



Espectroscopia de impedância

**LUÍS CADILLON COSTA
UNIVERSIDADE DE AVEIRO**

Estrutura da apresentação

Introdução

Modelos de relaxação

Circuitos equivalentes

Técnicas de medidas

Aplicações

Introdução

O que é?

Método de medida de propriedade eléctrica (Z^* , Y^* , ε^* , M^*) versus frequência.

$$Z^* = Z' - iZ''$$

$$\varepsilon^* = \varepsilon' - i\varepsilon''$$

$$Y^* = Z^{-1} = Y' + iY''$$

$$M^* = \varepsilon^{-1} = M' + iM''$$

Primeiros passos:

K. Cole, R. Cole, *J. Chem. Phys.* (1941).

Evolução:

Computadores rápidos, largura banda dos LCR.

Introdução

Vantagens:

Medida simples do ponto de vista eléctrico.

Fácil automatização.

Existência de modelos bem estudados.

Correlação com processos físicos e químicos.

Desvantagens:

Ambiguidade dos circuitos equivalentes.

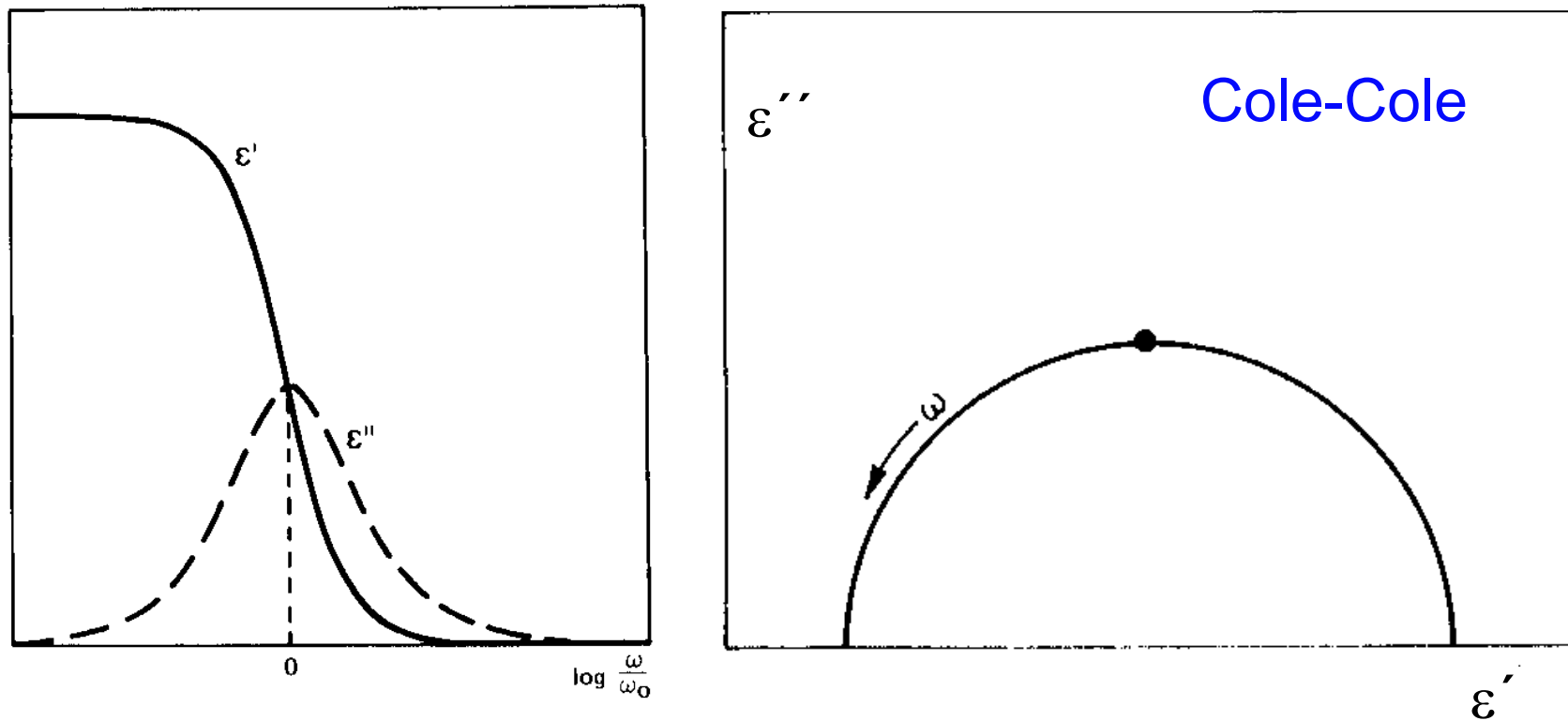
Interpretação física dos circuitos equivalentes.

Tempo de medida para baixas frequências e com temperatura.

Preço dos equipamentos.

Introdução

Como representar os dados?



K. Cole, R. Cole, *J. Chem. Phys.* (1941).

Modelos de relaxação

Debye



$$\Phi(t) = \Phi_0 \exp\left(-\frac{t}{\tau_D}\right)$$

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau_D}$$

$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2\tau_D^2}$$

$$\varepsilon''(\omega) = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau_D}{1 + \omega^2\tau_D^2}$$

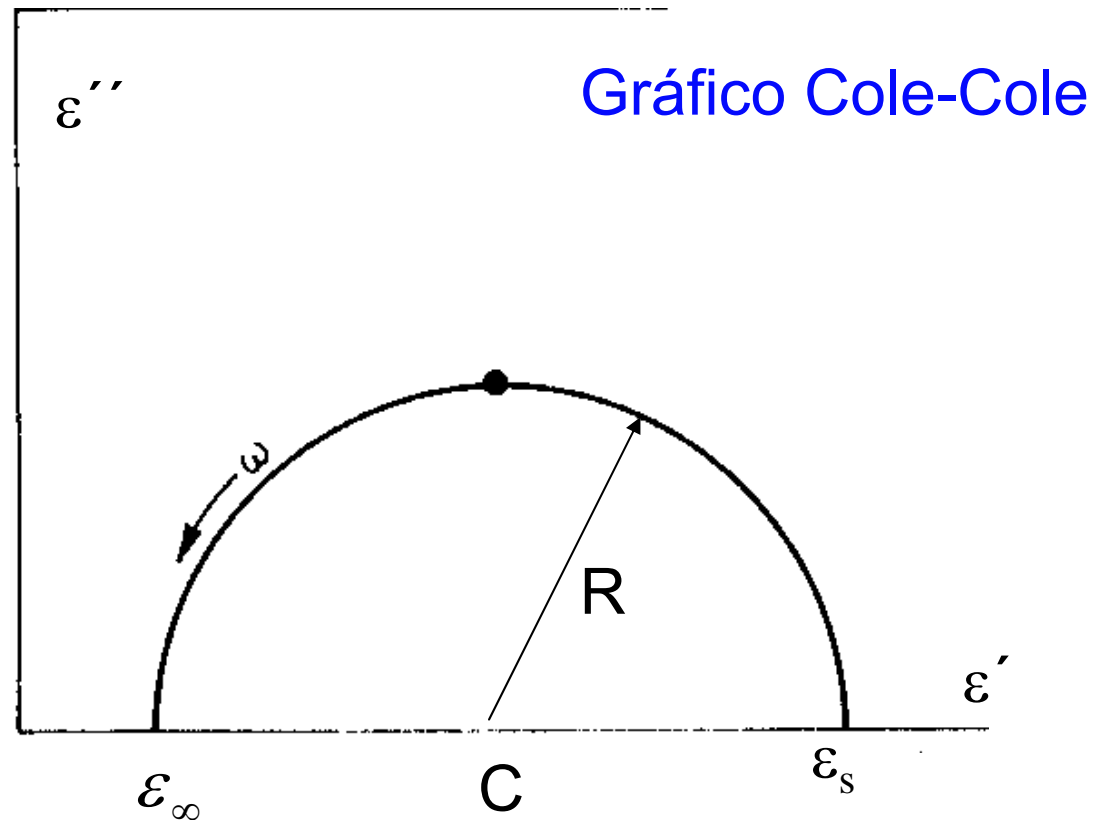
Modelos de relaxação

Debye

$$\left(\varepsilon'(\omega) - \frac{\varepsilon_s + \varepsilon_\infty}{2} \right)^2 + (\varepsilon''(\omega))^2 = \left(\frac{\varepsilon_s - \varepsilon_\infty}{2} \right)^2$$

$$C = \left(\frac{\varepsilon_s + \varepsilon_\infty}{2}, 0 \right)$$

$$R = \frac{\varepsilon_s - \varepsilon_\infty}{2}$$



Modelos de relaxação

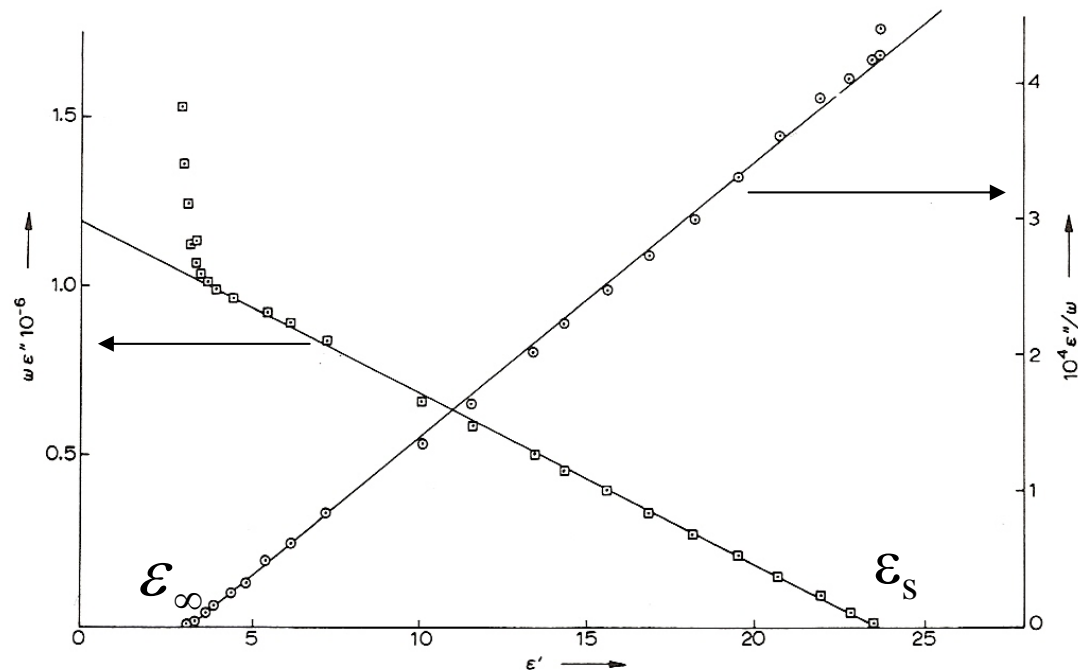
Debye

$$\varepsilon'(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_s - \varepsilon_{\infty}}{1 + \omega^2 \tau_D^2}$$

$$\varepsilon''(\omega) = \frac{(\varepsilon_s - \varepsilon_{\infty}) \omega \tau_D}{1 + \omega^2 \tau_D^2}$$

$$\omega \varepsilon''(\omega) = \frac{1}{\tau_D} (\varepsilon_s - \varepsilon'(\omega))$$

$$\frac{\varepsilon''(\omega)}{\omega} = \tau_D (\varepsilon'(\omega) - \varepsilon_{\infty})$$



Modelos de relaxação

Não-Debye ou a distribuição de τ :

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau_D}$$

Debye

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau_{cc})^{1-\alpha}}$$

Cole-Cole

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1 + i\omega\tau_{cd})^{1-\alpha}}$$

Cole-Davidson

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{\left(1 + (i\omega\tau_{hn})^\beta\right)^\gamma}$$

Havriliak-Negami

K. Cole, R. Cole, *J. Chem. Phys.* 9 (1941), 341.

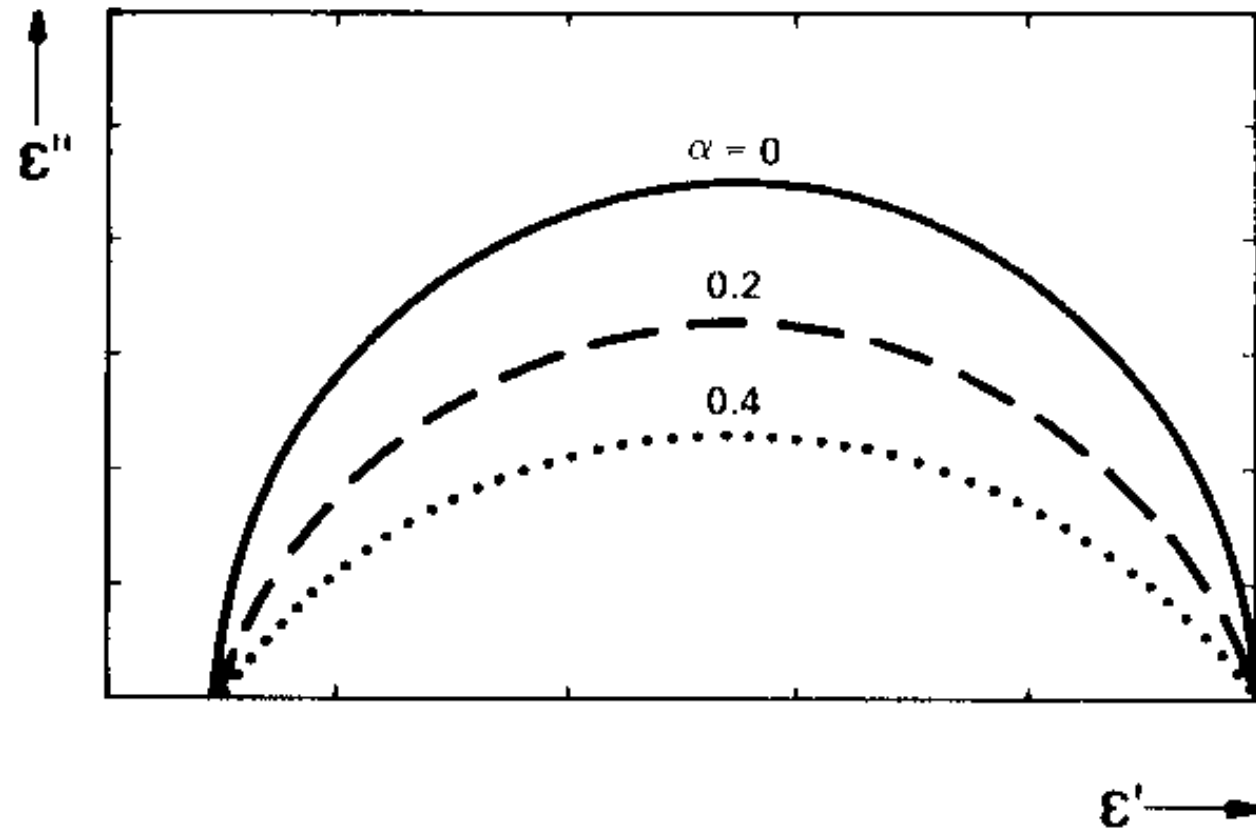
D. Davidson, R. H. Cole, *J. Chem. Phys.* 19 (1951), 1484.

