract tan δ_s by using equation (11), problems are encountered due to the high damping presented by the elastomers at room temperature. In fact, a high background signal was present in the output voltage and, consequently, the transference function of the composite was measured, to extract tan δ_t. The typical form for the transference function of the composite, at room temperature, is shown in *Figure 5*, which corresponds to the specimen cured up to 140%. A maximum is obtained at the resonant frequency but V_o/V_i does not go to zero at the antiresonant frequency. This is due to the fact that there are two contributions to the total transference function: the contribution due to the composite oscillator plus the transference function of the capacities C_o and C_p, shown in *Figure 2*. In fact, equation (9) can be written as:

$$V_o/V_i = Z_L\left[\left(\frac{1}{Z} + \omega C_t\right)^2 - 2(\omega C_t/Z)\right]^{1/2} \qquad (14)$$

and, on assuming that

$$(2\omega C_t/Z) \ll \left(\frac{1}{Z} + \omega C_t\right)^2 \qquad (15)$$

equation (14) reduces to

$$V_o/V_i = Z_L\left(\frac{1}{Z} + \omega C_t\right) \qquad (16)$$

which means that at resonance $(Z = R_c + R_s)$

$$Z_L/(R_c + R_s) \simeq \frac{V_o}{V_i} - Z_L\omega C_t \qquad (17)$$

where $Z_L\omega C_t$ is the transference produced by the capacitors in parallel with the composite oscillator. This transference can be obtained far from resonance since $Z \to \infty$ and equation (16) simplifies to:

$$V_o/V_i = Z_L\omega C_t \qquad (18)$$

at frequencies higher than the resonant frequency. Since $Z_L = R_L$, equation (18) shows that the contribution to the total transference function due to C_t changes linearly with the frequency, as indicated by the broken line in *Figure 5*. Then, on subtracting this contribution, it is possible to obtain the transference function of the composite oscillator. This is illustrated by the curves shown in *Figure 6*, where the net transference functions of the composite, at room temperature, for the three specimens, are indicated.

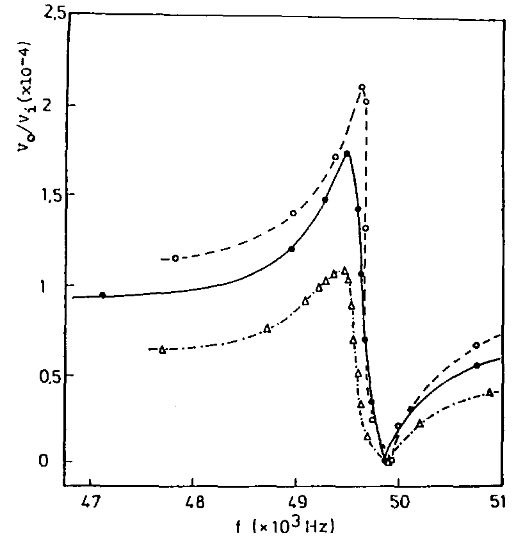

Figure 6 Net transference functions for the composite, at 298 K, for the three specimens: (○) 80% curring; (●) 140% curing; (△) 100% curing

It should be pointed out that the term $Z_L\omega C_t$, which for the case of elastomers is comparable to the contribution of the composite, is determined by the experimental set-up and is independent of the specimens studied. This value is known and does not differ much with the equipment used. C_p can be kept always below 5 pF and for the quartz crystals used $R_c = 10^3\ \Omega$ and $C_o < 5$ pF. Furthermore, for the equipment used: $C_o = 3.3$ pF, $C_p = 4.7$ pF and $R_s = 16^6\ \Omega$, indicating that equation (15) is satisfied.

Once the transference function of the composite is known, tan δ_t can be obtained from the transference functions shown in *Figure 6* by using equation (13). Moreover, equations (6), (11) and (12) and the

Table 1 Dynamic moduli and loss tangent, at 298 K, obtained in the vulcanized rubber specimens with different curing levels

Curing (%)	L_s (cm)	m_s (g)	f_s (kHz)	E'_s (GPa)	E''_s (GPa)	$\tan\delta_s$	$\tan\delta_t$	$\tan\delta_t$ (elec.)
80	1.10	0.240	46 725	1.02	0.15	0.15	0.10	0.096
100	1.45	0.348	46 349	2.10	0.35	0.17	0.16	0.146
140	1.20	0.288	45 847	1.42	0.21	0.15	0.12	0.117

relationship:

$$\tan\delta_s = E''_s/E'_s \tag{19}$$

where E''_s is the loss modulus, allow a calculation of the other parameters for the specimen. The results obtained through this procedure are shown in *Table 1*. The composite oscillator can also be used to obtain the attenuation coefficient for the material. In fact, the factor of merit, Q_t, of the composite is defined by:

