On the determination of phenomenological coefficients for dielectric materials

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Abstract

We show a method to express unknown phenomenological coefficients as functions of experimentally determinable quantities related to the dielectric response of materials. The equation proposed by Kluitenberg-Ciancio in [1]-[5] for dielectric relaxation is considered in one-dimensional form. Assuming a sinusoidal induction vector **D** (extensive variable = cause), the electric field **E** (intensive variable = effect) inside the system, which depends on unknown phenomenological coefficients, has been obtained by integration. This solution is expressed by phenomenological coefficients which are functions of experimentally determinable quantities. Moreover, a condition for the applicability of the theory is determined. Finally we carry out dielectric measurements on PMMA and PVC at different frequencies and fixed temperature in order to obtain the phenomenological coefficients as functions of the frequency. These data are found to be physically consistent.

Mathematics Subject Classification: 49M20, 74F15, 74D05.
Key words: Dielectric relaxations, electromagnetic effects, linear constitutive equations.

1 Experimental approach.

In [1]-[10] theoretical aspects of the dielectric relaxation phenomena are discussed and a phenomenological equation is proposed where four coefficients characterizing the medium appear.

In the framework of the linear response theory we will develop a method to relate univocally these coefficients to well known experimentally determinable quantities. Moreover we will determine the applicability conditions of Kluitenberg Ciancio model.

In particular we set four algebric equations on the four unknown phenomenological coefficients of the equation. This is possible by conceiving an experiment where a particular form of electric field is allowed to be set in terms of measurable quantities; so we think it is useful to describe conceptually the above mentioned experiment. In what follows the temperature will be considered as a constant parameter.

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If a sinusoidal voltage V is applied to a plane capacitor, we can observe a sinusoidal surface charge on his plates, the density of which is characterized by induction vector $\mathbf{D}$, generating a sinusoidal electric field inside capacitor. Linear response theory predicts that if the surface density charge (cause) evolves sinusoidally, i.e.

$$\mathbf{D} = \mathbf{D}_0 sin(\omega t) \tag{1.1}$$

the electric field (effect) inside the capacitor is also sinusoidal, and characterized by the same frequency but different phase and amplitude:

$$\mathbf{E} = \mathbf{E}_0 sin(\omega t + \phi) \tag{1.2}$$

and so

$$\mathbf{E} = \mathbf{D}_0\, s_1\, sin(\omega t) + \mathbf{D}_0\, s_2\, cos(\omega t)\,, \tag{1.3}$$

where [13]-[11]

$$s_1 = \frac{\mathbf{E}_0}{\mathbf{D}_0} cos\,\phi \tag{1.4}$$

$$s_2 = \frac{\mathbf{E}_0}{\mathbf{D}_0} sin\,\phi \tag{1.5}$$

¿From (1.3) the electric charge distribution on the plates is viewed as the cause determining the establishing of electric field inside capacitor. Then we can identify such a cause with the dielectric displacement $\mathbf{D}$ (which is an extensive variable). The effect will be identified with the electric field (which is an intensive variable) given by (1.2).

Such a viewpoint allows us to study dielectric relaxation phenomena:

input $\mathbf{D}$ *"cause"*$\rightarrow$ output $\mathbf{E}$ *"effect"*

Defining the *reciprocal complex dielectric constant*:

$$s^* = \frac{\mathbf{E}^*}{\mathbf{D}^*} = s_1 + i\, s_2\,, \tag{1.6}$$

the *complex dielectric constant* shall be [11]:

$$\frac{1}{s^*} = \varepsilon^* = \varepsilon' - i\,\varepsilon''\,, \tag{1.7}$$

where

$$\varepsilon' = \frac{s_1}{s_1^2 + s_2^2}\,,\quad \varepsilon'' = \frac{s_2}{s_1^2 + s_2^2}\,, \tag{1.8}$$

by virtue of (1.4),(1.5) and (1.8) we obtain:

$$\varepsilon' = \frac{\mathbf{D}_0}{\mathbf{E}_0} cos\phi \qquad \varepsilon'' = \frac{\mathbf{D}_0}{\mathbf{E}_0} sin\phi\,, \tag{1.9}$$

The quantities (1.9) are experimentally measurable and can be proved to be proportional to stored and dissipated energy, respectively.