S. Havriliak, S. Negami, *J. Polymer Sci.* C14 (1966), 99.

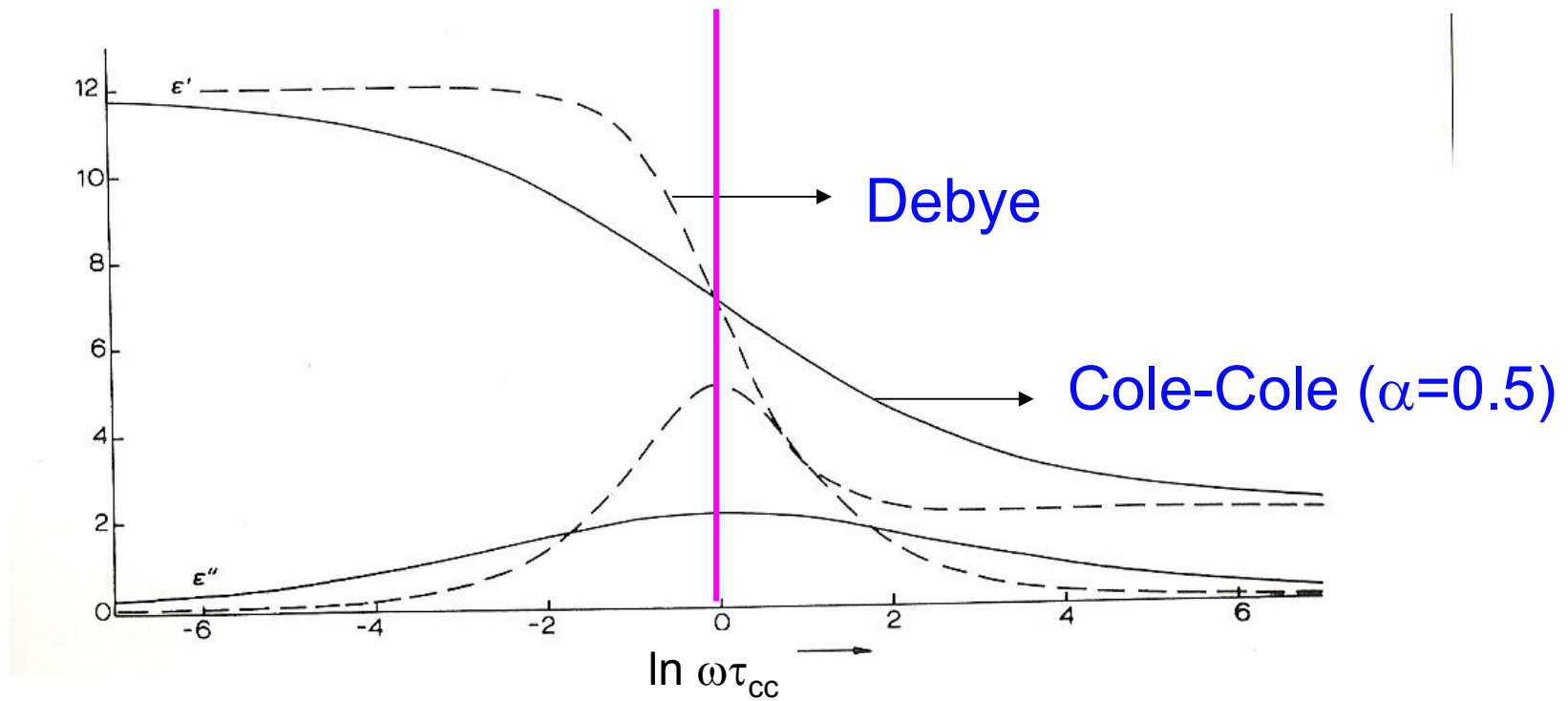
Modelos de relaxação

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau_{cc})^{1-\alpha}}$$

Cole-Cole



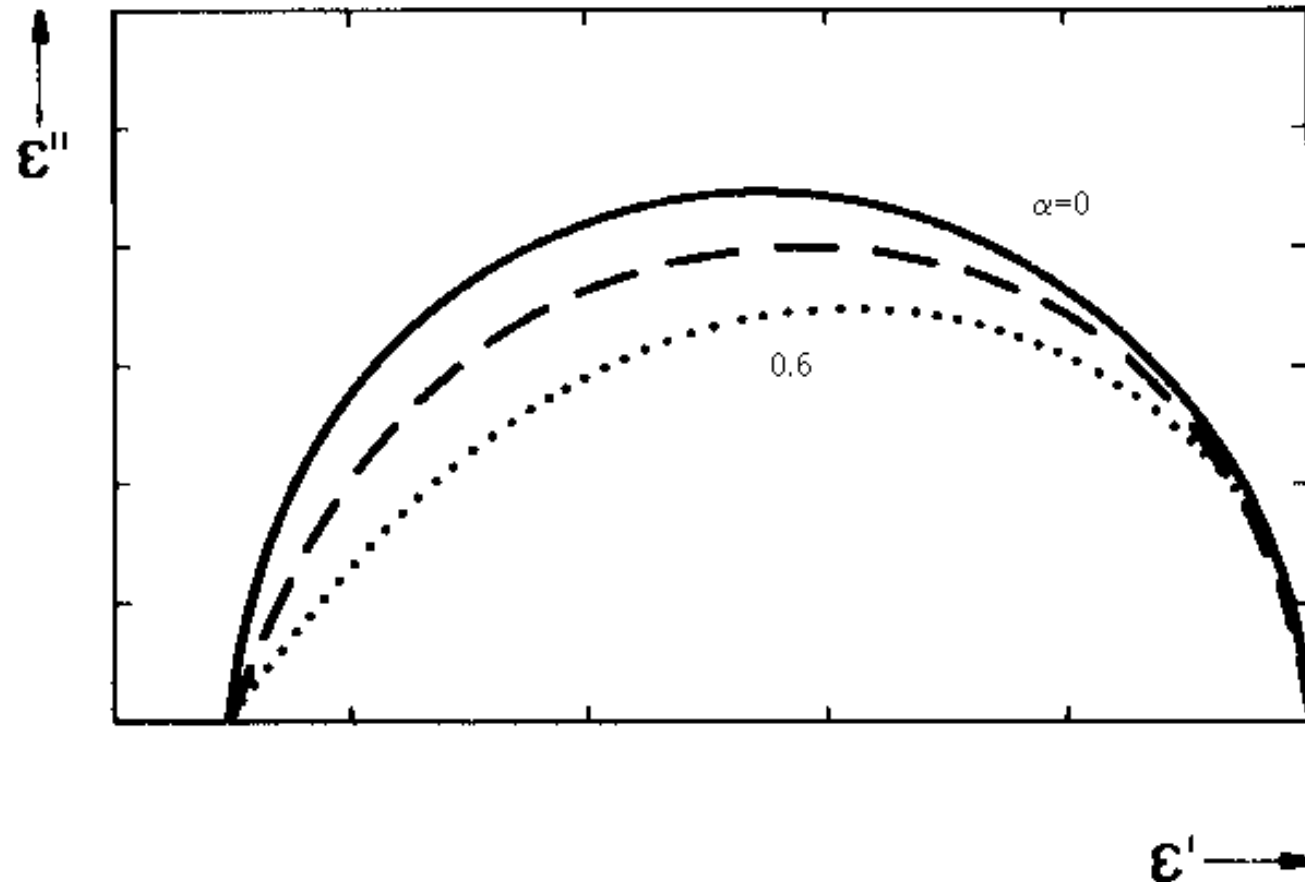
Modelos de relaxação



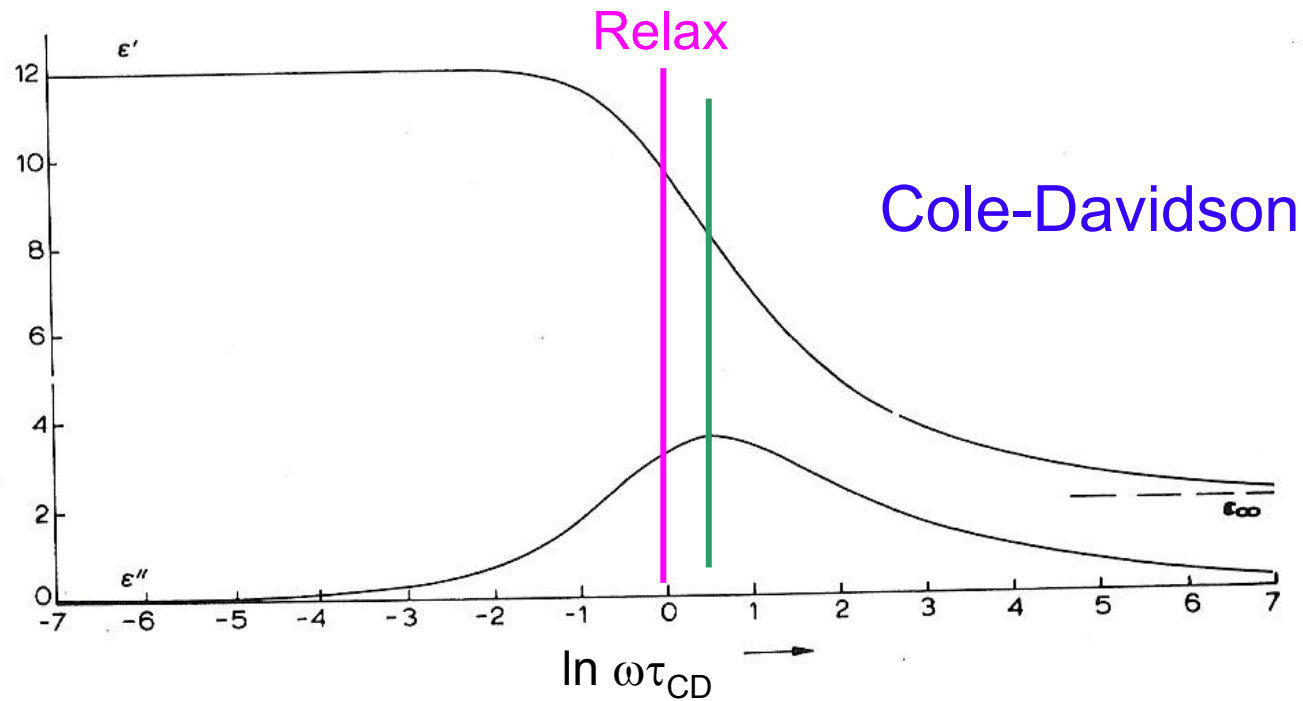
Modelos de relaxação

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1 + i\omega\tau_{cd})^{1-\alpha}}$$

Cole-Davidson



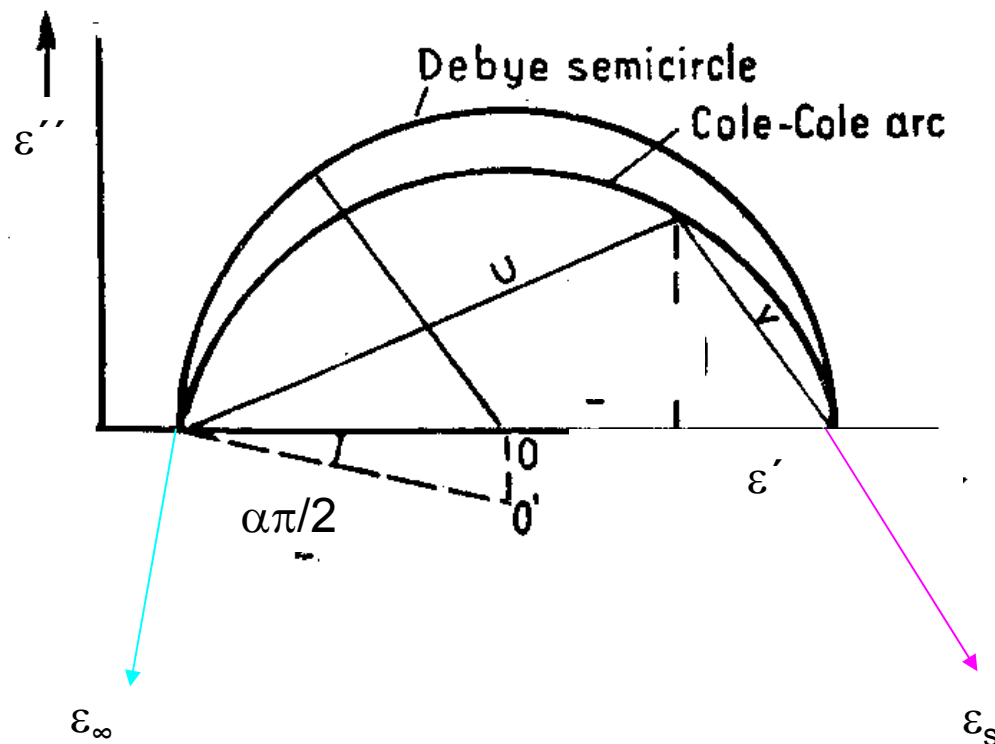
Modelos de relaxação



Modelos de relaxação

O parâmetro α

ângulo de descentragem



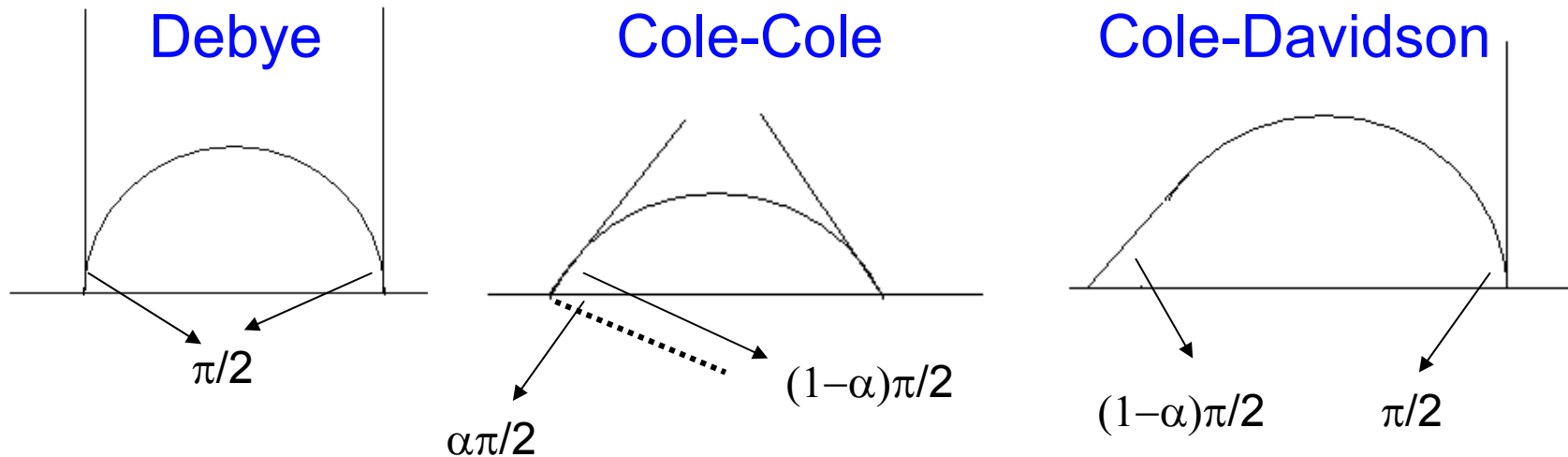
Heterogeneidade

$\alpha = 0$ \rightarrow Debye

T. Kirschen et. al., *Phys. Chem. Chem. Phys.* 5 (2003), 5243.
K. Ngai et. al., *Phys. Rev. B* 39 (9) (1989), 6169.

Modelos de relaxação

Como escolher o modelo?



$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau_D}$$

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau_{cc})^{1-\alpha}}$$

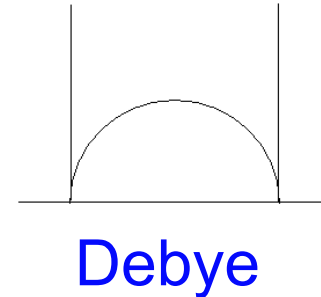
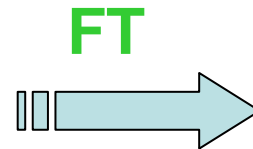
$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1 + i\omega\tau_{cd})^{1-\alpha}}$$

lim CD ($\omega \rightarrow 0$) = Debye

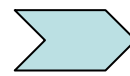
Modelos de relaxação

Tempo versus frequência

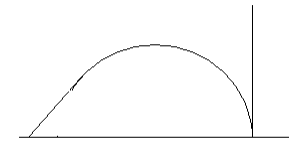
$$\Phi(t) = \Phi_0 \exp\left(-\frac{t}{\tau_D}\right)$$



$$\Phi(t) = \Phi_0 \exp\left[-\left(\frac{t}{\tau_D}\right)^\beta\right]$$



Cole-Cole

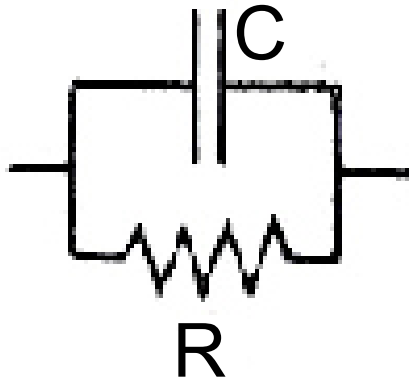


Cole-Davidson

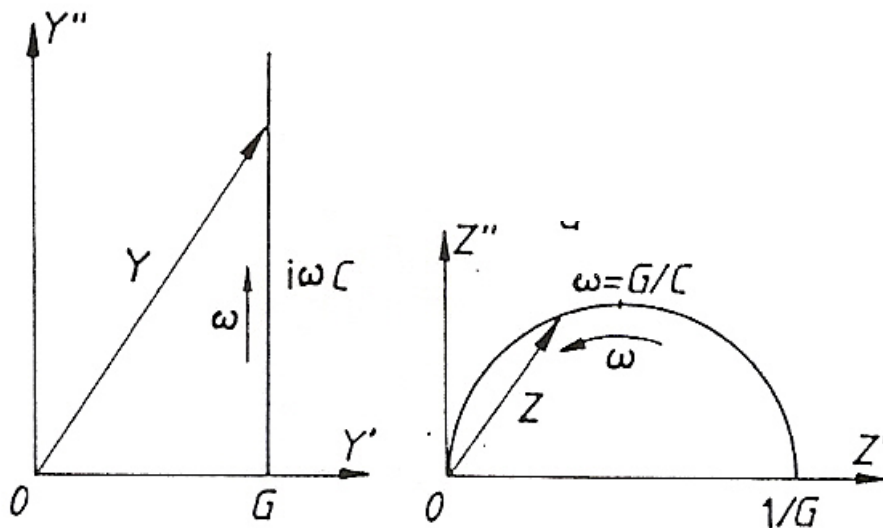
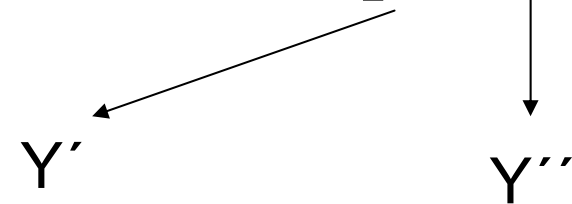
$\beta \longleftrightarrow \alpha$

Circuitos equivalentes

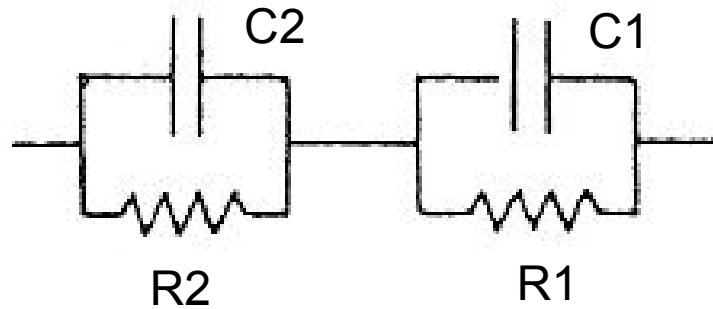
Um circuito simples



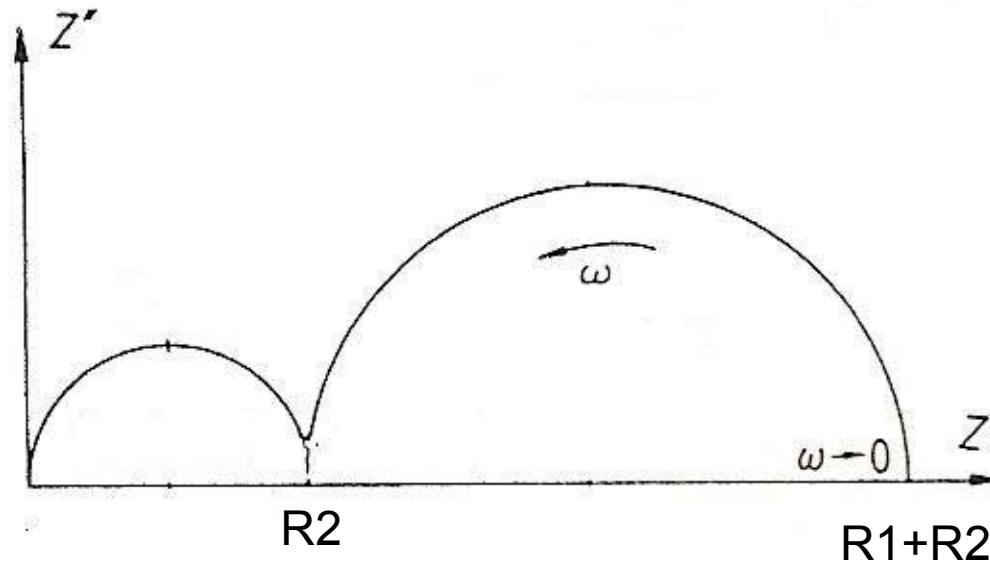
$$I(\omega) = \frac{V(\omega)}{Z(\omega)} = V(\omega)Y(\omega) = V(\omega) \left[\frac{1}{R} + i\omega C \right]$$



Circuitos equivalentes

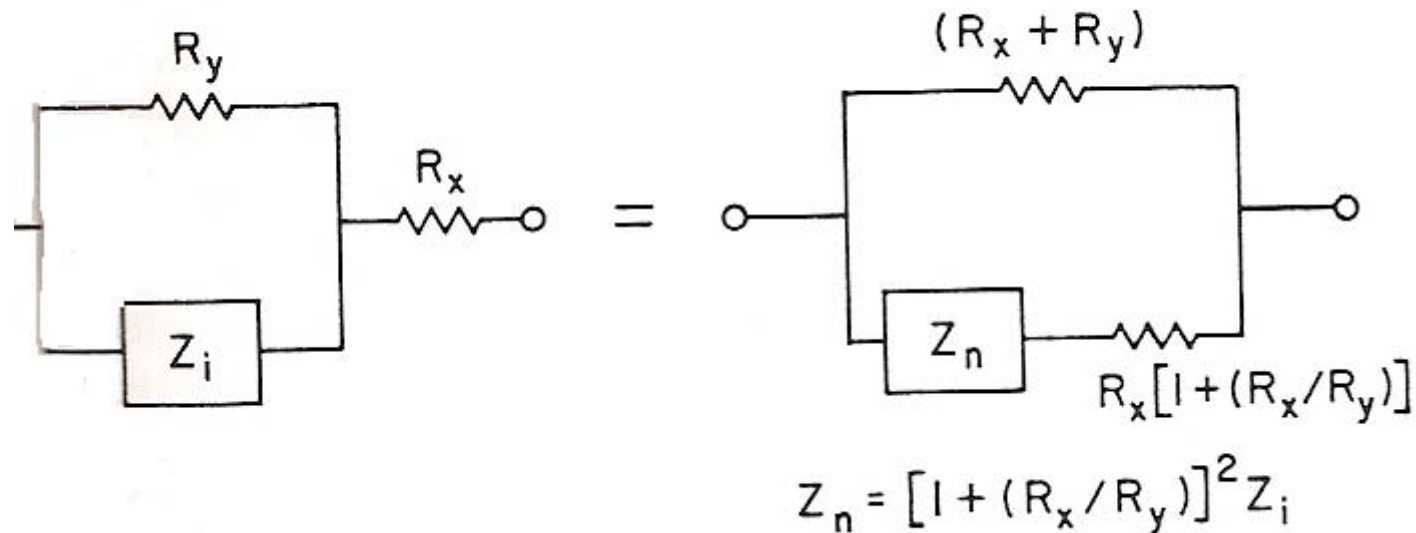


$$\tau_1 \ll \tau_2$$



Circuitos equivalentes

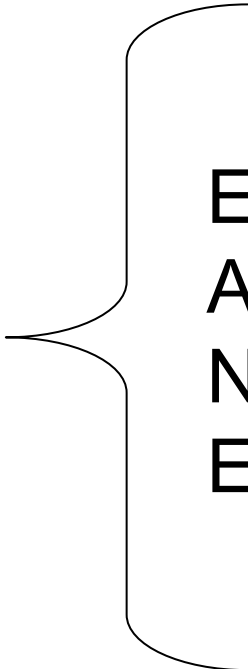
Ambiguidade nos circuitos



Como escolher?