$$\begin{aligned} Q_t &= 2\pi W^t_{st}/W^t_{diss} = 2\pi(W^c_{st} + W^s_{st})/(W^c_{diss} + W^e_{diss}) \\ &= \tan\delta_t \end{aligned} \tag{20}$$

where W_{st} and W_{diss} indicate the stored and dissipated energy per cycle, respectively. The superscripts c and s indicate the corresponding quantities in each component of the composite. On calculating the corresponding energies for each component, taking into account that displacement maxima are present at the extremes of each of them, and that the viscosity of the crystal is very low, that is, $E''_c = 0$, equation (20) can be written as:

$$\begin{aligned} Q_t = \frac{E'_s}{E''_s} &+ 2\pi^2 E'_c/\alpha_s E''_s L_c[2 + (k_s/\alpha_s)^2] \\ &\times [1 + \exp(-2\alpha_s L_s)] \end{aligned} \tag{21}$$

where L_c is the length of the crystal. Then, α_s can be obtained by fitting equation (21) to the experimental data, which is a complicated procedure. If the specimen is large, however, in such a way that the term $\exp(\alpha_s x)$ in equation (2) is higher than one it means that above a given length of specimen, L_{sf}, the elastic waves are completely attenuated and, consequently, there are no more changes in the loss of the composite, leading to a constant $\tan\delta_t$ for $L_s > L_{sf}$. This effect is illustrated in *Figure 7* for the specimen cured 80%, measured at room temperature. This curve was obtained by the following procedure. A specimen with a length equal to several half wavelengths was joined to the piezoelectric crystal. The transference function was measured and $\tan\delta_t$ was obtained by using equation (13); $(\tan\delta_t)^{-1}$ gives Q_t directly. The specimen was shortened by segments of a half wavelength in successive steps and the transference function and $\tan\delta_t$ were measured at each step, until the specimen had a length equal to one half wavelength. The measurements are indicated by the solid circles in *Figure 7*. It can be noticed that for $L_s > 3$ cm, Q_t remains constant within experimental error. This procedure was used due to the fact that the composite system operates only in resonance. From *Figure 7* it can be concluded that: (1) the reciprocal of α_s has a maximum value of three times the length needed for the fundamental resonance, that is,

$$(k_s/\alpha_s) \simeq 3\pi$$

and (2) $2\alpha_s L_c \rho_c/\rho_s \gg 1$, where $\rho_c = 2.28\ \mathrm{g\,cm^{-3}}$ and $\rho_s = 1.17\ \mathrm{g\,cm^{-3}}$. On taking into account these two approximations, equation (21) can be written as:

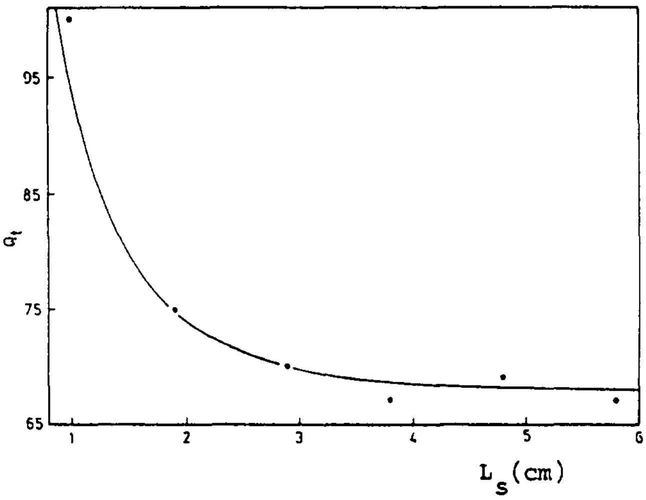

Figure 7 Quality factor against specimen length, at 298 K, for a rubber specimen cured up to 80%

$$Q_t = (E'_s/E''_s)2\alpha_s L_c(\rho_c/\rho_s)[1 - \exp(-2\alpha_s L_s)]^{-1} \tag{22}$$

This equation cannot be fitted directly to the experimental data since E'_{ss}/E''_s is not known. The fitting can be performed, however, by considering the asymptotic value of equation (22), that is, the value of Q_t when $L_s \rightarrow \infty$, given by:

$$Q_{tf} = (E'_s/E''_s)2\alpha_s L_c(\rho_c/\rho_s) = 68 \tag{23}$$

Then, combining equations (22) and (23) leads to:

$$\ln[1 - (Q_{tf}/Q_t)] = -2\alpha_s L_s \tag{24}$$

The fitting of the experimental data of *Figure 7* to this equation gives

$$\alpha_s = 0.63 \tag{25}$$

with a correlation coefficient of 0.9991. The curve described by equation (24) is indicated by the curve in *Figure 7*.