2 Phenomenological coefficients and frequency.

In [6] Kluitenberg and Ciancio consider dielectric relaxation phenomena in a medium, which is at rest respect to an inertial refernce frame, and by thermodynamical considerations the following phenomenological equation is determined:

$$\chi^{(0)}_{(EP)}\mathbf{E} + \dot{\mathbf{E}} = \chi^{(0)}_{(PE)}\mathbf{P} + \chi^{(1)}_{(PE)}\dot{\mathbf{P}} + \chi^{(2)}_{(PE)}\ddot{\mathbf{P}}\,. \tag{2.10}$$

In (2.10) the dot up the vectors mean derivative to respect to time and $\mathbf{P}$ is the polarization vector define by:

$$\mathbf{P} = \mathbf{D} - \varepsilon_0\,\mathbf{E} \tag{2.11}$$

where $\mathbf{D}$ is the dielectric displacement and ε_0 the dielectric constant in vacuum.
In [6] it was shown that the phenomenological coefficients which occur in (2.10) satisfy the following inequalities:

$$\chi^{(0)}_{(EP)} \geq 0\,,\ \chi^{(0)}_{(PE)} \geq 0\,,\ \chi^{(2)}_{(PE)} \geq 0\,, \tag{2.12}$$

$$\chi^{(1)}_{(PE)} - \chi^{(0)}_{(EP)}\,\chi^{(2)}_{(PE)} \geq 0\,, \tag{2.13}$$

$$\chi^{(1)}_{(PE)} \geq 0\,, \tag{2.14}$$

$$\chi^{(1)}_{(PE)}\,\chi^{(0)}_{(EP)} - \chi^{(0)}_{(PE)} \geq 0\,, \tag{2.15}$$

Setting

$$h_i = \chi^{(i)}_{(PE)}\ \ (i = 0,1,2)\,, \qquad k_0 = \chi^{(0)}_{(EP)} \tag{2.16}$$

dimensionally we have:

$$[k_0] = t^{-1}\,, \qquad [h_0] = \frac{m\,l^3\,t^{-3}}{Q^2} \tag{2.17}$$

$$[h_1] = \frac{1}{\varepsilon_0} = \frac{m\,l^3\,t^{-2}}{Q^2}\,, \qquad [h_2] = \frac{m\,l^3\,t^{-1}}{Q^2} \tag{2.18}$$

In one dimension the equation (2.10) can be written:

$$h_2\varepsilon_0\ddot{E} + (1 + h_1\varepsilon_0)\dot{E} + (h_0\varepsilon_0 + k_0)E = h_2\ddot{D} + h_1\dot{D} + h_0 D\,. \tag{2.19}$$

Dividing by $h_2\varepsilon_0 \neq 0$ and putting:

$$a = \frac{h_0\varepsilon_0 + k_0}{h_2\varepsilon_0} \qquad b = \frac{1 + h_1\varepsilon_0}{h_2\varepsilon_0} \tag{2.20}$$

from (2.19) follows:

$$\ddot{E} + b\dot{E} + aE = \frac{1}{\varepsilon_0}\ddot{D} + \frac{h_1}{h_2\varepsilon_0}\dot{D} + \frac{h_0}{h_2\varepsilon_0}D\,. \tag{2.21}$$

Using (1.1) and putting:

$$\alpha = D_0\Big(\frac{h_0}{h_2\varepsilon_0} - \frac{\omega^2}{\varepsilon_0}\Big)\,, \qquad \beta = D_0\Big(\frac{h_1\omega}{h_2\varepsilon_0}\Big) \tag{2.22}$$

the equation (2.21) becomes:

$$\ddot{E} + b\dot{E} + aE = \alpha\, sin(\omega t) + \beta\, cos(\omega t)\,. \tag{2.23}$$