Técnicas de medida

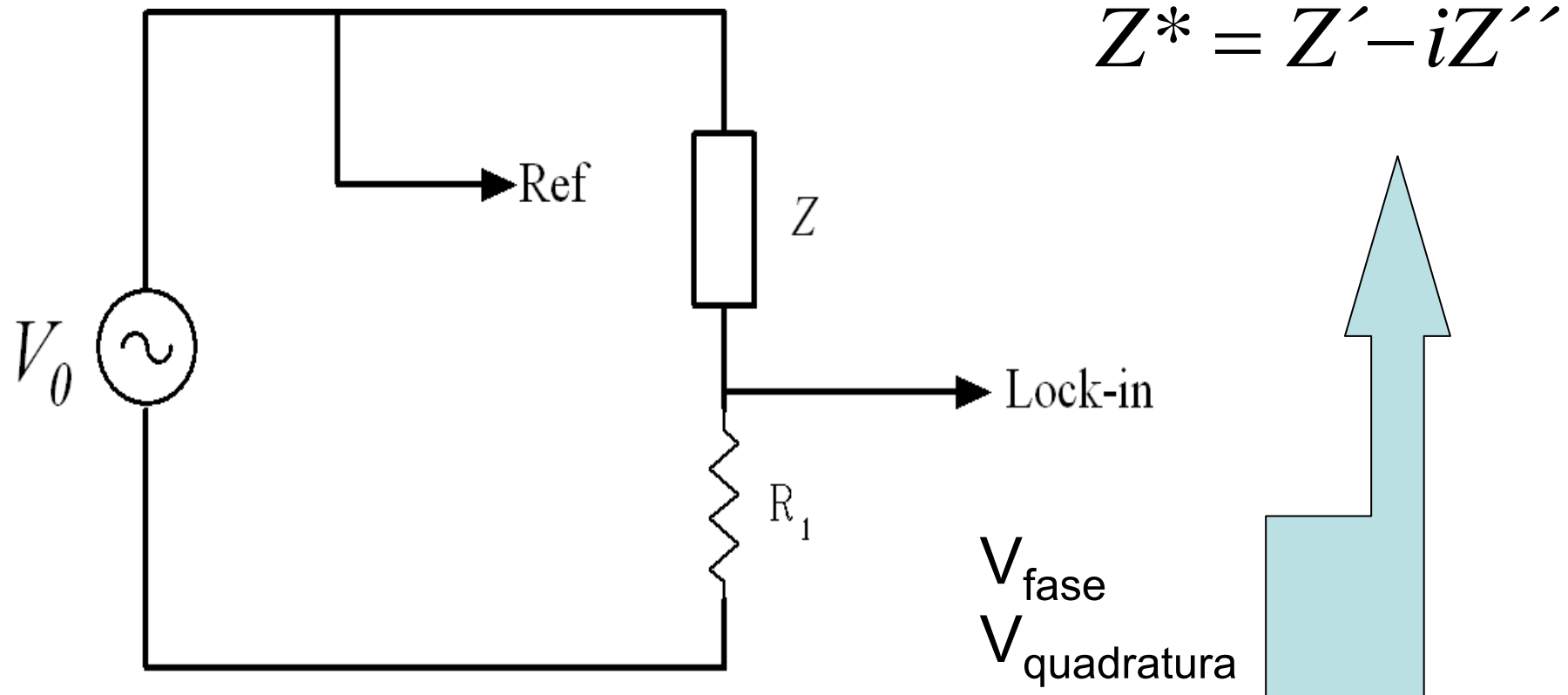
Lock-in



- Elevado S/N (eliminação ruído freq.)
- Alta impedância entrada(efeito carga)
- Necessidade de referência
- Esfasamento desejado

Técnicas de medida

Lock-in

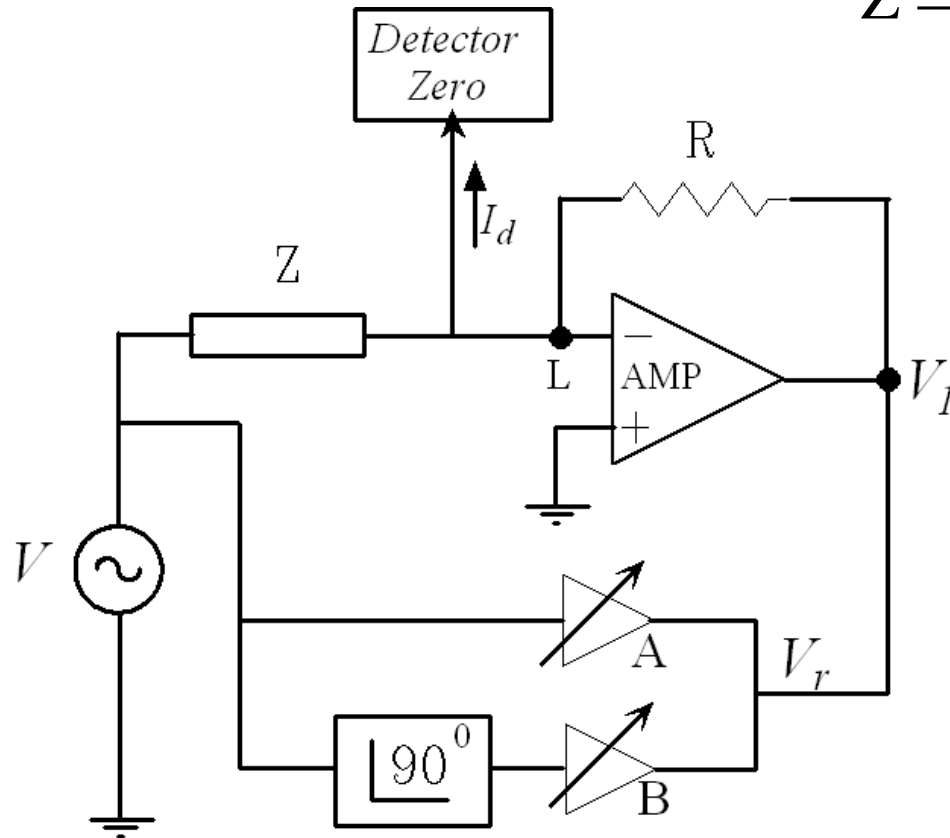


Técnicas de medida

LCR

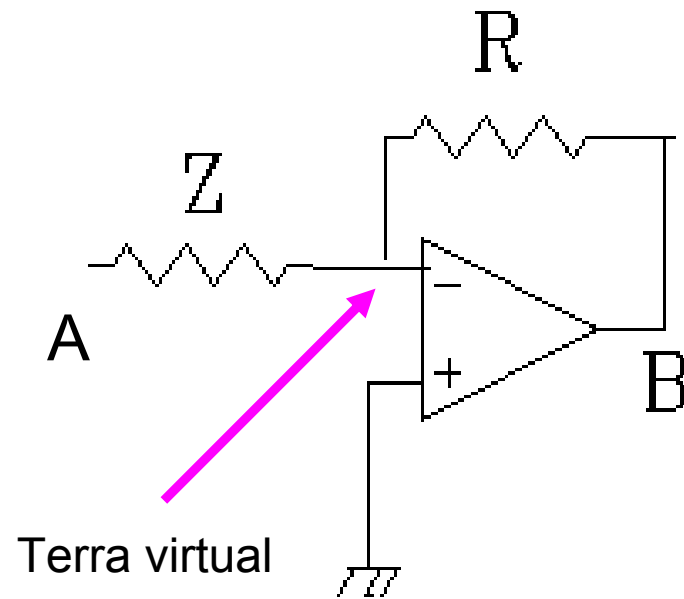
$$V_1 = -\frac{R}{Z}V$$

$$Z = -R\frac{V}{V_1} = -R\frac{V}{AV + iBV} = -\frac{R}{A + iB}$$



Técnicas de medida

LCR



$$Z_{in} \gg Z, R$$

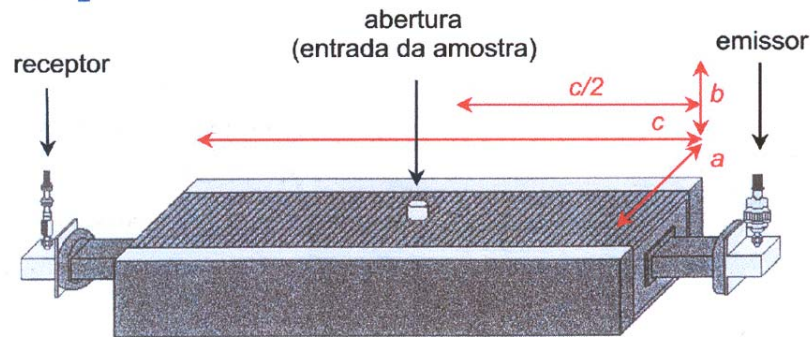
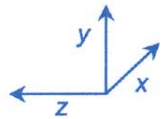
$$I_Z = I_R$$

$$V_B = -\frac{R}{Z} V_A$$

Técnicas de medida

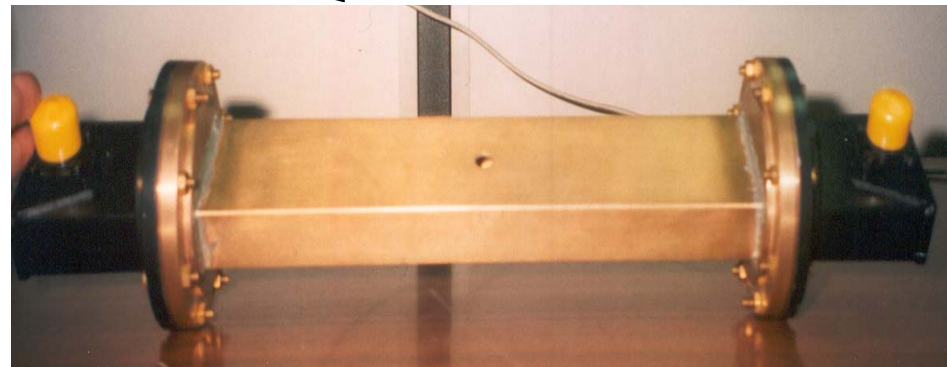
Microondas

$$\frac{\partial^2 E_y}{\partial x^2} + \frac{\partial^2 E_y}{\partial y^2} + \frac{\partial^2 E_y}{\partial z^2} - \frac{1}{c^2} \frac{\partial^2 E_y}{\partial t^2} = 0$$

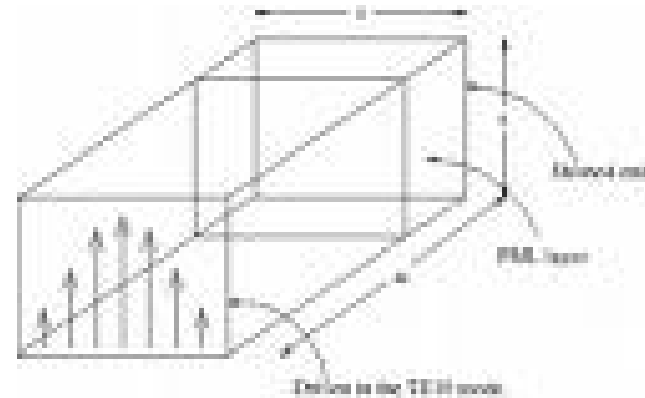
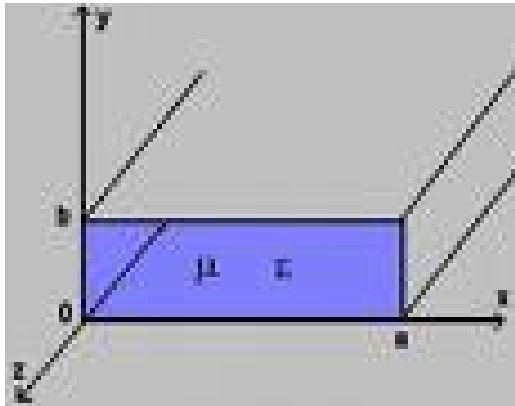


$$f = \frac{1}{2\sqrt{\mu\epsilon}} \sqrt{\left(\frac{m}{a}\right)^2 + \left(\frac{n}{b}\right)^2 + \left(\frac{p}{c}\right)^2}$$

TE_{mnp}



TE_{mnp}

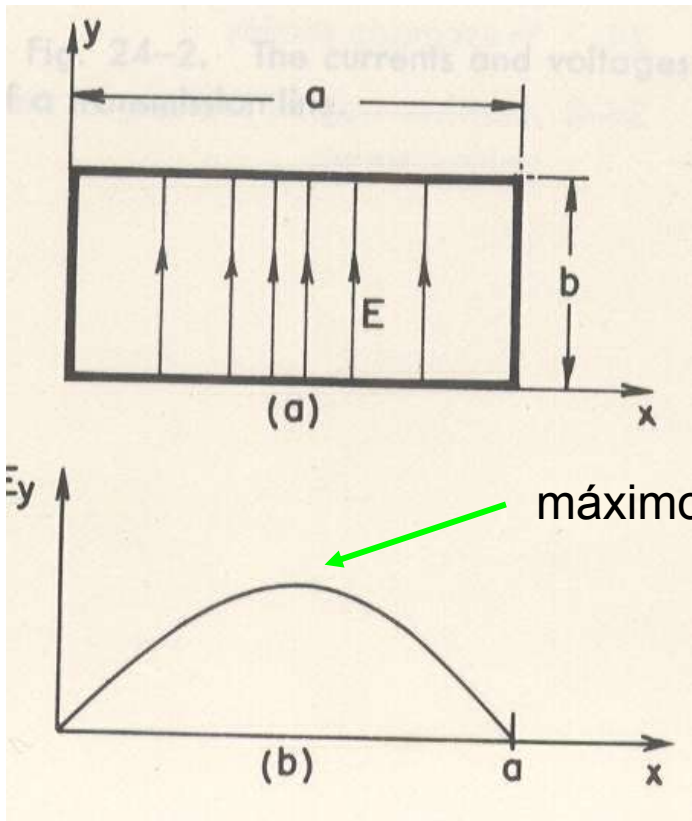


TE_{10p}

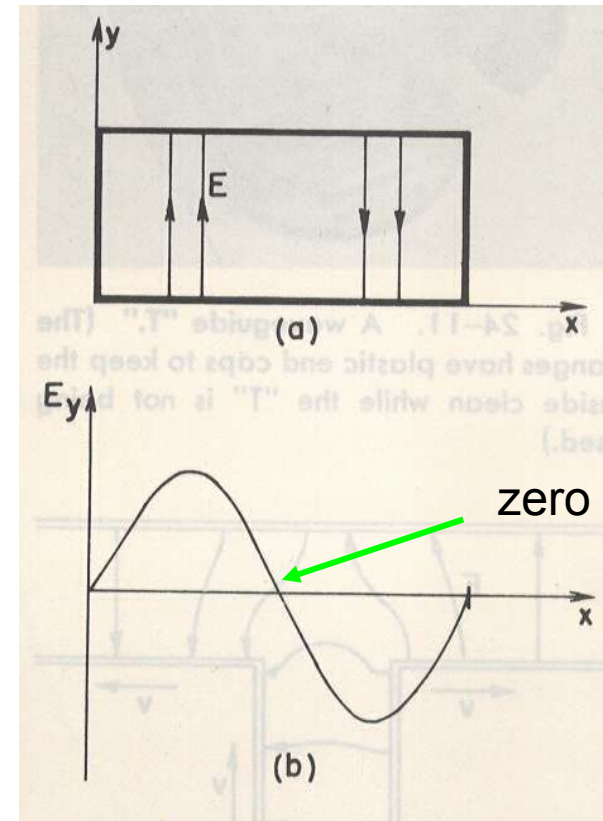
$E_t=0$ é uma condição fronteira!

Técnicas de medida

Microondas



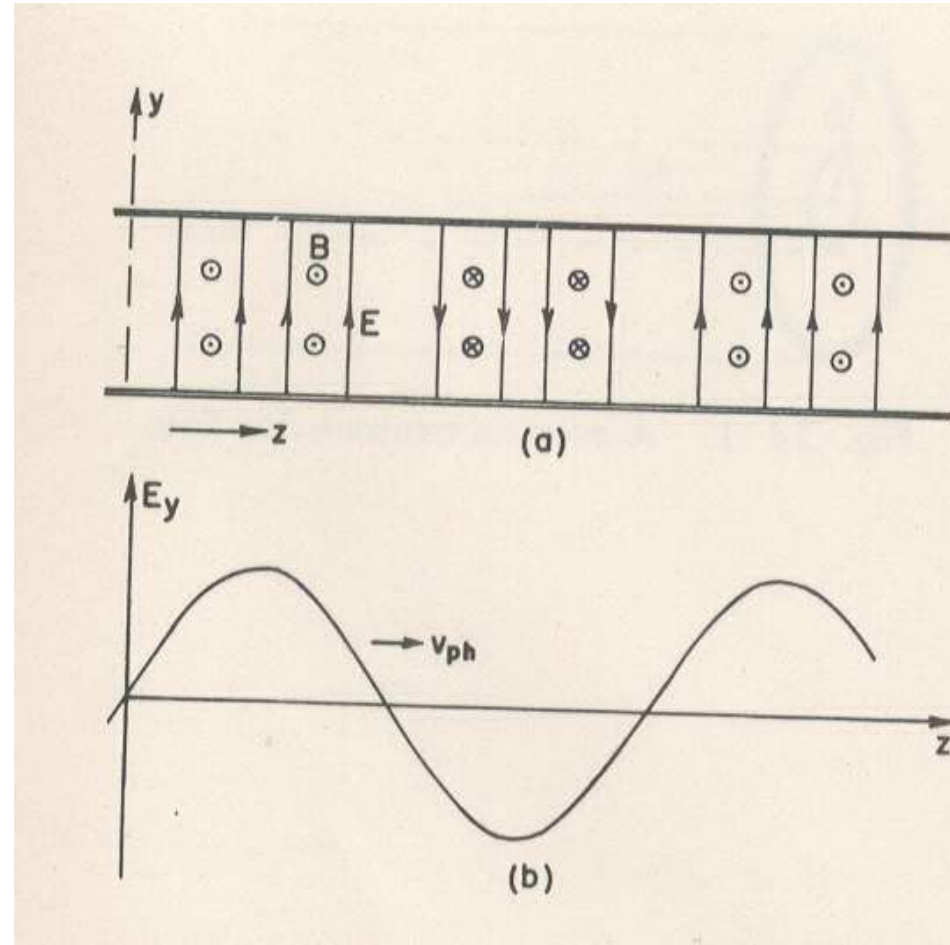
TE_{10}



TE_{20}

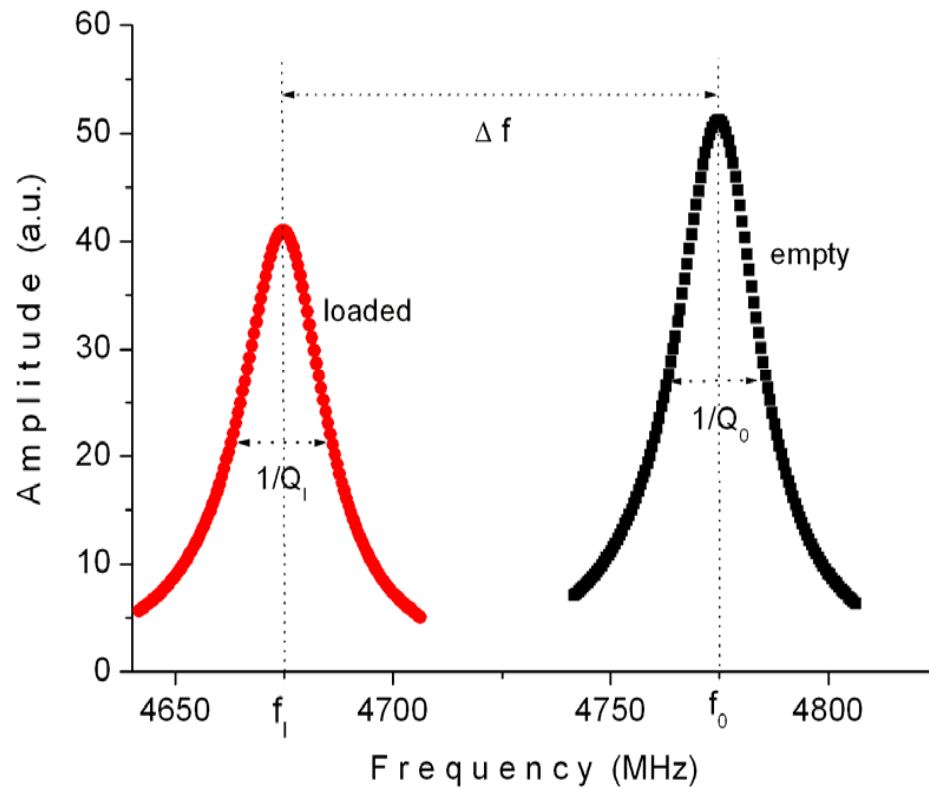
Técnicas de medida

Microondas



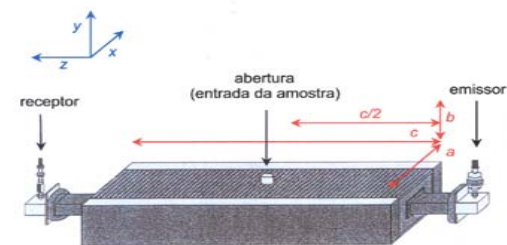
Técnicas de medida

$$\varepsilon^* = \varepsilon' - i\varepsilon''$$



$$\varepsilon' = K \frac{\Delta f}{f_0} \frac{V}{v} + 1$$


$$\varepsilon'' = \frac{K}{2} \Delta \left(\frac{1}{Q} \right) \frac{V}{v}$$



Técnicas de medida

$$\varepsilon' = K \frac{\Delta f}{f_0} \frac{V}{v} + 1$$

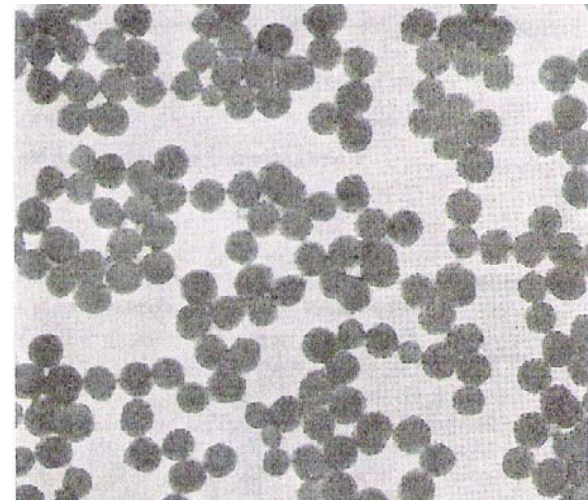
$$\varepsilon'' = \frac{K}{2} \Delta \left(\frac{1}{Q} \right) \frac{V}{v}$$