Once α_s is known, E'_s can be calculated by using equation (3) and $\tan\delta_s$ by using equation (23), leading to

$$E'_s = 1.02\ \text{GPa} \qquad \tan\delta_s = 0.19 \tag{26}$$

The value of E'_s coincides exactly with the value given in *Table 1* for the same material, as expected, since $r^2 \ll 1$. Tan δ_s does not differ much from the value reported in *Table 1*, on taking into account the experimental errors and the approximations made. Finally, $\tan\delta_t$ can also be obtained from the electrical analogue of the composite oscillator, shown in *Figure 2*. In fact[21]

$$\tan\delta_t = \omega_t R_t C_{cs} \tag{27}$$

with $R_t = R_c + R_s$ and $C_{cs} = C_s C_c/(C_c + C_s)$. In addition,

$C_{cs} \simeq C_c$, ω_t is measured directly and R_t is obtained from the relationship:

$$R_t = (V_i - V_o)/\{(V_o/R_L)^2 - [(V_i - V_o)\omega_t C_t]^2\}^{1/2} \quad (28)$$

The values calculated for $\tan\delta_t$ by using equations (27) and (28) are indicated by $\tan\delta_t$(elec.) in *Table 1*. It is seen that good agreement is obtained with the values calculated from the transference function.

DISCUSSION

The values of E' and E'' given in *Table 1* are similar to those obtained by applying the time–temperature superposition to the data measured at low frequencies in vulcanized rubber[22] and the values C_1 and C_2, for the Williams–Landel–Ferry equation, reported on page 277 in reference 1. It should be pointed out, however, that non-linear effects have been observed in the dynamic mechanical behaviour of elastomers[23], that is, the dynamic moduli and the loss tangent are amplitude-dependent, reaching a plateau at low strain amplitudes. Consequently, a direct comparison of the data reported in *Table 1* with those given in the literature should be performed, in principle, only for experiments carried out at very low strains. Arai and Ferry[24,25], in fact, reported G', G'' and $\tan\delta$ data for carbon black filled styrene–butadiene rubbers, both in cured and uncured specimens. The experiments were performed with a torsion pendulum ($\sim$1 Hz) operating at very low strain amplitudes. The following values are obtained, at 50 kHz, from the master curves reported for 298 K in cured specimens:

$$G' = 2.0 \text{ GPa} \qquad G'' = 0.25 \text{ GPa} \qquad \tan\delta = 0.20$$

These values are of the order of those shown in *Table 1* for E'_s, E''_s and $\tan\delta_s$. It should be mentioned, in any case, that these are only order of magnitude estimates since the time–temperature superposition is not strictly valid[26].

E' varies with curing as expected since as vulcanization advances from 80 to 100% more sulphur links are formed and the storage modulus increases. Between 100 and 140% the process reverses and some sulphur links are destroyed inducing a decrease in the modulus, which is the trend[27] observed in *Table 1* for E'_s. In principle, the composite oscillator can be used to simply determine the loss tangent and the resonant frequency of the specimen by using equations (10) and (11). This is not the case, however, for hard polymeric solids and metals where the damping is very low. In fact, in materials with high damping, that is, with high R_s, the transference of the composite oscillator is of the order of the transference due to C_t (*Figure 2*). If R_s is small, on the contrary, $1/Z \gg \omega C_t$ equation (9) reduces to $V_o/V_i \simeq Z_L/Z$ and the measured transference function depends only on the impedance of the composite, since $Z_L = R_L$ is fixed. It has been shown, however, how the composite oscillator can be used to obtain the loss tangent of the specimen also for high damping materials.

Finally, the composite oscillator can also be used to measure the attenuation coefficient of the specimen by using the method leading to *Figure 7*, provided the attenuation is sufficiently high. Even if the accuracy of this procedure might be slightly lower than the one obtained with the traditional methods of propagation of continuous waves or pulses, the experimental requirements are much simpler in the case of the composite oscillator.

CONCLUSIONS

A composite oscillator driven by a piezoelectric crystal, working in longitudinal oscillation and at a frequency of 50 kHz, has been presented. The mechanical and electrical response of the composite oscillator, which involves the specimen and the piezoelectric crystal, have been studied in detail, to show how the dynamic mechanical properties of the specimen can be obtained from the measured mechanical and electrical response of the composite. Finally, some measurements on vulcanized rubber specimens have been reported to illustrate the applicability and reliability of the device.

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