The integration of this equation gives the electric field to be compared with (1.3) in order to obtain two of the four equation which we are seeking.
The general solution of this differential equation is

$$\begin{aligned} E(t) \;=\; c_1 e^{r_1 t} + c_2 e^{r_2 t} \quad &+ \quad \Big[\frac{\alpha(r_1 r_2 - \omega^2) - \beta\omega(r_1 + r_2)}{(r_1^2 + \omega^2)(r_2^2 + \omega^2)}\Big] sin(\omega t) \\ &+ \quad \Big[\frac{\beta(r_1 r_2 - \omega^2) + \alpha\omega(r_1 + r_2)}{(r_1^2 + \omega^2)(r_2^2 + \omega^2)}\Big] cos(\omega t)\,, \end{aligned} \tag{2.24}$$

where c_1 and c_2 are two arbitrary integration constans, while $-r_1^{-1}$ and $-r_2^{-1}$ are two relaxation times. Of course r_1 and r_2 are solutions of the algebric associated equation:

$$r^2 + br + a = 0\,. \tag{2.25}$$

i.e.

$$r_1 + r_2 = -b\,, \tag{2.26}$$

$$r_1\, r_2 = a\,. \tag{2.27}$$

Since the aim is to find a functional relation between the phenomenological coefficients (2.16) and the quantities expressed by (1.4), (1.5) and (1.9), which are experimentally measurable, it is reasonable to neglect any transitory phenomenon, so that eq. (2.24) can be rewritten:

$$E = E_0\, sin(\omega t + \phi) \tag{2.28}$$

in which:

$$E_0 = \frac{\sqrt{(\alpha^2 + \beta^2)\Big[(\omega^2 - r_1 r_2)^2 + \omega^2(r_1 + r_2)^2\Big]}}{(r_1^2 + \omega^2)(r_2^2 + \omega^2)} \tag{2.29}$$

$$cos\,\phi = \frac{\alpha(r_1 r_2 - \omega^2) - \beta\omega(r_1 + r_2)}{\sqrt{(\alpha^2 + \beta^2)\Big[(\omega^2 - r_1 r_2)^2 + \omega^2(r_1 + r_2)^2\Big]}} \tag{2.30}$$

$$sin\,\phi = \frac{\beta(r_1 r_2 - \omega^2) + \alpha\omega(r_1 + r_2)}{\sqrt{(\alpha^2 + \beta^2)\Big[(\omega^2 - r_1 r_2)^2 + \omega^2(r_1 + r_2)^2\Big]}} \tag{2.31}$$

Taking into account that from (2.25) we can obtained:

$$(r_1^2+\omega^2)(r_2^2+\omega^2) \;=\; a^2+\omega^2(b^2-2a)+\omega^4\,. \tag{2.32}$$

The equation (1.9), by virtue of (2.26),(2.27) and (2.29)-(2.32), provide the following expressions:

$$\varepsilon' = \frac{h_2\varepsilon_0\omega^4-\Big[2h_0h_2\varepsilon_0+k_0h_2-h_1(1+h_1\varepsilon_0)\Big]\omega^2+h_0^2\varepsilon_0+h_0k_0}{h_2\omega^4-(2h_0h_2-h_1)\omega^2+h_0^2}\,, \tag{2.33}$$

$$\varepsilon'' = \frac{h_2\omega^3+(h_1k_0-h_0)\omega}{h_2\omega^4-(2h_0h_2-h_1)\omega^2+h_0^2}\,, \tag{2.34}$$

As (2.28) and (1.3) are two mathematical representation of the same phenomenon,identifing these equations one has:

$$D_0s_1 \;=\; \frac{\alpha(r_1r_2-\omega^2)-\beta\omega(r_1+r_2)}{(r_1^2+\omega^2)(r_2^2+\omega^2)} \tag{2.35}$$

$$D_0s_2 \;=\; \frac{\beta(r_1r_2-\omega^2)+\alpha\omega(r_1+r_2)}{(r_1^2+\omega^2)(r_2^2+\omega^2)} \tag{2.36}$$