- Determinar K  Usar PTFE
- Pequena perturbação!
- Modo TE_{10p} , p ímpar

Aplicações

Efeito da introdução de PPy
 $X < 1\%$

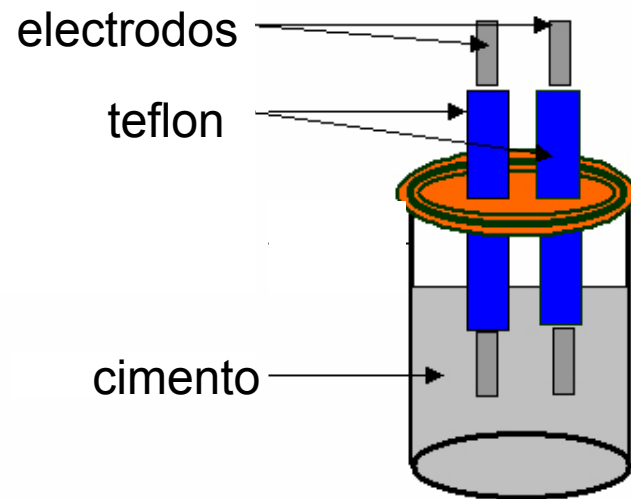
- CEM I 52.5N
- Cimento + PPy: Mistura 300 rpm, 3 min
- PPy dedopado e lavado
- $D \sim 200$ nm
- Inicial $w/c = 0.4$



PPy (SEM)

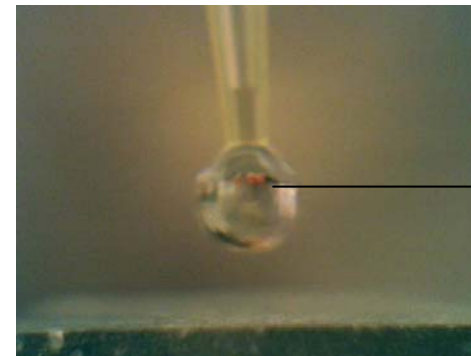
Aplicações

Espectroscopia de impedância

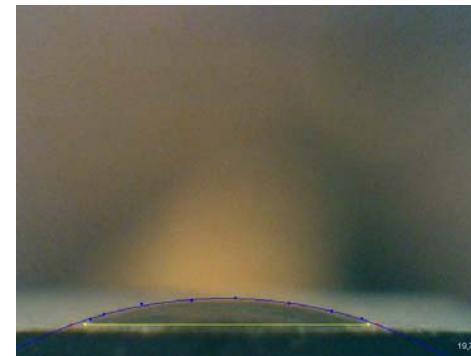


$Z^* = f(\omega)$, durante a presa
 $1\text{Hz} < f < 5\text{MHz}$

Ângulo de contacto

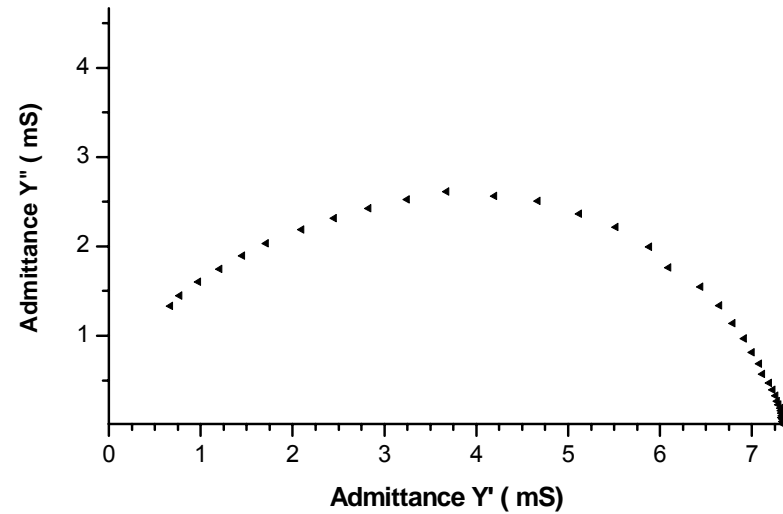
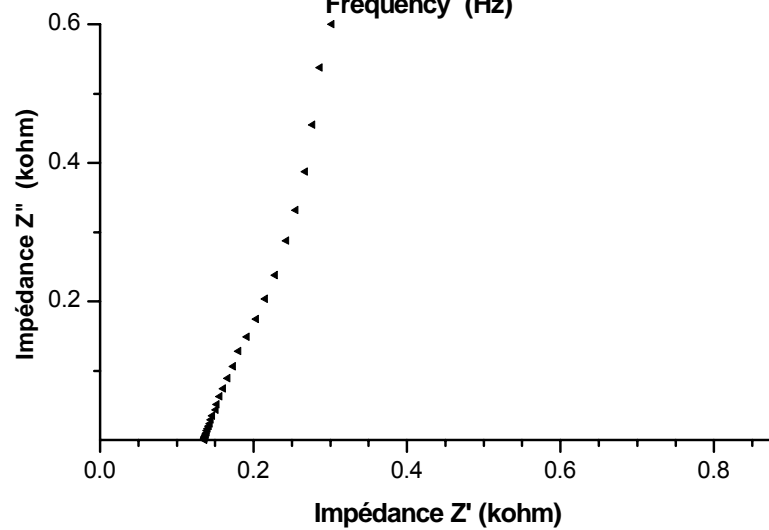
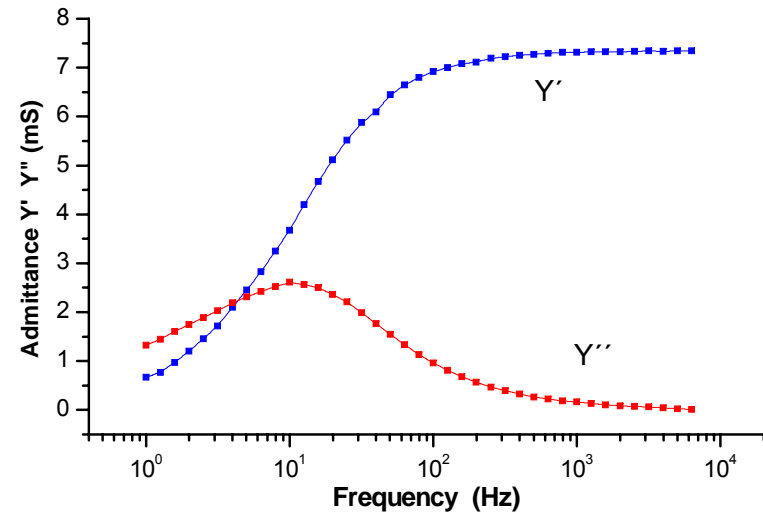
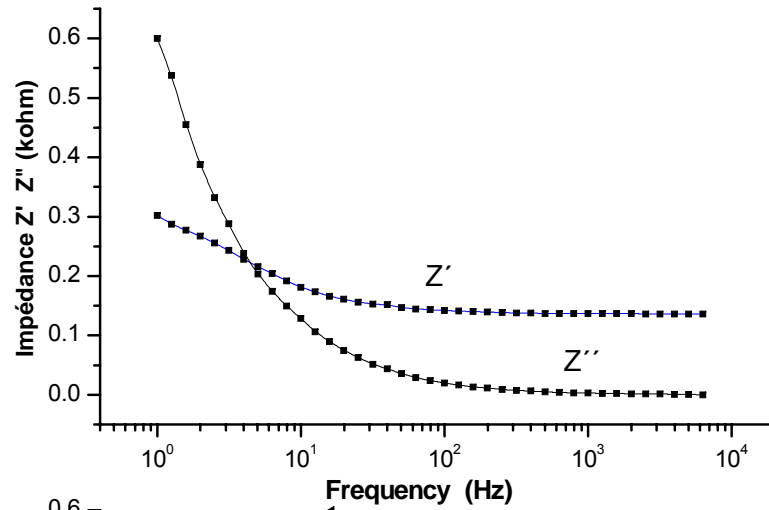