Using (2.26),(2.27),(2.32),(2.20),(2.22),(1.8), from (2.35) and (2.36) we obtain:

$$h_1 \;=\; \frac{k_0\varepsilon''+\omega(\varepsilon'-\epsilon_0)}{\omega\Big[(\varepsilon'-\varepsilon_0)^2+\varepsilon''^2\Big]}\,, \tag{2.37}$$

$$h_2 \;=\; \frac{h_0}{\omega^2}+\frac{k_0(\varepsilon-\varepsilon')+\varepsilon''\omega}{\omega^2\Big[(\varepsilon'-\varepsilon_0)^2+\varepsilon''^2\Big]}\,. \tag{2.38}$$

Now we observe that in static conditions the equation (2.10), by virtue of (2.11) and (2.16), gives:

$$D=\Big(\frac{h_0\varepsilon_0+k_0}{h_0}\Big)E\,. \tag{2.39}$$

¿From this last equation we deduce the expression for dielectric constant:

$$\varepsilon=\frac{h_0\varepsilon_0+k_0}{h_0} \tag{2.40}$$

and then

$$k_0=h_0(\varepsilon-\varepsilon_0)\,. \tag{2.41}$$

We remark that the left side of (2.40) can be determined experimentally.

If the surface charge on the plate of capacitor is constant, i.e.

$$D=D_0=\text{constant} \tag{2.42}$$

neglecting the second derivative in (2.10) and using (2.11) we have

$$\dot{E} + \frac{h_0\varepsilon_0 + k_0}{1 + h_1\varepsilon_0}\, E = \frac{h_0 D_0}{1 + h_1\varepsilon_0}\,, \tag{2.43}$$

from which the following relaxation time is obtained:

$$\tau = \frac{1 + h_1\varepsilon_0}{h_0\varepsilon_0 + k_0}\,. \tag{2.44}$$

The left hand side of (2.44) is determined experimentally through

$$\tau = \frac{\varepsilon'}{\omega\varepsilon''}\,. \tag{2.45}$$

The equations (2.37),(2.38),(2.41) and (2.44) form an complete algebraic system in four unknowns k_0, h_0, h_1, h_2.

3 Some inequalities.

In [6] it was shown that the phenomenological coefficients must soddisfy to inequalities (2.12)-(2.15). In this section we are using these relations for obtain any inequalities for the quantities which have introduced in the previous sections.

With the help of (2.45)the solutions of the system (2.37),(2.38),(2.41),(2.44) are:

$$k_0 = \frac{\omega(\varepsilon - \varepsilon_0)(\varepsilon'^2 + \varepsilon''^2 - \varepsilon'\varepsilon_0)}{\varepsilon\omega\tau\Big[(\varepsilon' - \varepsilon_0)^2 + \varepsilon''^2\Big] - (\varepsilon - \varepsilon_0)\varepsilon''\varepsilon_0}\,, \tag{3.46}$$

$$h_0 = \frac{\omega(\varepsilon'^2 + \varepsilon''^2 - \varepsilon'\varepsilon_0)}{\varepsilon\omega\tau\Big[(\varepsilon' - \varepsilon_0)^2 + \varepsilon''^2\Big] - (\varepsilon - \varepsilon_0)\varepsilon''\varepsilon_0}\,, \tag{3.47}$$

$$h_1 = \frac{(\varepsilon - \varepsilon_0)\varepsilon'' + \varepsilon\omega\tau(\varepsilon' - \varepsilon_0)}{\varepsilon\omega\tau\Big[(\varepsilon' - \varepsilon_0)^2 + \varepsilon''^2\Big] - \varepsilon_0\varepsilon''(\varepsilon - \varepsilon_0)}\,, \tag{3.48}$$

$$h_2 = \frac{h_0}{\omega^2}\Big[\frac{(\varepsilon' - \varepsilon)(\varepsilon' - \varepsilon_0) + \varepsilon''^2}{(\varepsilon' - \varepsilon_0)^2 + \varepsilon''^2}\Big] + \frac{\varepsilon''}{\omega\Big[(\varepsilon' - \varepsilon_0)^2 + \varepsilon''^2\Big]}\,. \tag{3.49}$$

It is well known that the following inequalities hold:

$$\varepsilon' - \varepsilon_0 > 0\,, \tag{3.50}$$

$$\varepsilon - \varepsilon_0 > 0\,, \tag{3.51}$$

$$\varepsilon - \varepsilon' > 0\,, \tag{3.52}$$

and from (3.46),(3.47) and (3.48) one obtains

$$k_0 > 0\,, \tag{3.53}$$

$$h_0 > 0\,, \tag{3.54}$$

$$h_1 > 0\,, \tag{3.55}$$

$$\text{(3.56)} \qquad \text{if} \qquad \varepsilon\omega\tau\Big[(\varepsilon'-\varepsilon_0)^2+\varepsilon''\Big]-(\varepsilon-\varepsilon_0)\varepsilon''\varepsilon_0>0\,.$$

Using (3.53)-(3.56) from (3.49) it follows:

$$\text{(3.57)} \qquad h_2>0\,,$$

if

$$\text{(3.58)} \qquad \begin{aligned}(\varepsilon' \;-\; &\varepsilon_0)\Big[\varepsilon'(\varepsilon'-\varepsilon_0)(\varepsilon'-\varepsilon)+\varepsilon''^2(2\varepsilon'-\varepsilon)\Big]+\varepsilon''^4+\\ +\;\; &\varepsilon''\varepsilon\omega\tau\Big[(\varepsilon'-\varepsilon_0)^2+\varepsilon''^2\Big]-\varepsilon''^2\varepsilon_0(\varepsilon-\varepsilon_0)>0\,.\end{aligned}$$

We can conclude that the inequalities (3.56) and (3.58) define the class of dielectric media which are described in the theory developed in [6].

4 Experimental date.

We have applied this method to PMMA (PolyMethylMetaCrylate) and PVC (PolyVinylChloride) polymers in order to obtain phenomenological coefficients for such materials.
Then dielectric measurements were perfomed by Rheometric Scientific Analyser (DETA).
The analysis chamber is purged with nitrogen and spanned frequencies in the range 1 Hz - 100 for PMMA and 3 Hz - 300 Hz for PVC.
The PMMA and PVC samples [12],in the shape of suitable disks, are previously metallised with gold to ensure a good matching with stainless steel blocking electrodes of the DETA; ε' and ε'' were determined at the temperature of $90C$ and $100C$, respectively.
The experimental results are shown in appendix A: Figures (1)-(8) and are physically meaningful.

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APPENDIX A : FIGURES

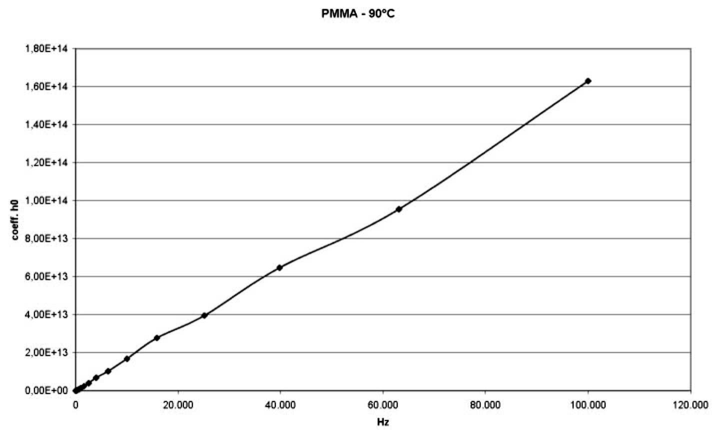

Figure 1: k_0 for PolyMethylMetaCrylateat at $90\,C$ in the range 1–100 Khz .