Gota de
água

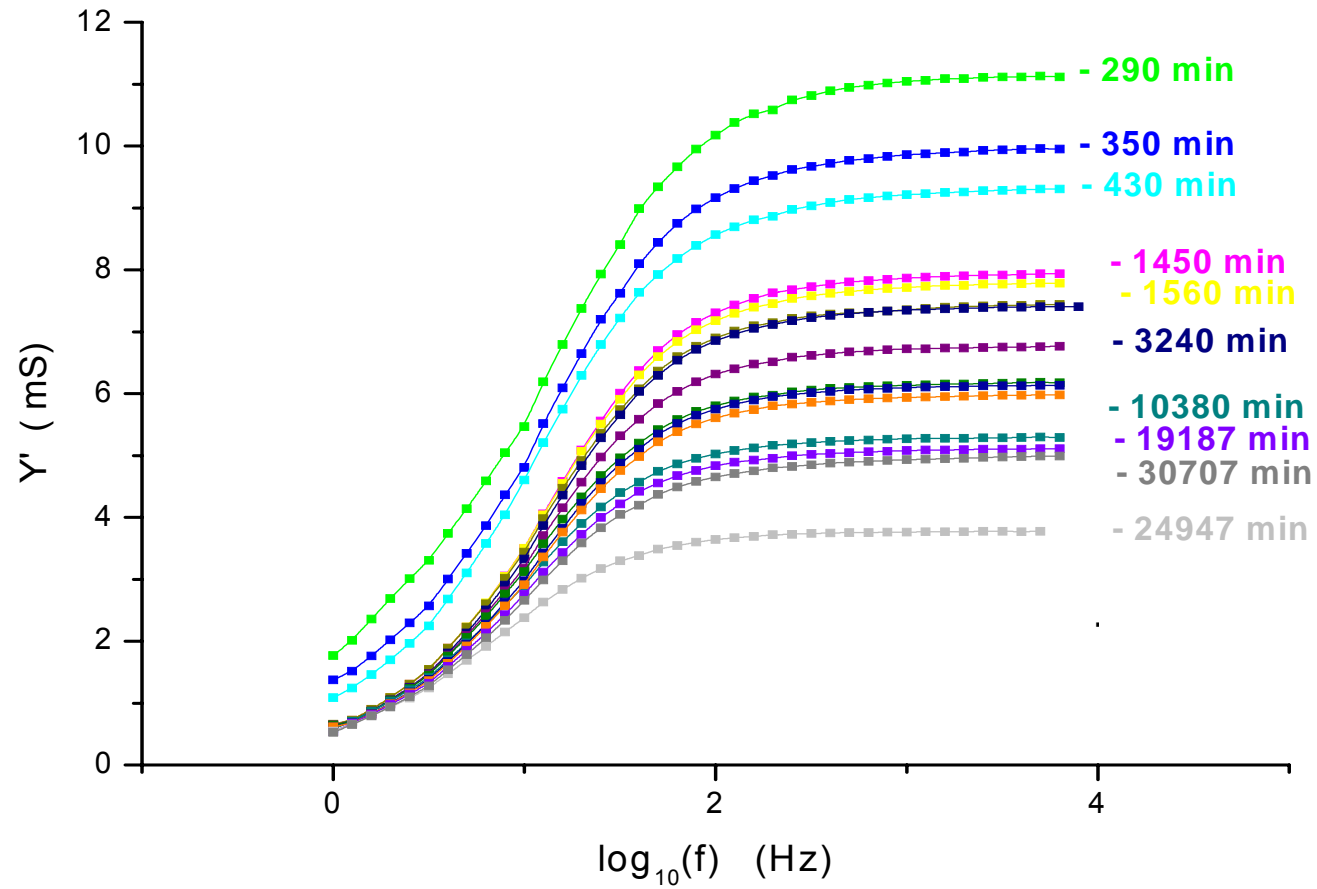


$\delta = f(t)$, após 2 meses de presa

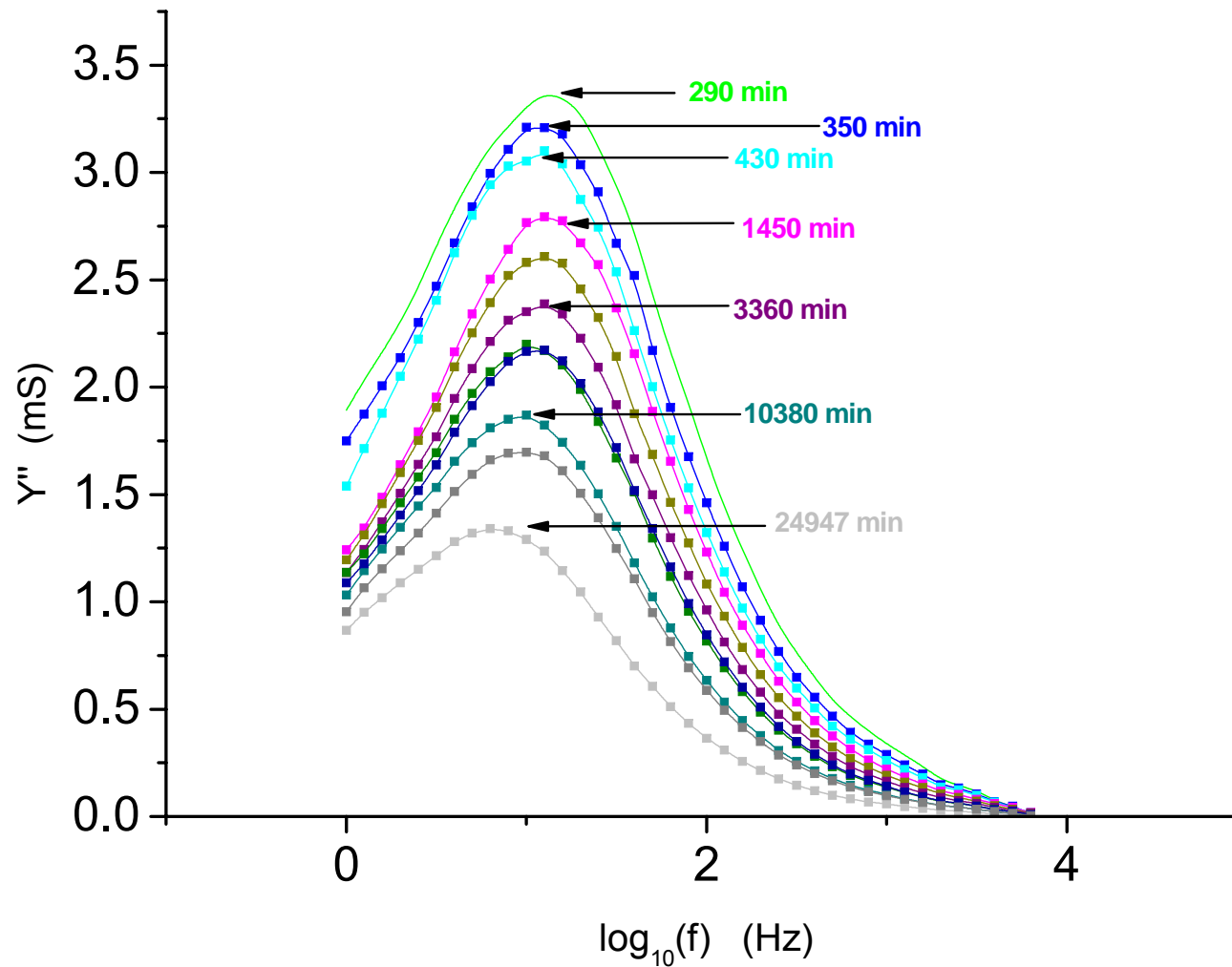
Aplicações



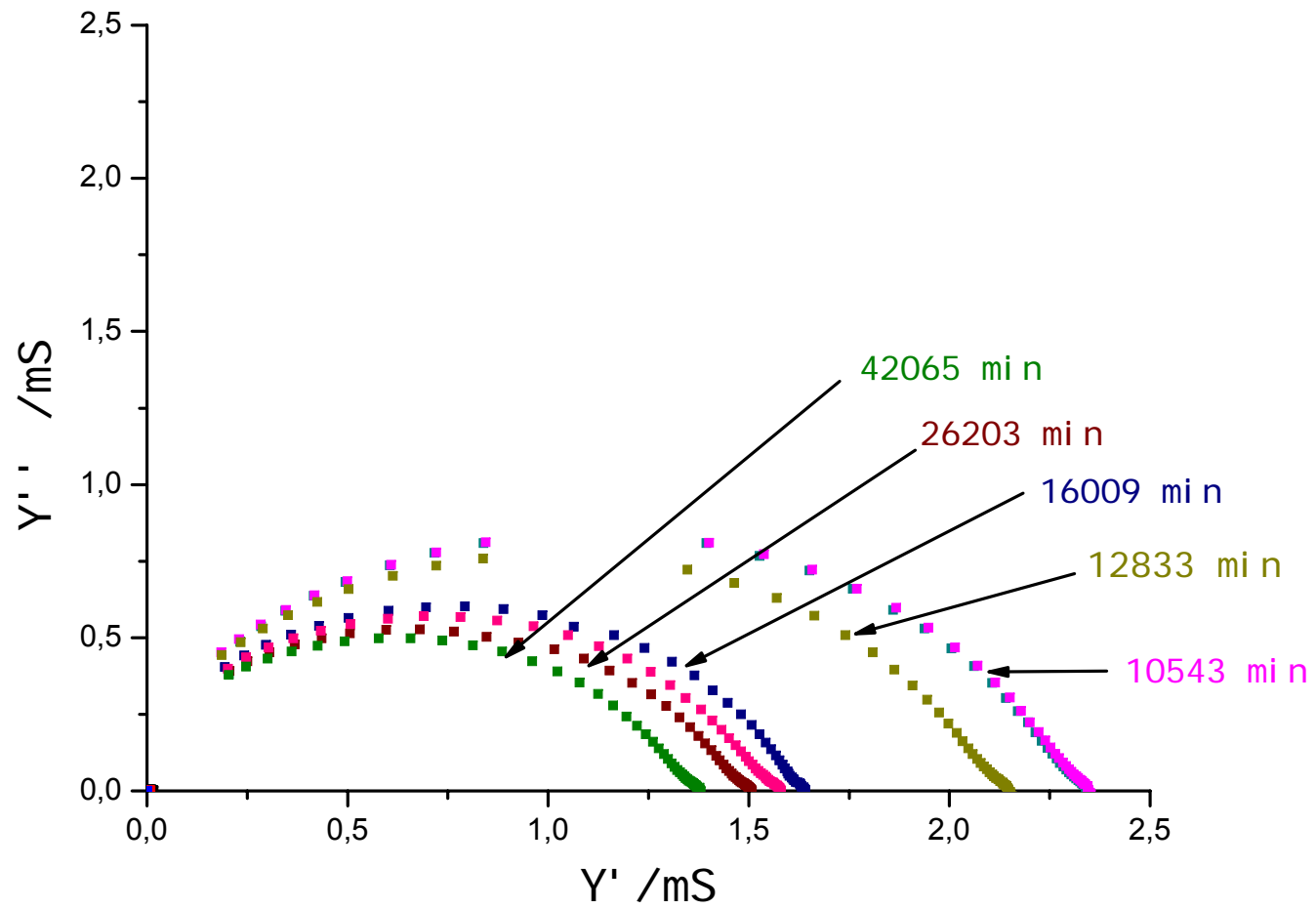
Aplicações



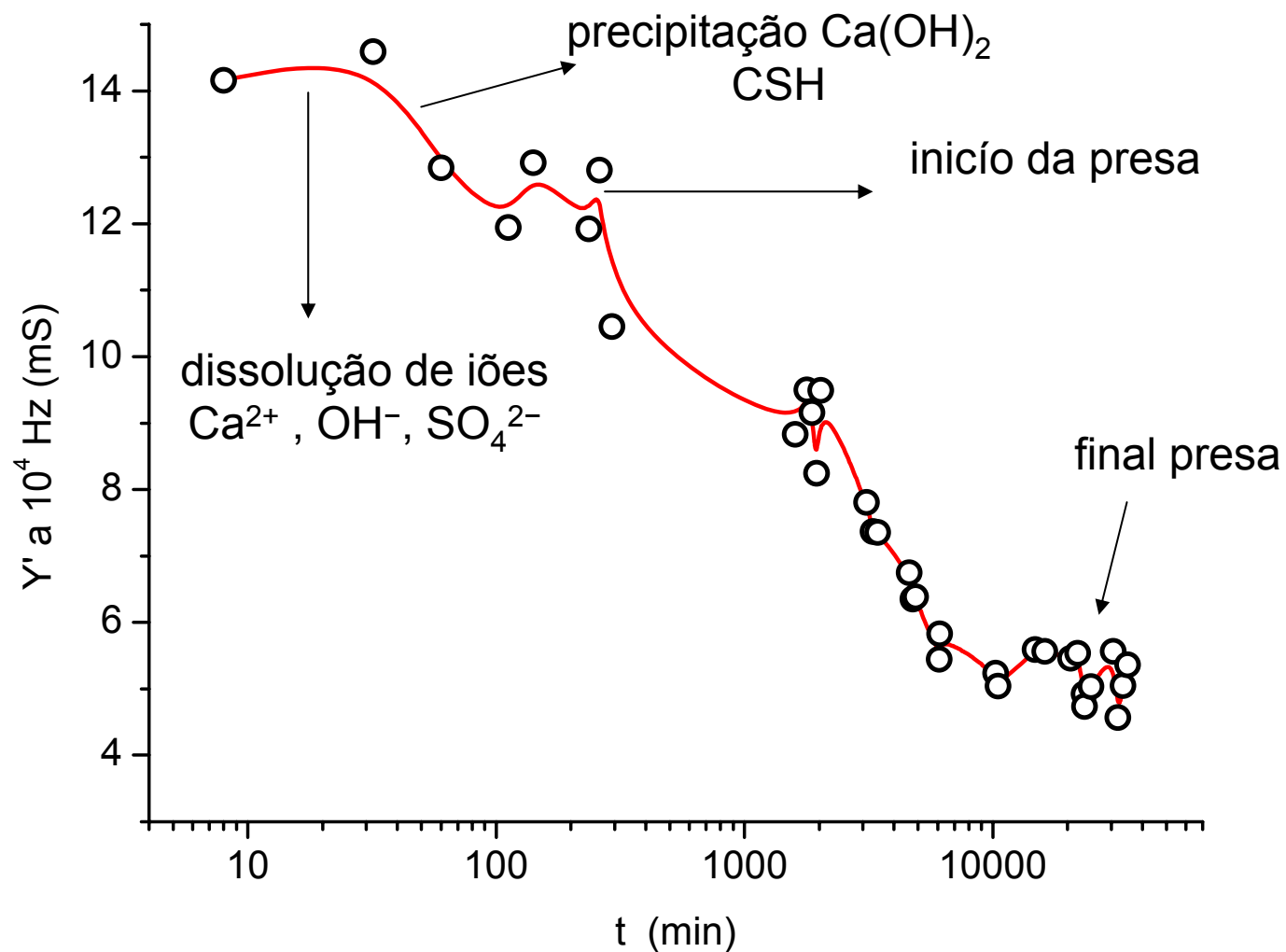
Aplicações



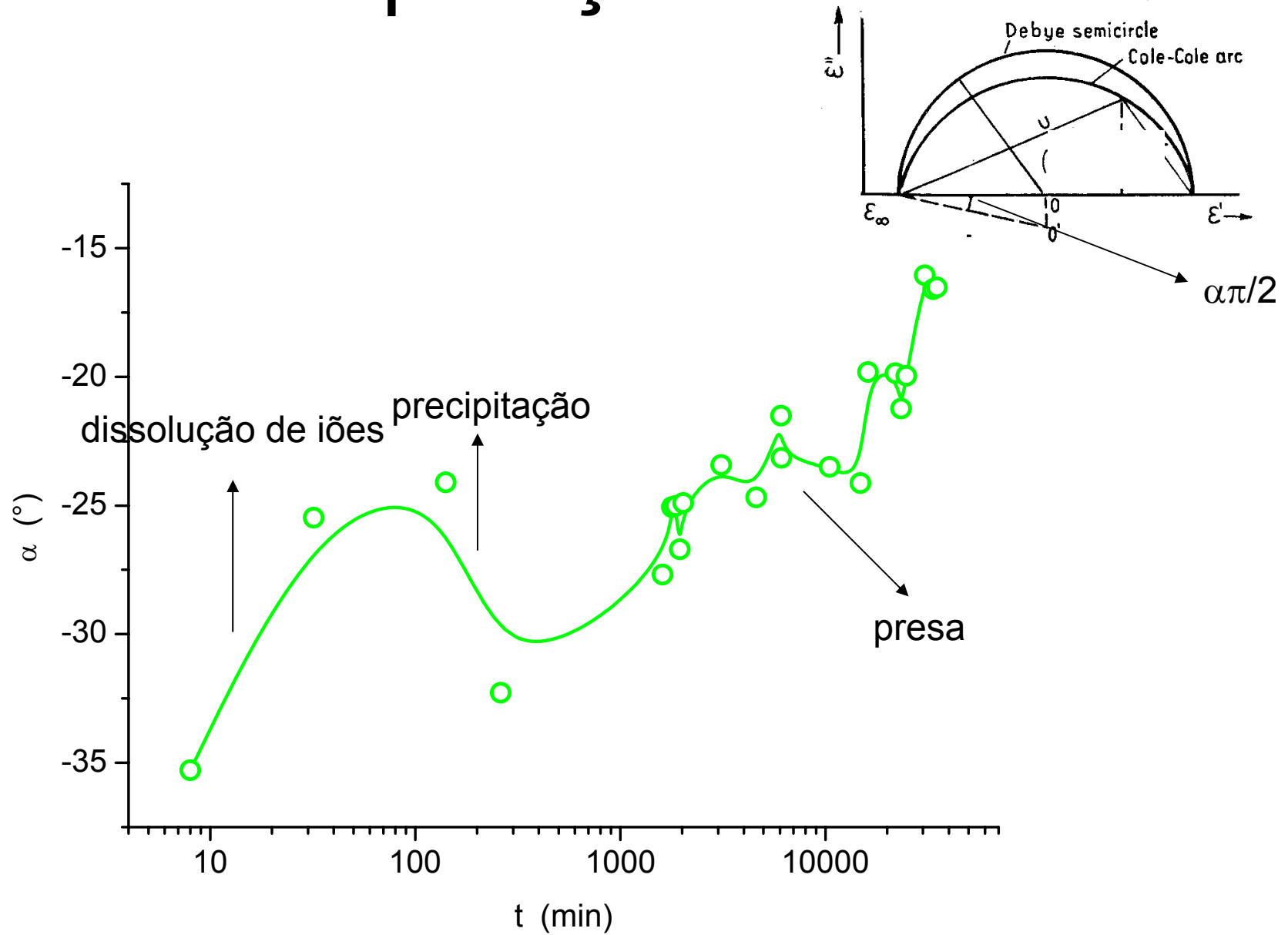
Aplicações



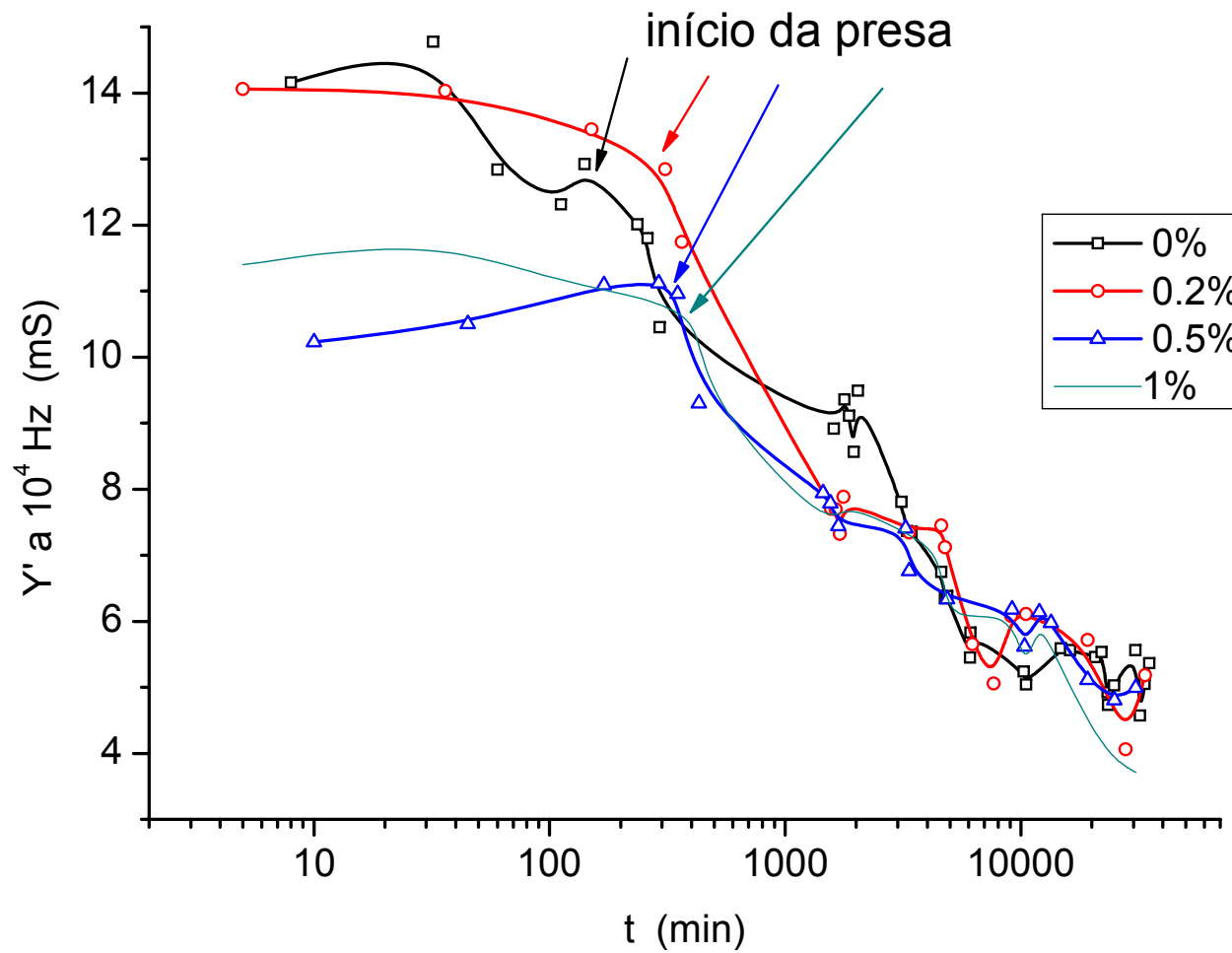
Aplicações



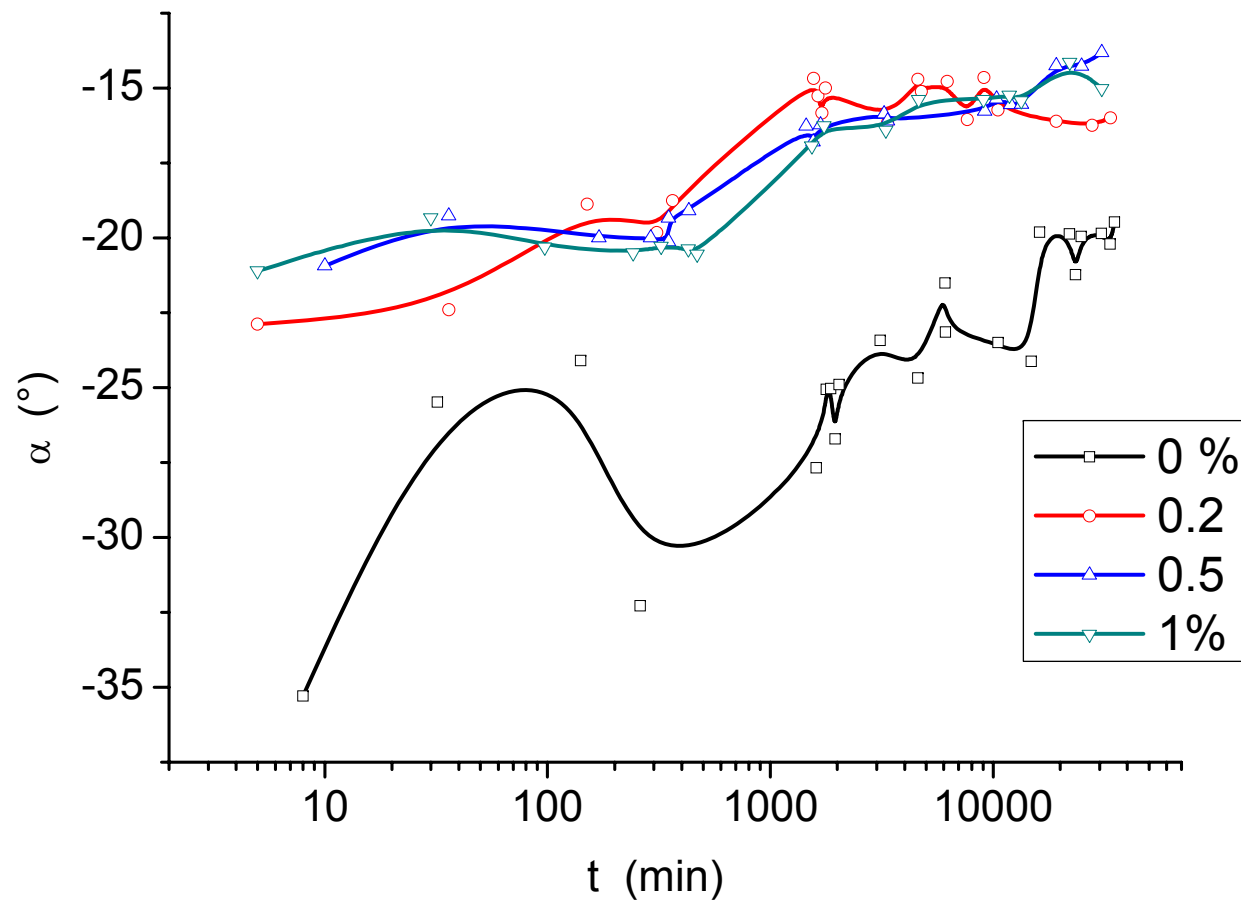
Aplicações



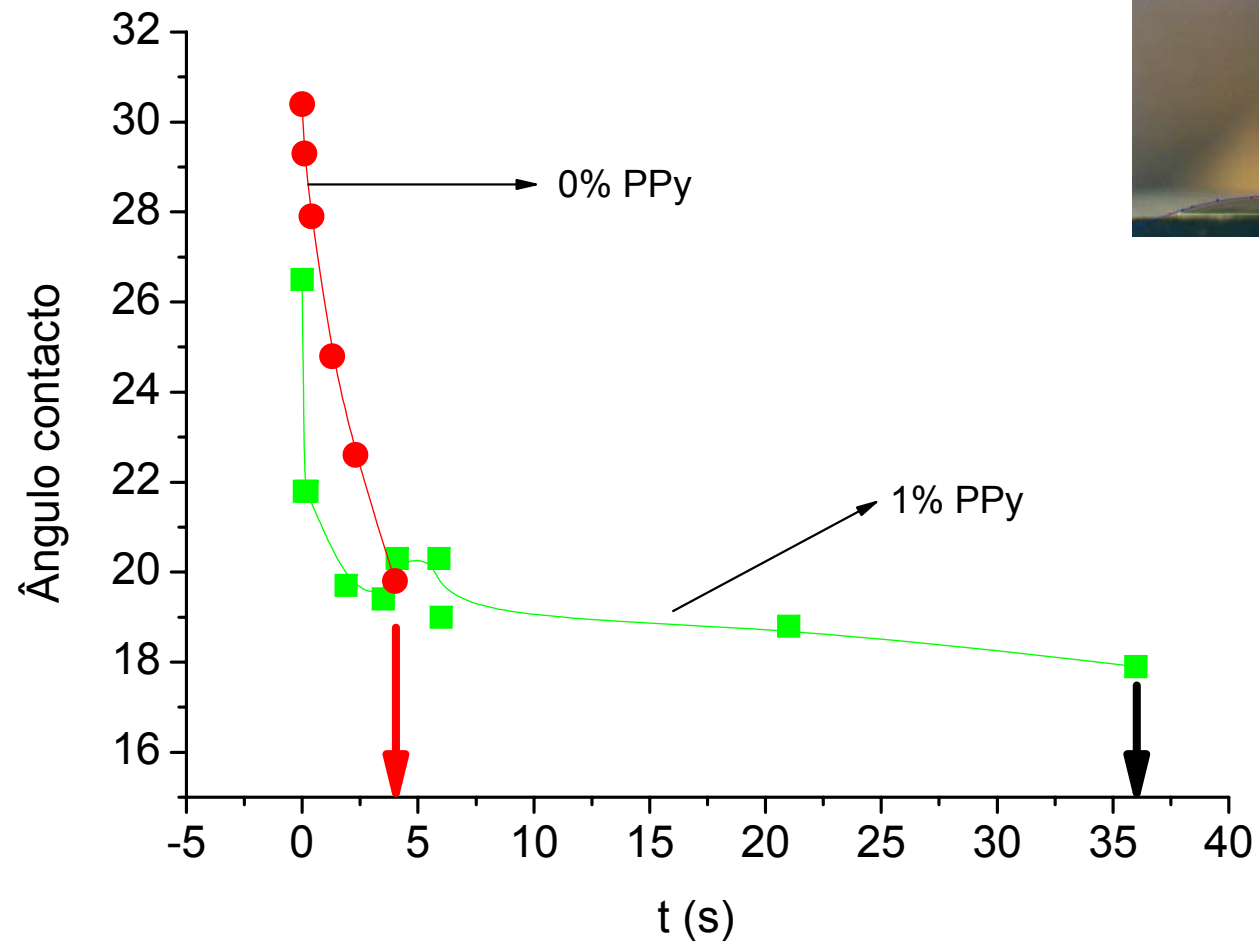
Aplicações



Aplicações



Aplicações



Aplicações

Conclusão

Espectroscopia de Impedância permite:

Seguir a presa do cimento.

Observar a alteração do início da presa devido à introdução de PPy.

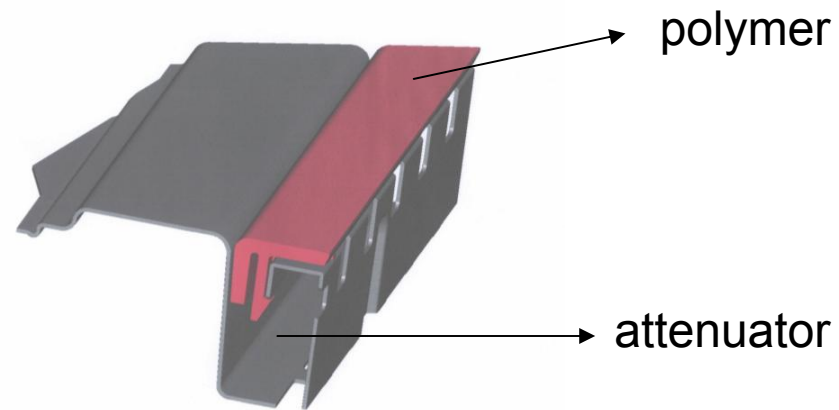
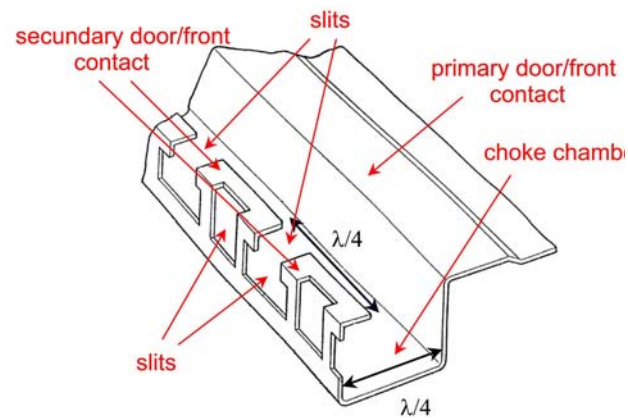
Observar a diminuição de porosidade devido à introdução de PPy.

Os resultados foram correlacionados com medidas de ângulo de contacto e Mecânicas.

Efectuaram-se testes em 4x4x16 (industria).