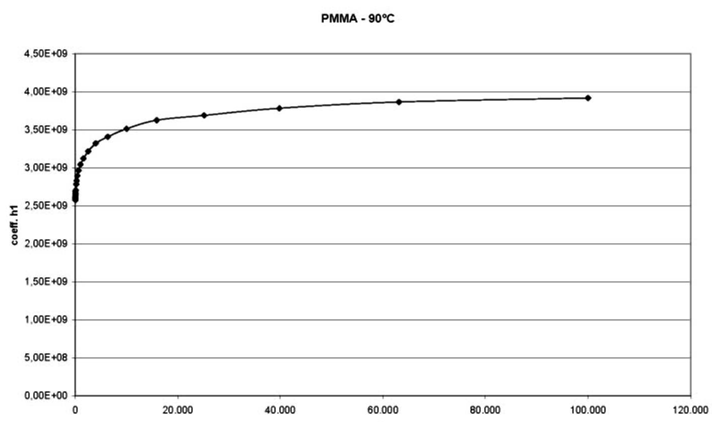

Figure 2: h_0 for Polymethylmetacrylateat $90\,C$ in the range 1–100 KHz.

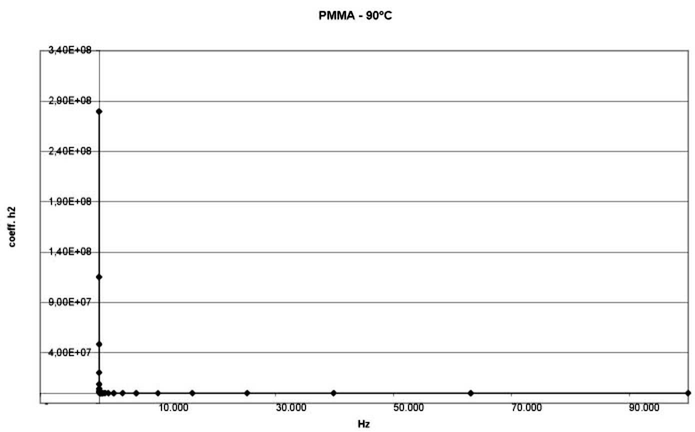

Figure 3: h_1 for Polymethylmetacrylateat $90\,C$ in the range 1–100 KHz.

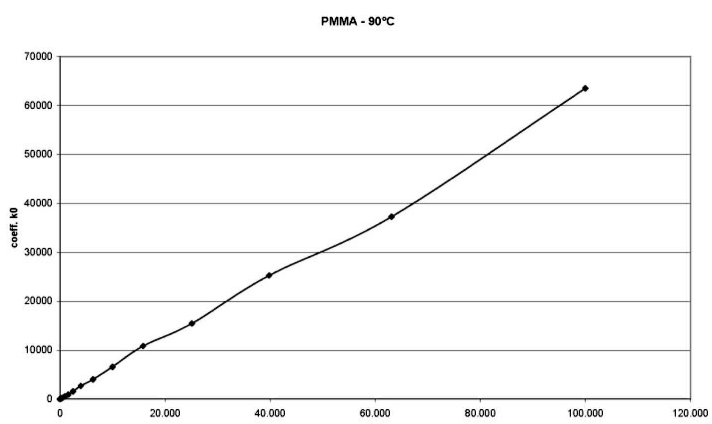

Figure 4: h_2 for PolyMethylMetaCrylate at $90\,C$ in the range 1–100 KHz.

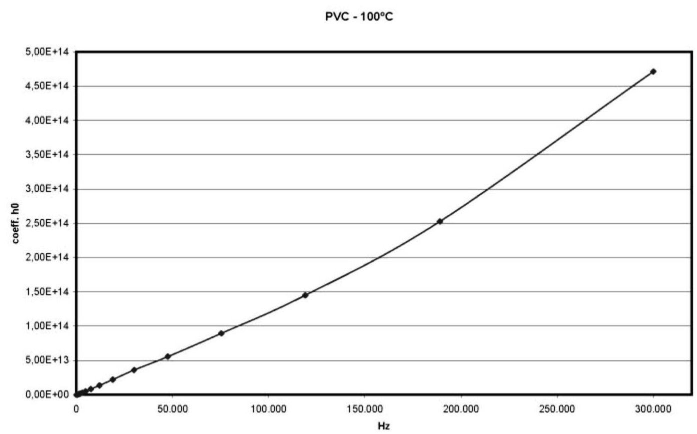

Figure 5: k_0 for PolyVinylChloride at $100\,C$ in the range 3–300 KHz.

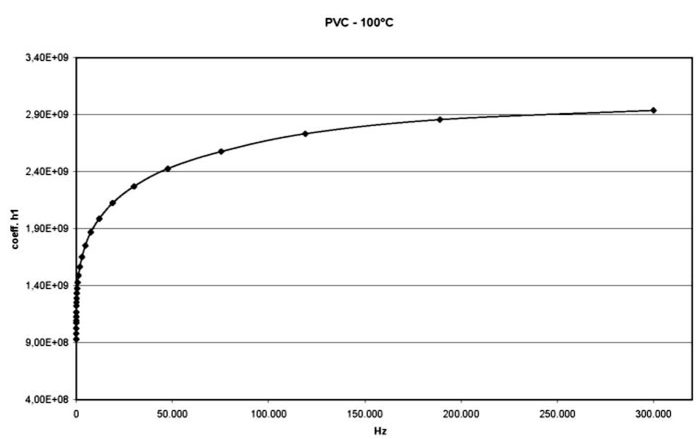

Figure 6: h_0 for PolyVinylChloride at $100\,C$ in the range 3–300 KHz.

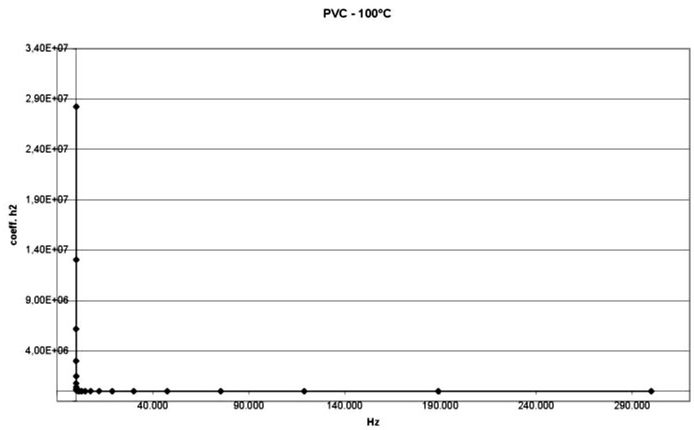

Figure 7: h_1 for PolyVinylChloride at $100\,C$ in the range 3–300 KHz.

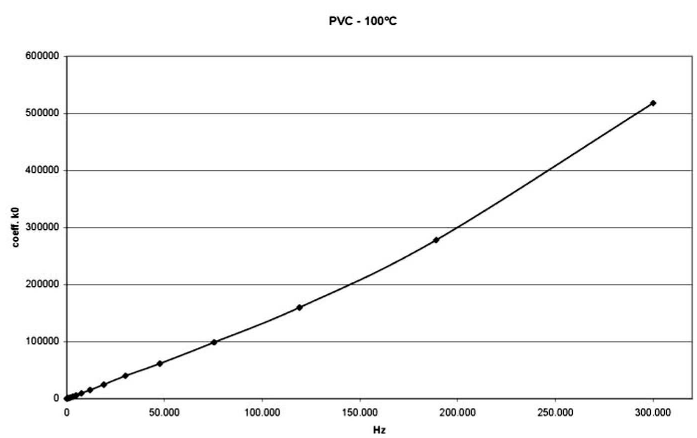

Figure 8: h_2 for PolyVinylChloride at $100\,C$ in the range 3–300 KHz.