Aplicações

Porta de forno de microondas



The filler of the cavity with a polymer:

1. prevents the entrance of soil
2. reduces the dimensions of the choke cavity

Aplicações

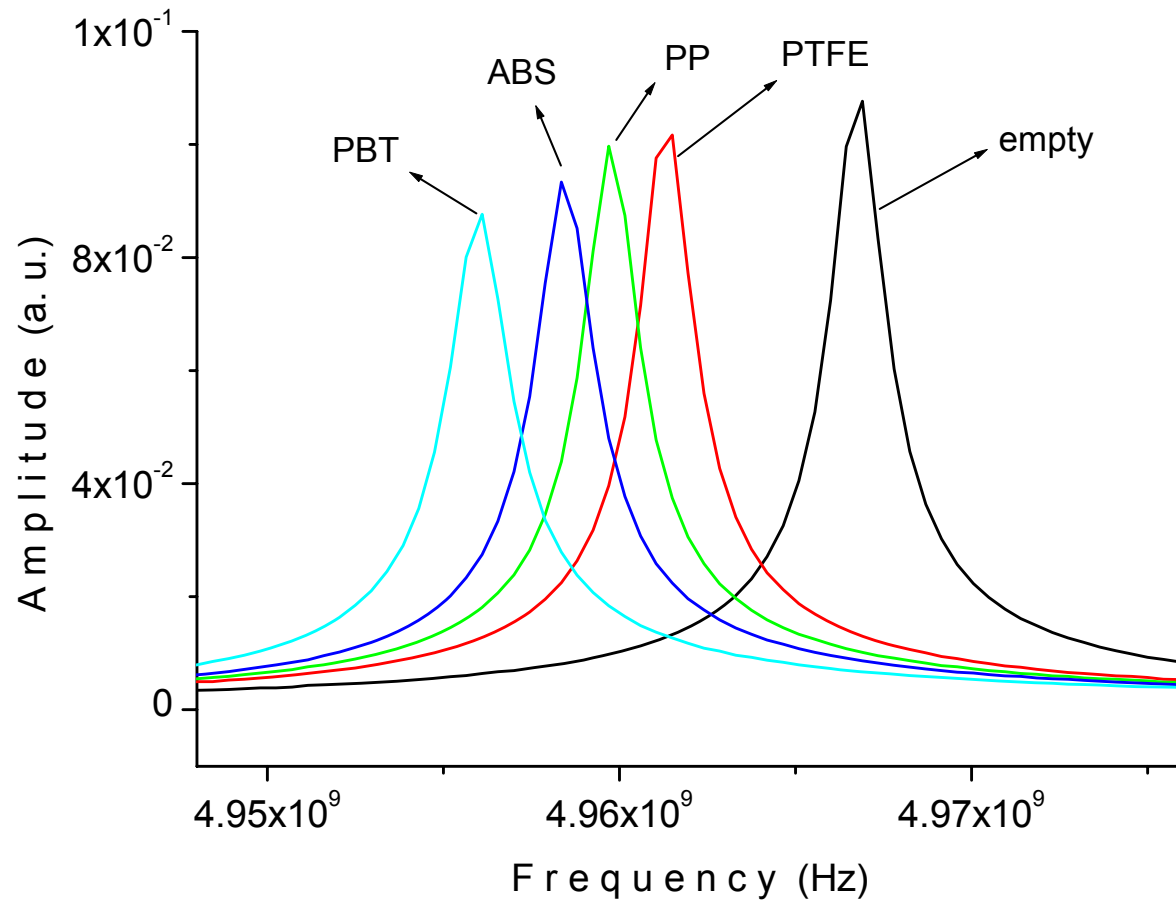
Que polímero usar?

$$P = \frac{1}{2} [(\sigma + \omega \epsilon'') E^2 + \omega \mu'' H^2] \quad \Rightarrow \quad \epsilon'' \downarrow$$

$$\lambda_{ef} = \frac{\lambda}{\sqrt{\epsilon'}} \quad \Rightarrow \quad \epsilon' \uparrow$$

ABS, PBT, PP

Aplicações



$$\varepsilon' = K \frac{\Delta f}{f_0} \frac{V}{v} + 1$$

$$\varepsilon'' = \frac{K}{2} \Delta \left(\frac{1}{Q} \right) \frac{V}{v}$$

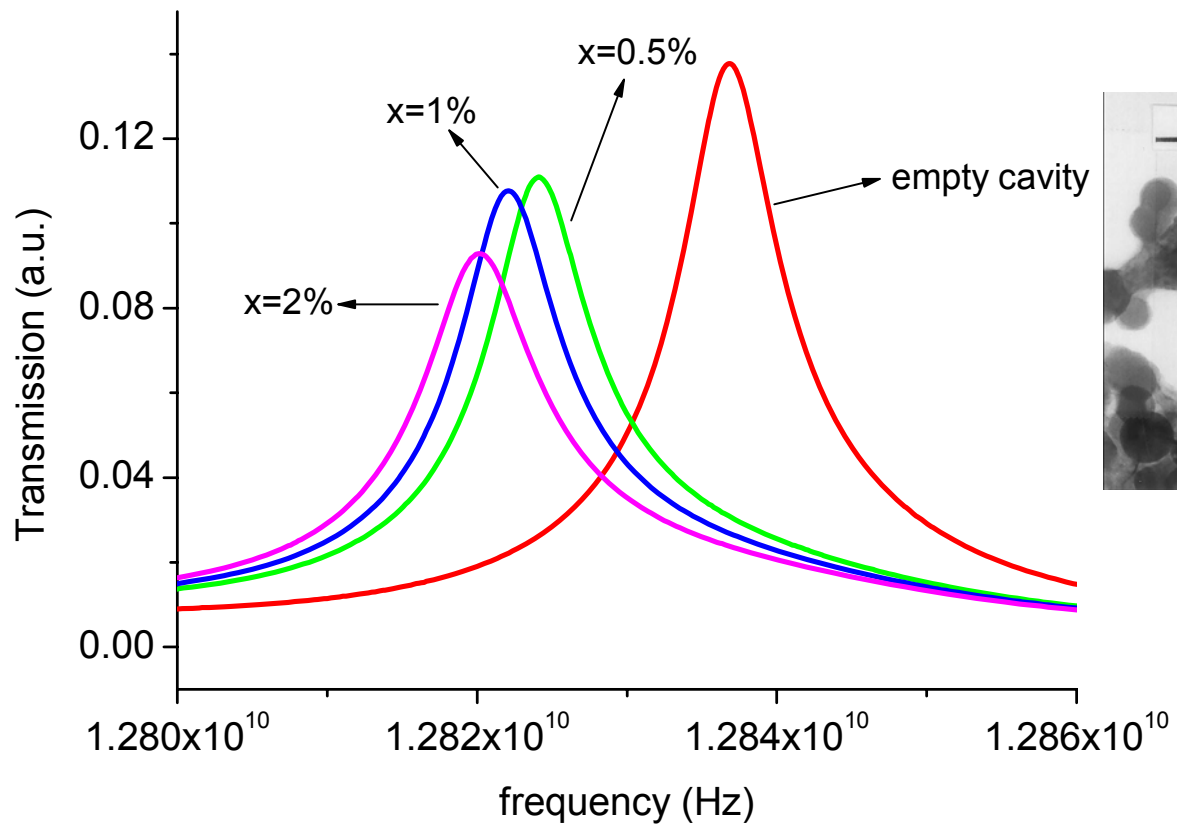
Aplicações

$$\varepsilon^* = \varepsilon' - i\varepsilon''$$

	2.45 GHz		12.8 GHz	
	ε'	$\varepsilon''(10^{-4})$	ε'	$\varepsilon''(10^{-3})$
PP	2.46	11	2.40	11
ABS	2.96	23	2.73	53
PBT	3.68	45	3.24	109

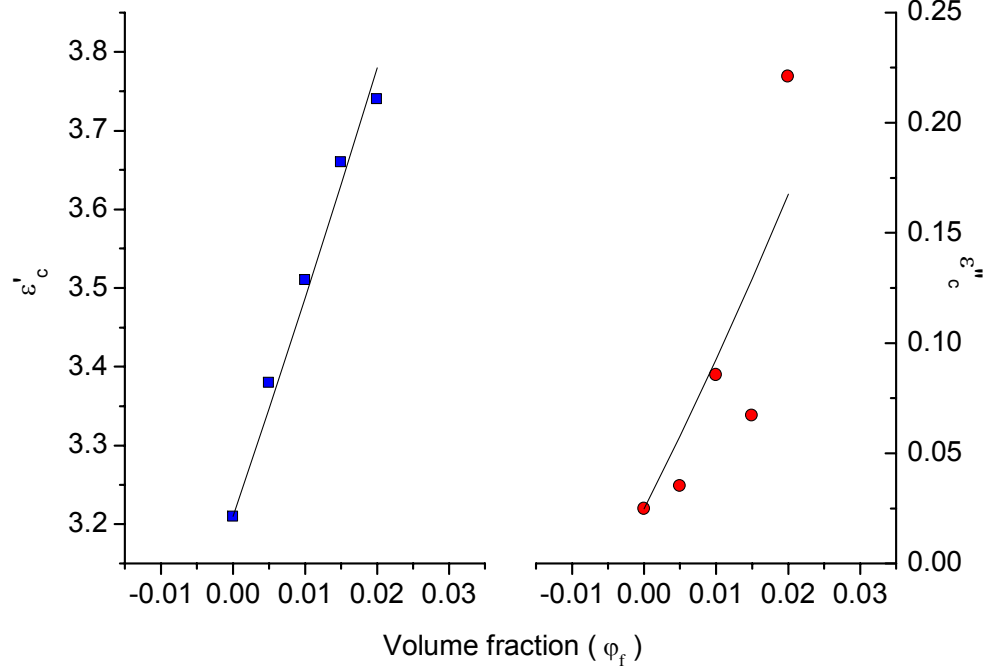
Aplicações

Introdução de carbono em PBT



Aplicações

Modelo de mistura



Generalised
Looyenga

$$\epsilon_c * (\omega)^{1/t} = \varphi_1 \epsilon_1 * (\omega)^{1/t} + \varphi_2 \epsilon_2 * (\omega)^{1/t}$$

$t \sim 3$ (spherical particles)

Aplicações

Conclusões

- Small perturbation to calculate complex permittivity, using a resonant cavity
- PBT is an adequate polymer to prevent leakage in the attenuator hole ($\lambda/4$)
- Introduce 1.5% black carbon particles to optimize the properties
- Generalised Loyenga law to fit the data

Aplicações



Tomato seed (~3 mg)

The price of 1 kg of tomato seed? 50.000 euros!!

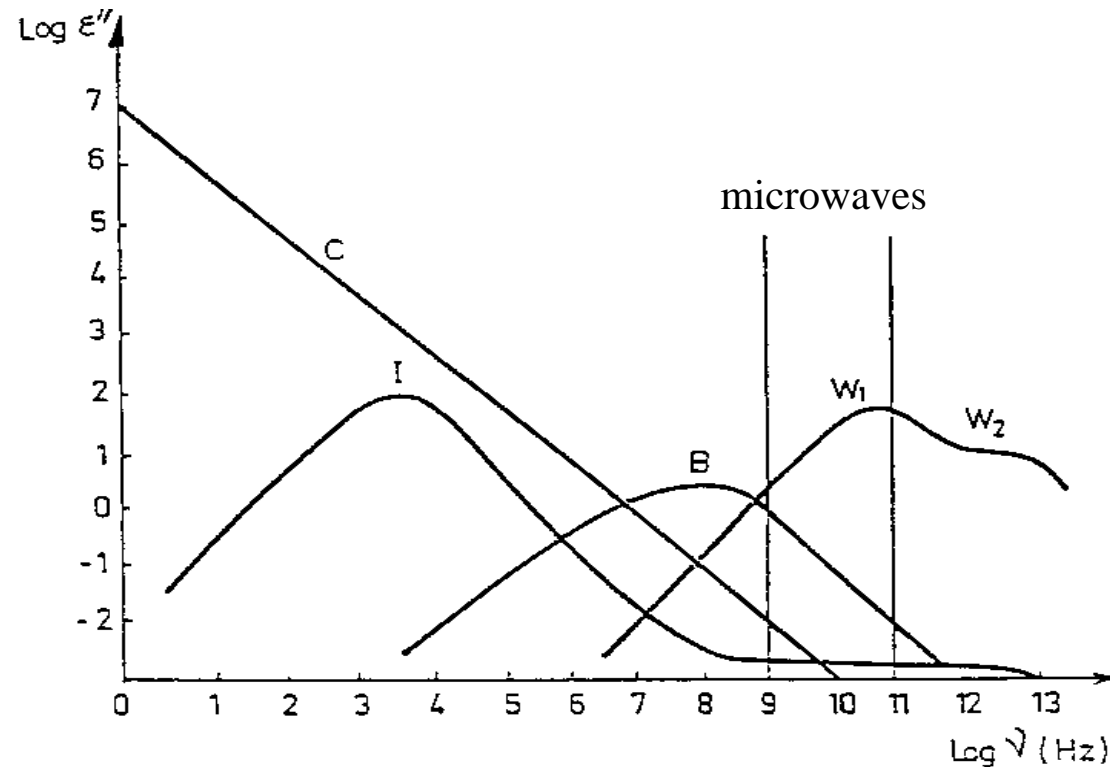
1 kg of seeds \longrightarrow 300.000 seeds

1 germinated seed \longrightarrow 20 tomatoes \longrightarrow 3 kg \longrightarrow 5 euros

1 kg of seeds **produces** 1.5 millions euros

Aplicações

A água

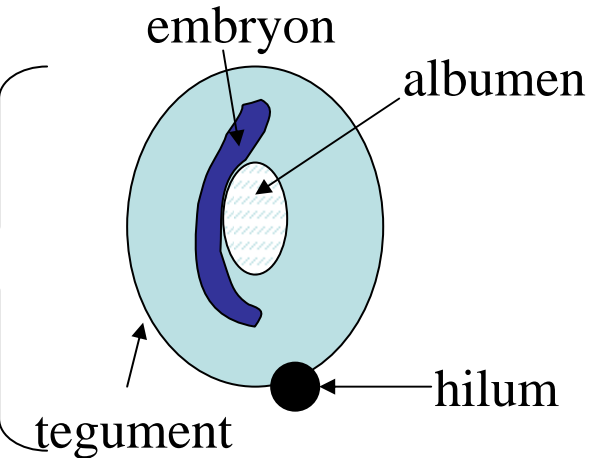
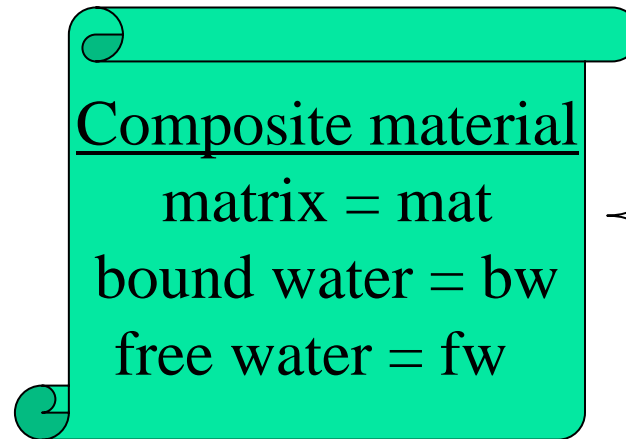


- I kHz domain : Solid Water (ice)
- B MHz domain : Bound or Adsorbed Water
- W GHz domain : Free Water
- C Contribution of the conductivity

Aplicações

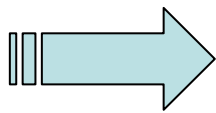
Lei de Wiener

Seed



Using Wiener law we postulate :

- the addition of dielectric contributions
- no dependence with the morphology



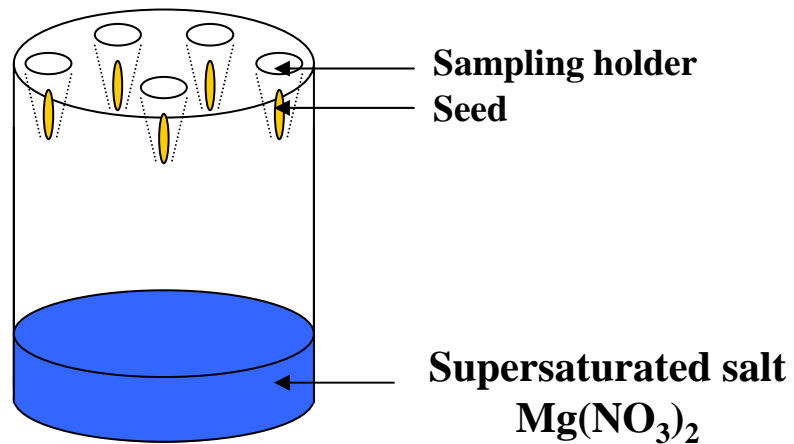
$$\begin{aligned}\varepsilon'' &= \varepsilon''_{\text{mat}} \cdot \varphi_{\text{mat}} + \varepsilon''_{\text{bw}} \cdot \varphi_{\text{bw}} + \varepsilon''_{\text{fw}} \cdot \varphi_{\text{fw}} \\ \varepsilon' &= \varepsilon'_{\text{mat}} \cdot \varphi_{\text{mat}} + \varepsilon'_{\text{bw}} \cdot \varphi_{\text{bw}} + \varepsilon'_{\text{fw}} \cdot \varphi_{\text{fw}}\end{aligned}$$

Aplicações

			Living seed			Death seed		
	ϵ'	ϵ''	%	partial ϵ'	partial ϵ''	%	partial ϵ'	partial ϵ''
Matrix	3	0.01	80	2.4	$0.8 \cdot 10^{-2}$	80	2.4	$0.8 \cdot 10^{-2}$
Bound water	10	0.1	18	1.8	$1.8 \cdot 10^{-2}$	2	0.2	$0.2 \cdot 10^{-2}$
Free water	70	30	2	1.4	$60 \cdot 10^{-2}$	18	12.6	$540 \cdot 10^{-2}$
Total				5.6	$62.6 \cdot 10^{-2}$		16.2	$541 \cdot 10^{-2}$

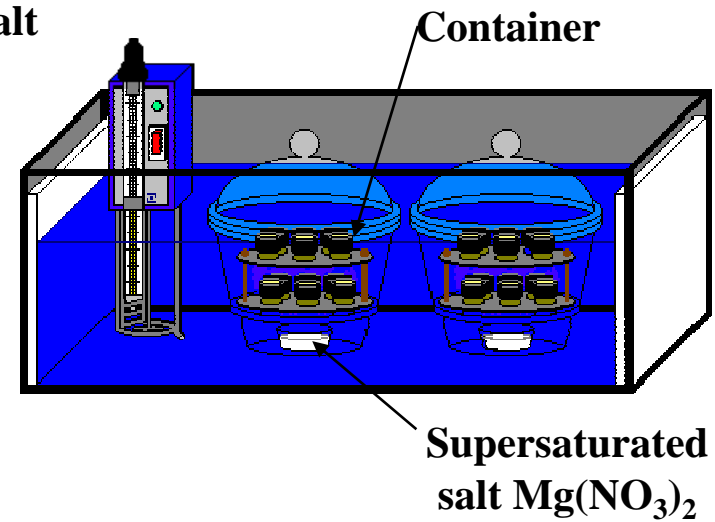
Aplicações

Condicionamento de sementes

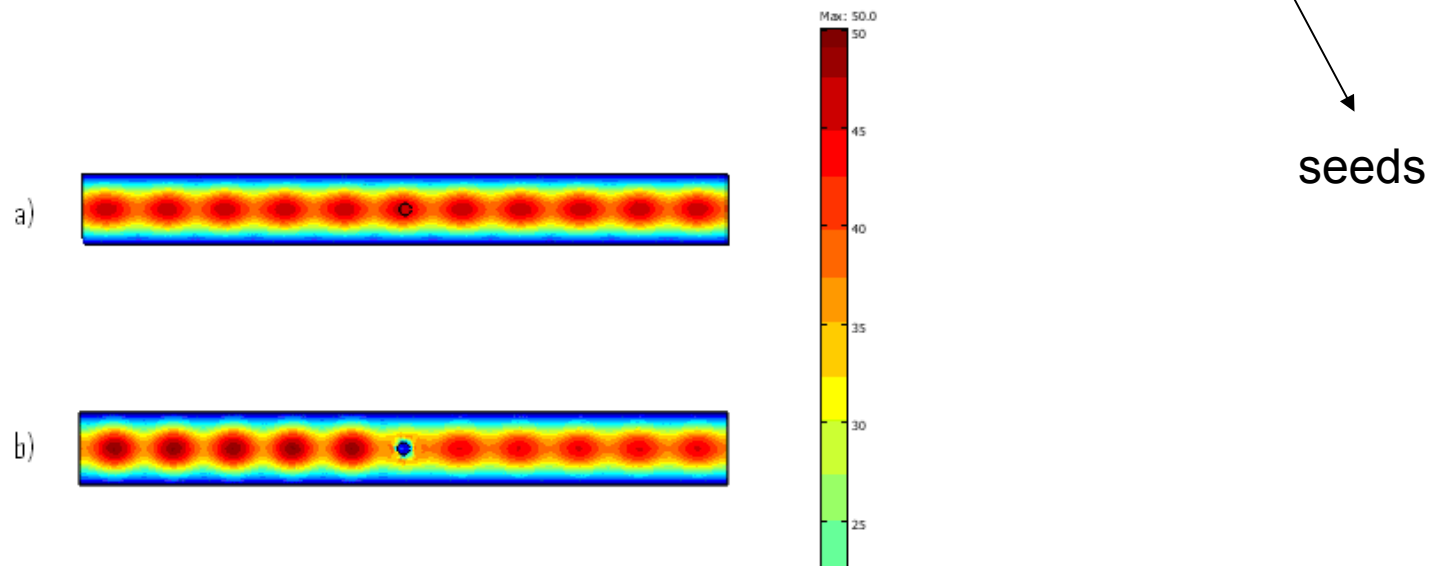
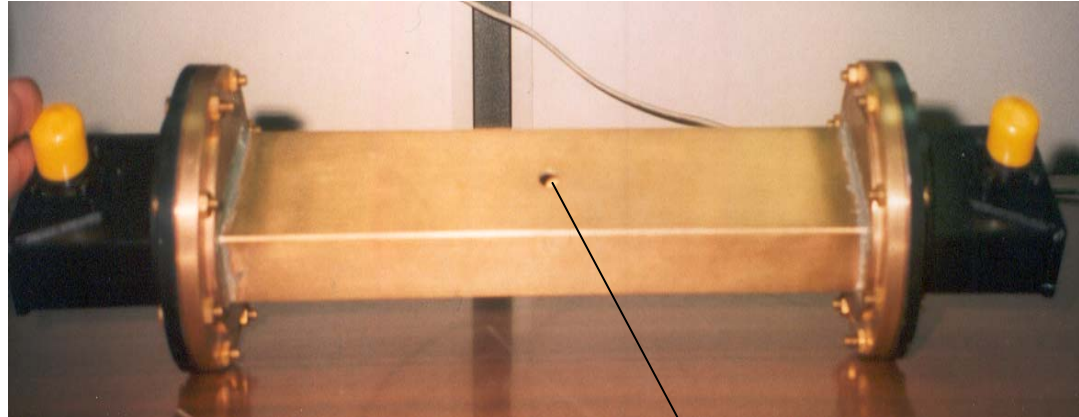


$T=25^\circ\text{C}$

$\text{RH}=50\%$

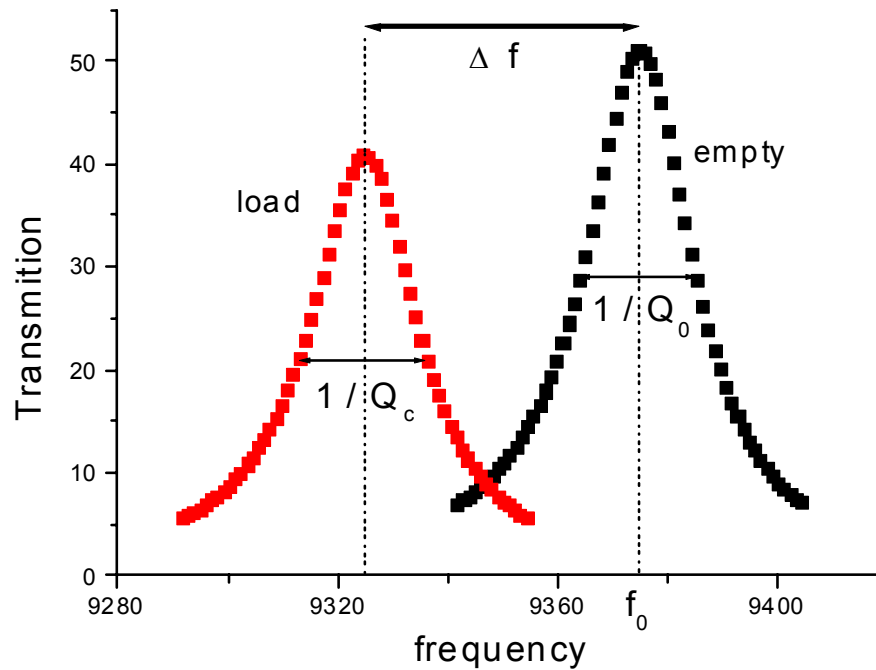


Aplicações



seeds

Aplicações



$$(\epsilon' - 1) \frac{v}{V} = K \frac{\Delta f}{f_0}$$

$$\epsilon'' \frac{v}{V} = \frac{K}{2} \Delta \left(\frac{1}{Q} \right)$$

v = Volume of the sample

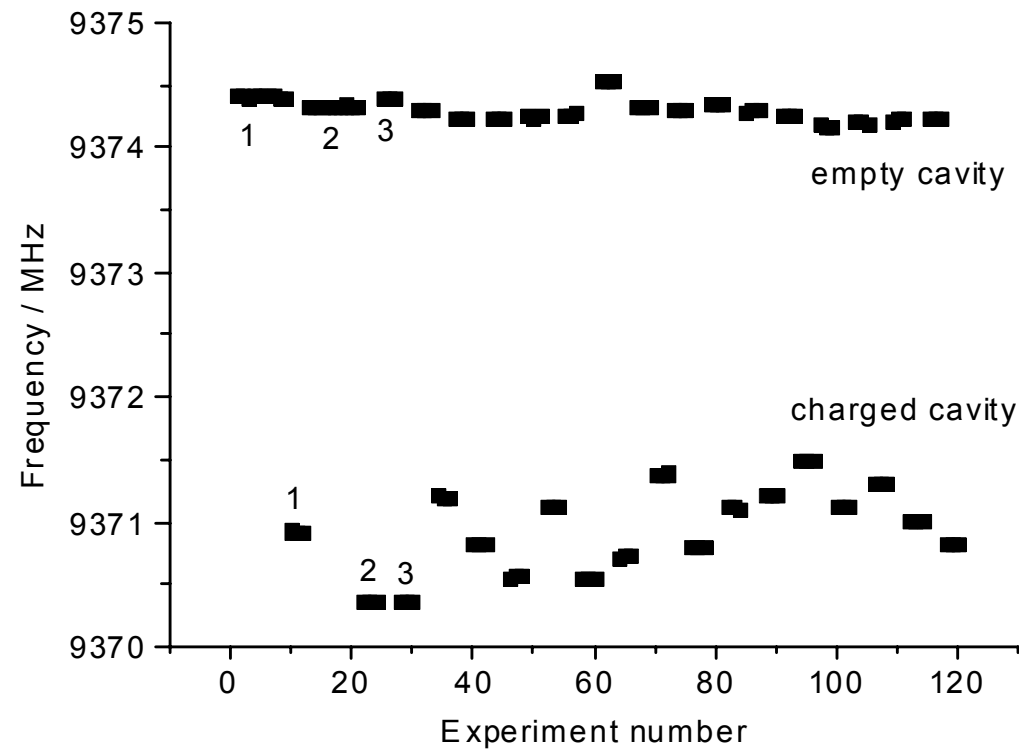
V = Volume of the cavity

K = Depolarisation
or coupling factor

Teoria das pequenas perturbações

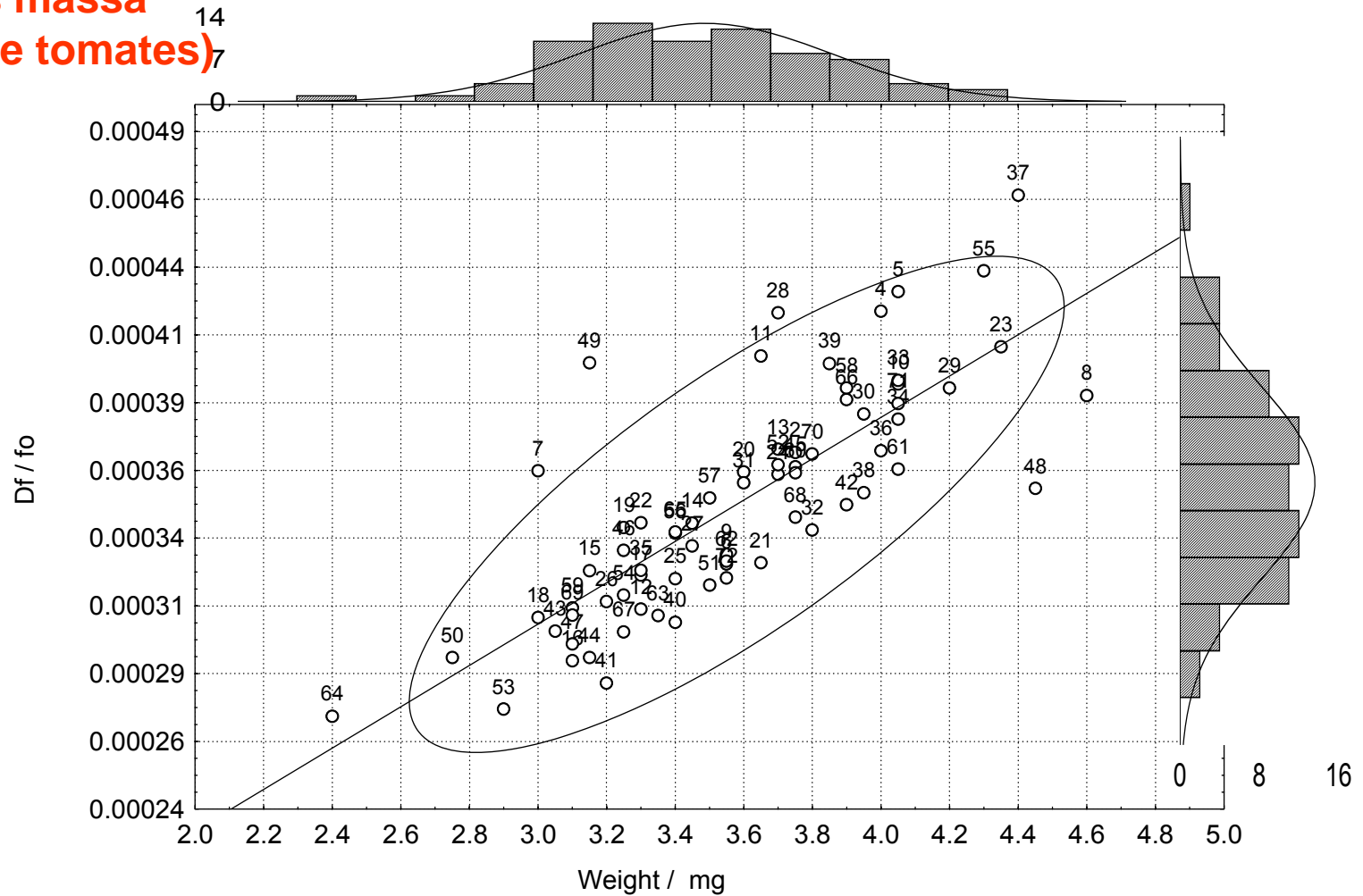
Aplicações

Cavidade em carga



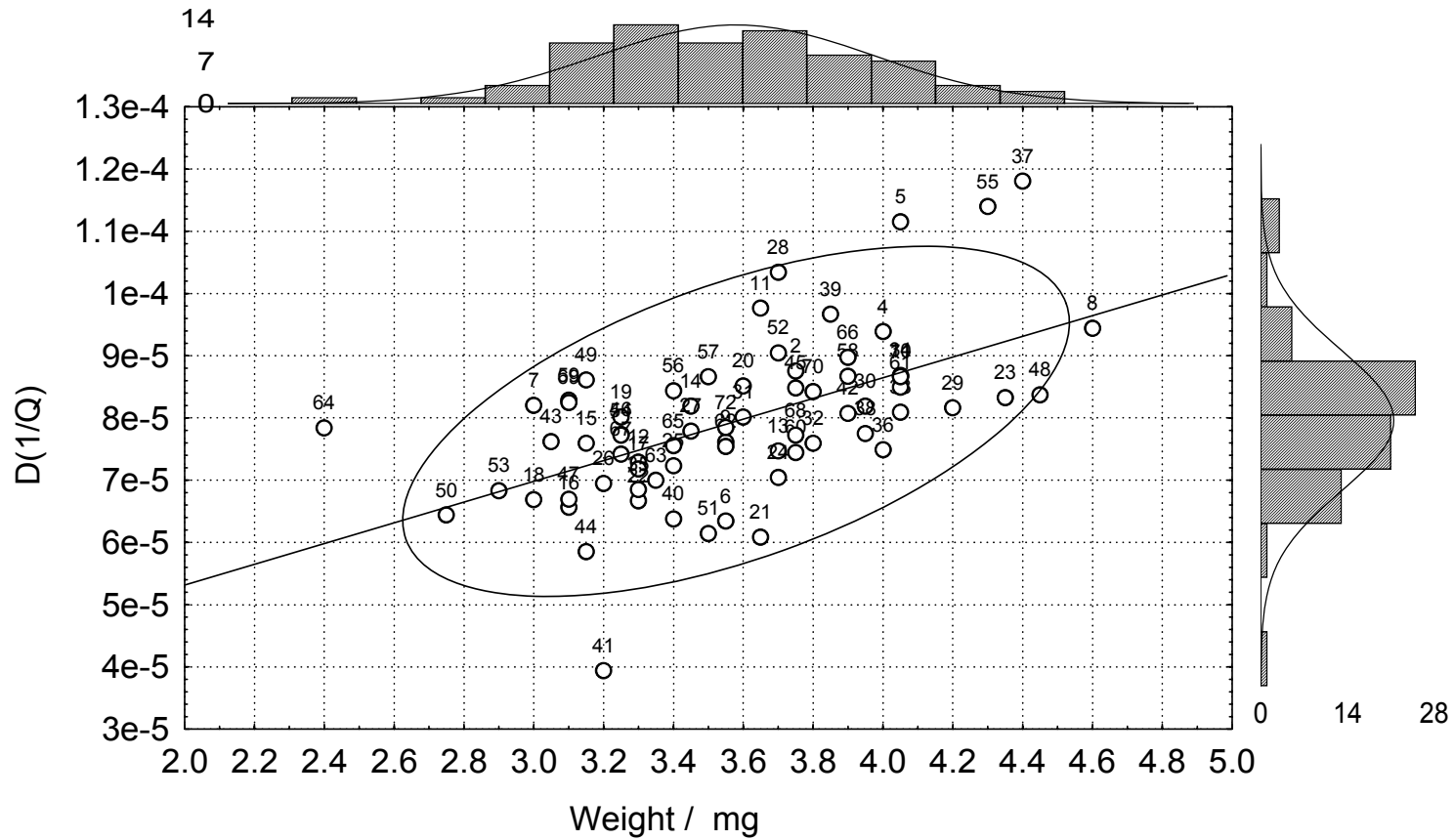
Aplicações

$\Delta f/f_0$ versus massa
(semente de tomates)

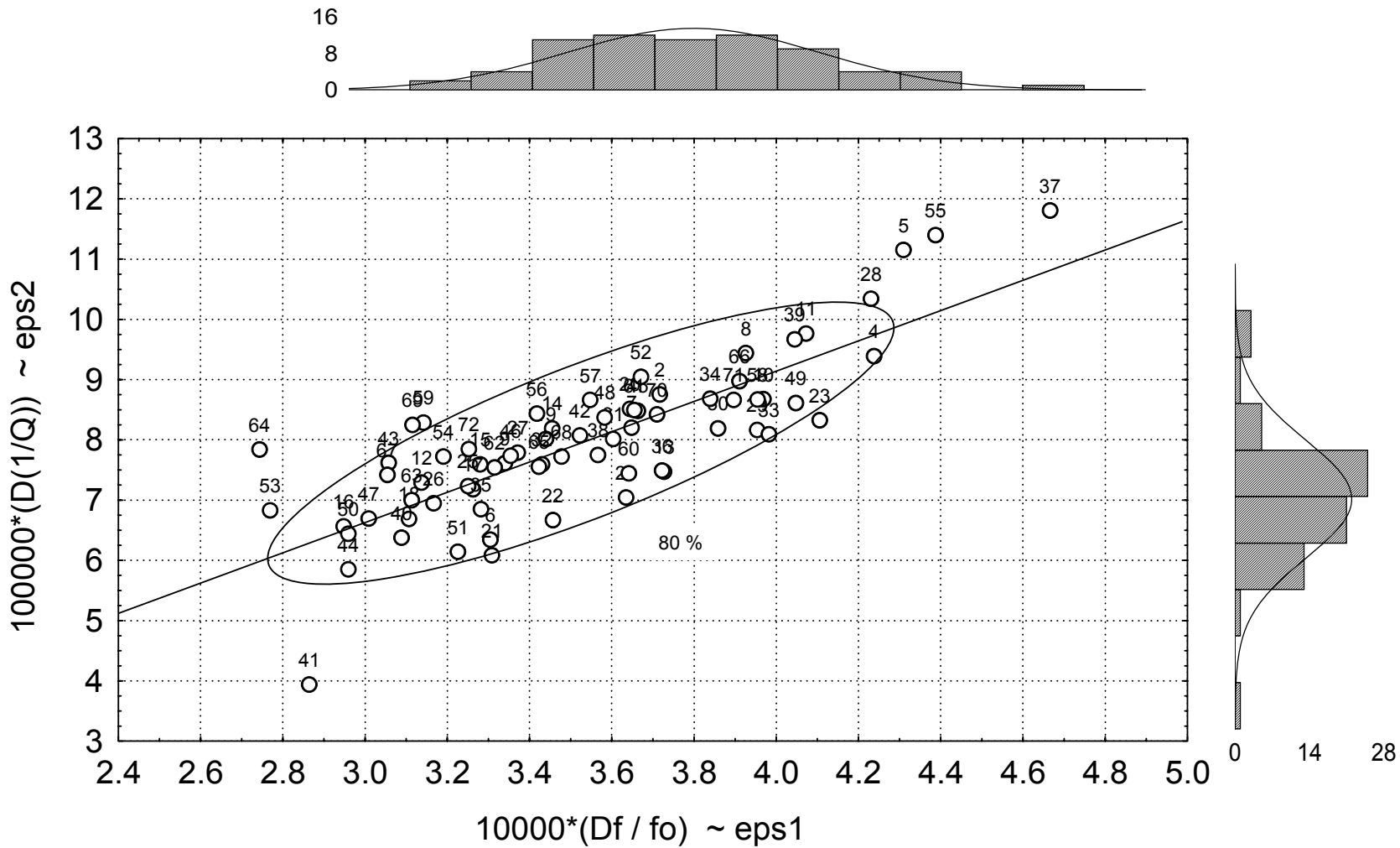


Aplicações

$\Delta(1/Q)$ versus massa
(semente de tomates)

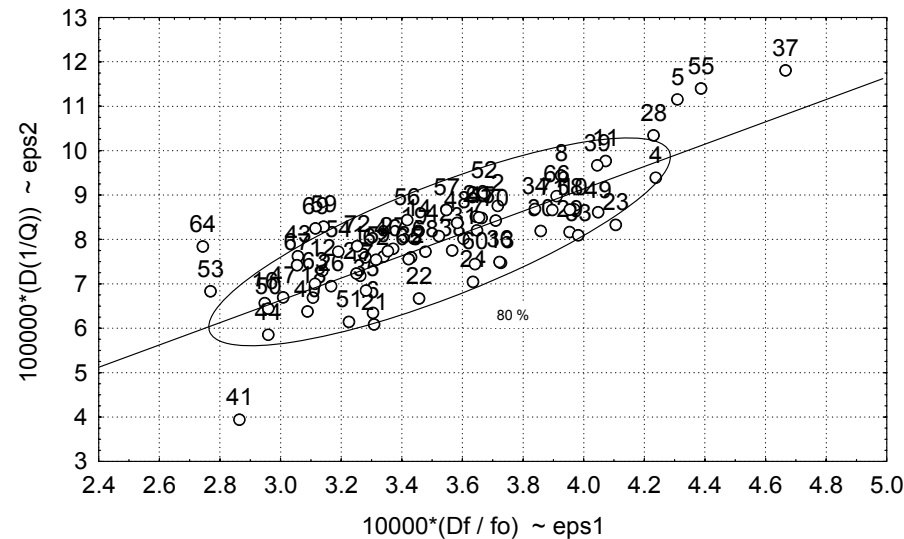


Aplicações



Aplicações

1st critério de eliminação

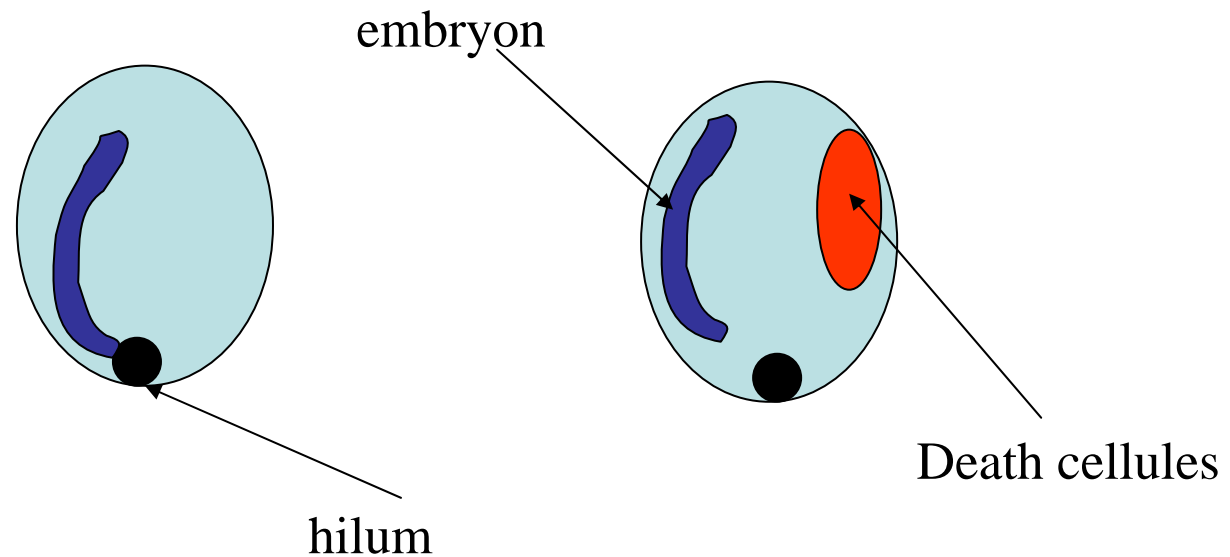


The seeds outside the ellipsoid of statistical dispersion are probably death!

Aplicações

Anisotropia da semente

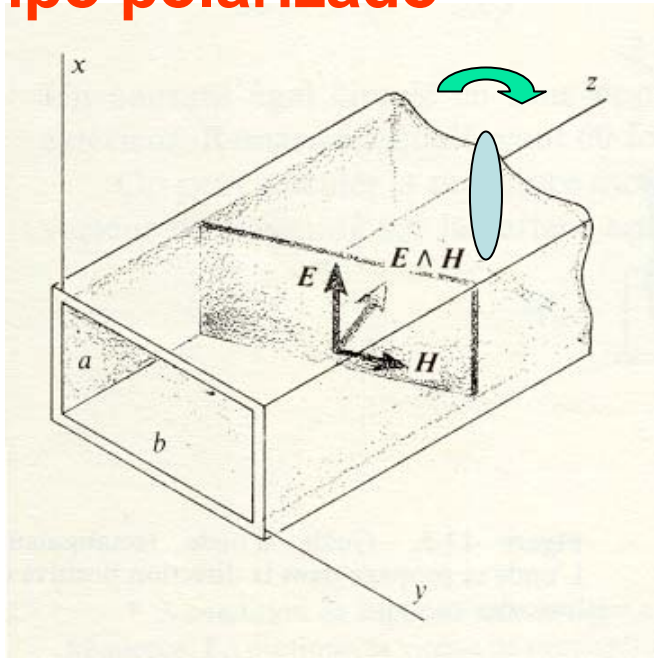
- a) asymmetric morphology
- b) dielectric heterogeneity



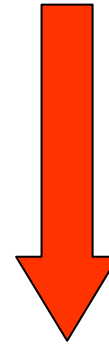
Death cellules ➡ Increasing of heterogeneity ➡ Anisotropy

Aplicações

Campo polarizado



E is strongly polarised

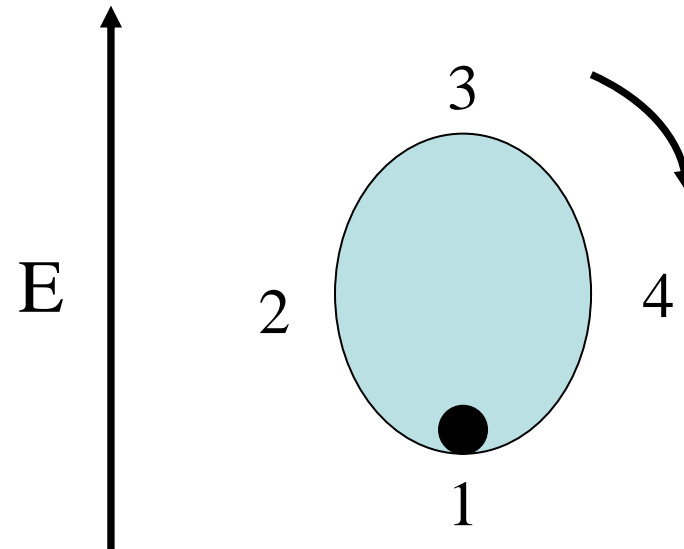


The rotation of seed show us, with the measurement of variation of coupling factor (K), the anisotropy or dielectric heterogeneity

Aplicações

Medida da anisotropia

Rotation of the seed inside the cavity
(4 perpendicular positions)



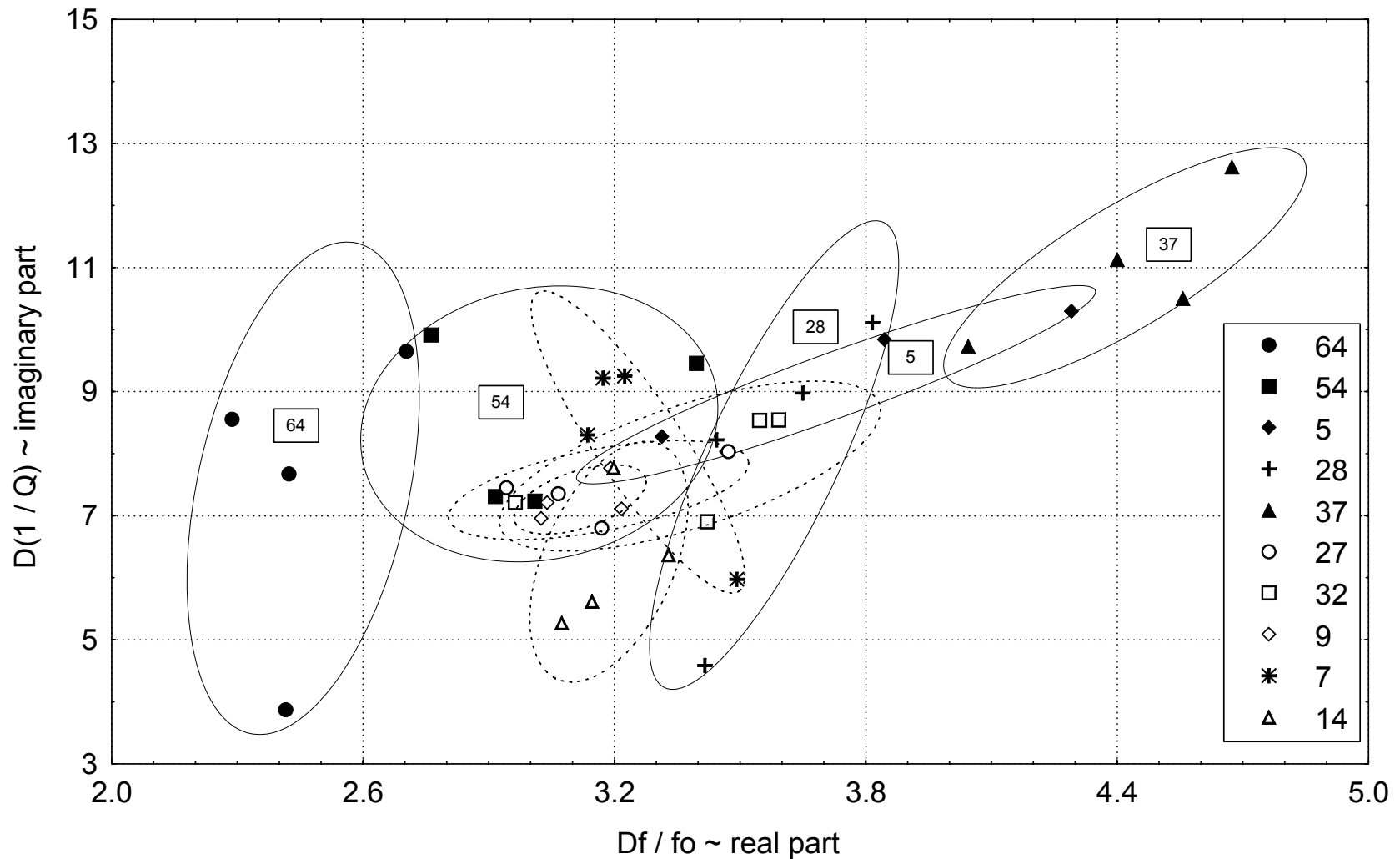
In the ellipsoid distribution we choose:

5 seeds outside + 5 seeds inside
(64,54,5,37,28) (7,9,14,27,32)

Aplicações

2º critério de eliminação

Tomatoes (K 4330 medium) (9 GHz 25°C RH=50%)



Aplicações

Eliminação de sementes

1st criterion – The high quantity of death cellules (seeds outside the ellipsoid) probably implies a death seed!

2nd criterion – The seeds (inside or outside the ellipsoid) with high anisotropy are probably death!

Aplicações

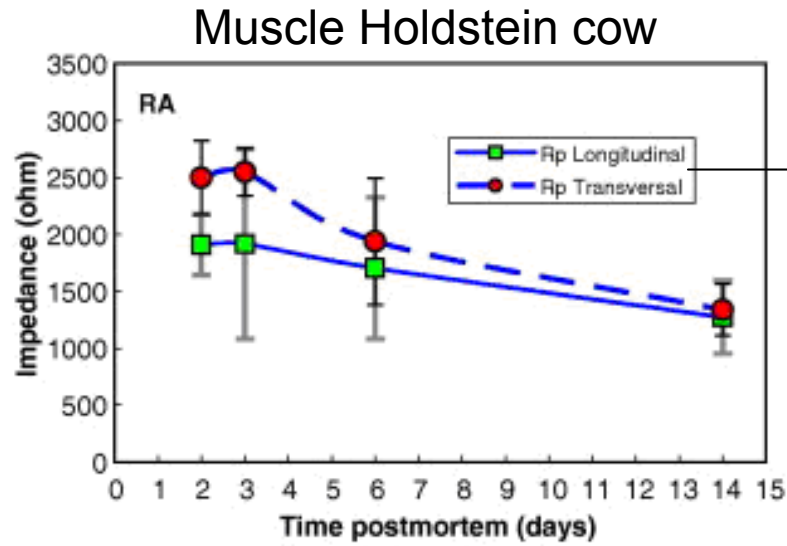
Conclusões

The statistical discrimination with these criteria is rather good

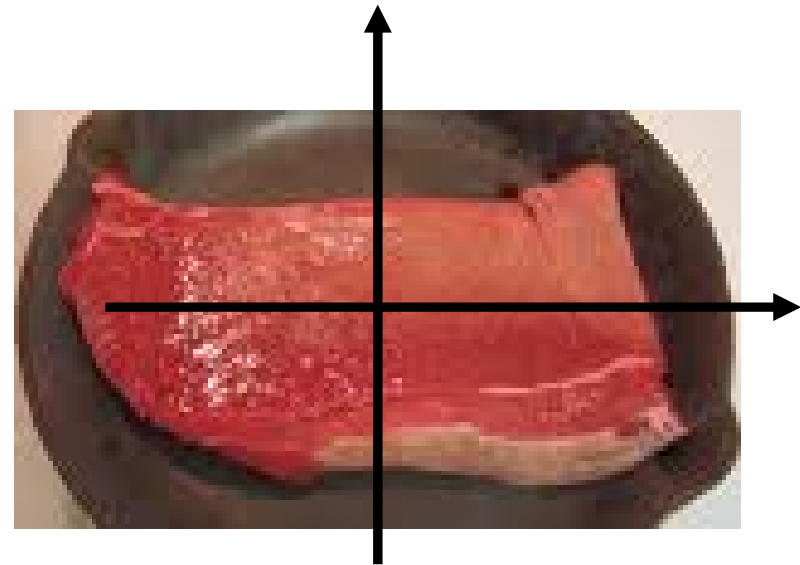
The germination of the seeds confirm this discrimination

This lab methodology can be implemented in industry

Sementes e

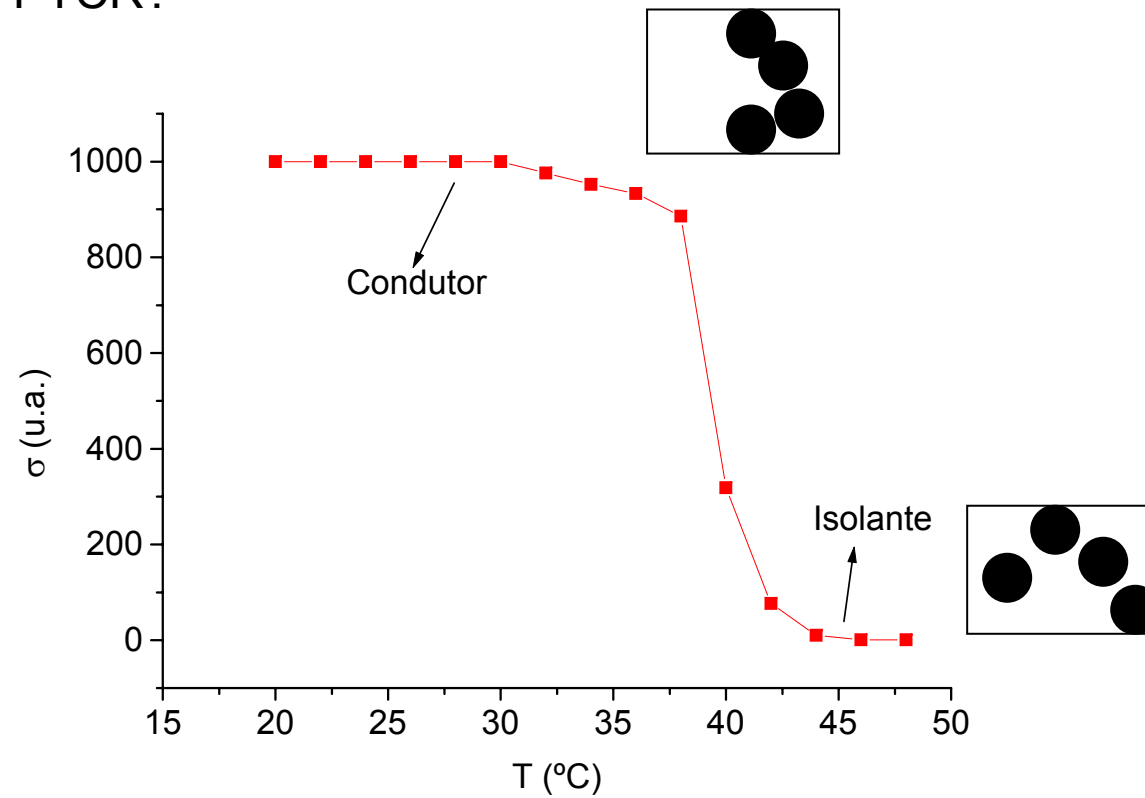


$\alpha \epsilon''$

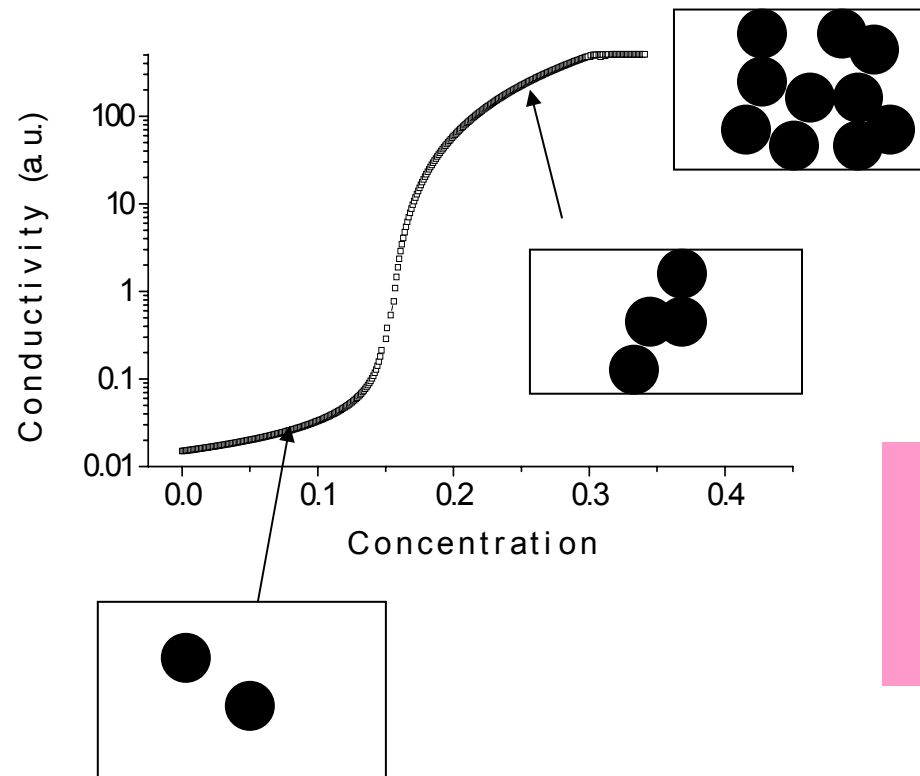


Aplicações

O que é o efeito PTCR?



Aplicações



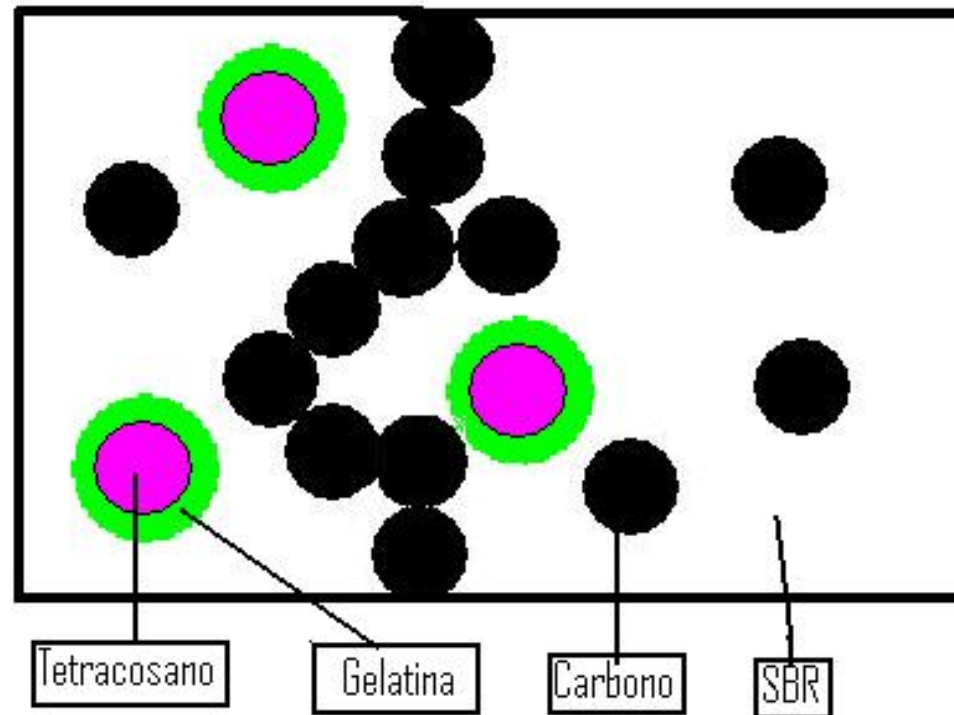
A percolação

Matriz isolante: PS, SBR

Condutor: C, Fe, PPy

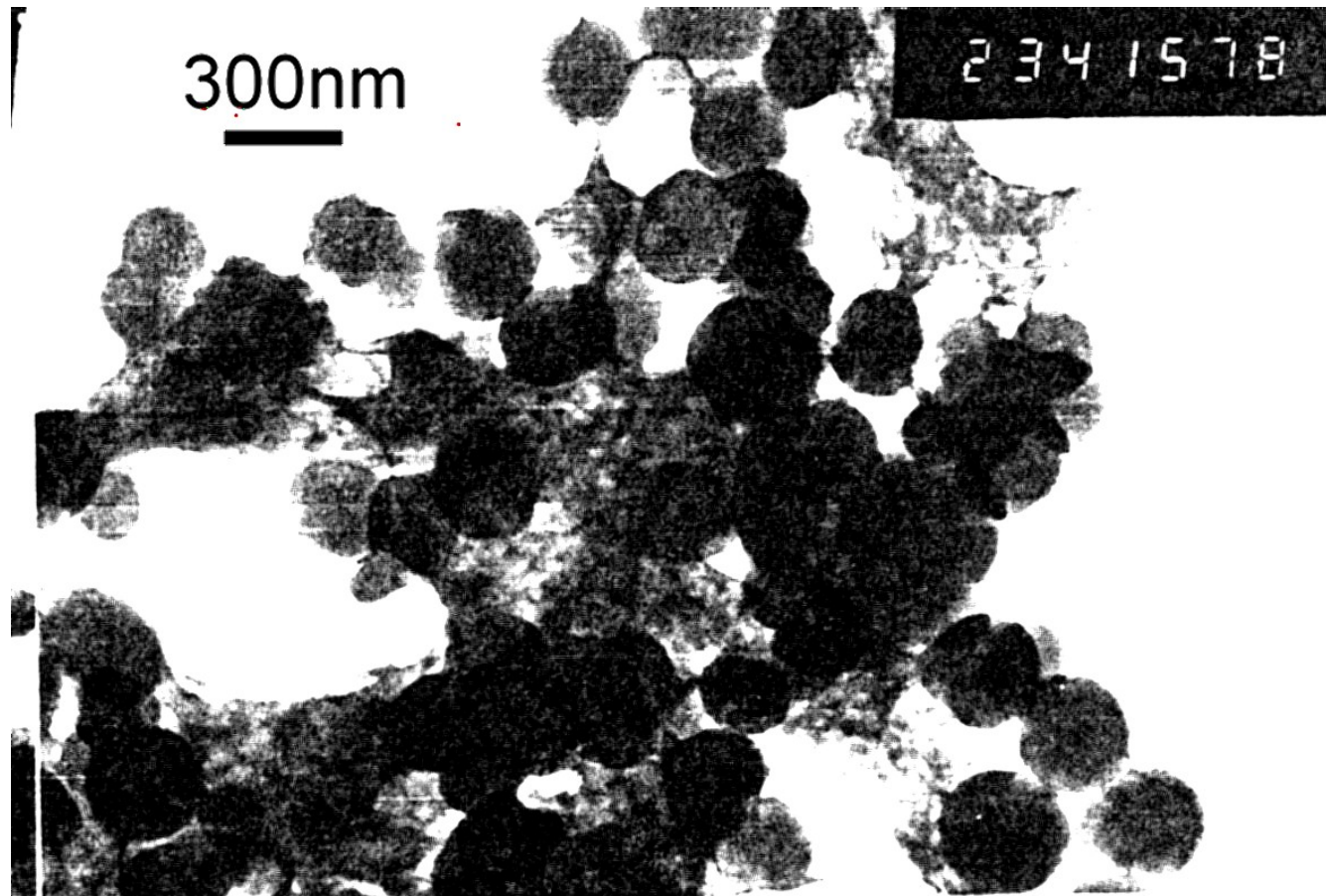
Aplicações

Como conseguir o efeito PTCR?



Aplicações

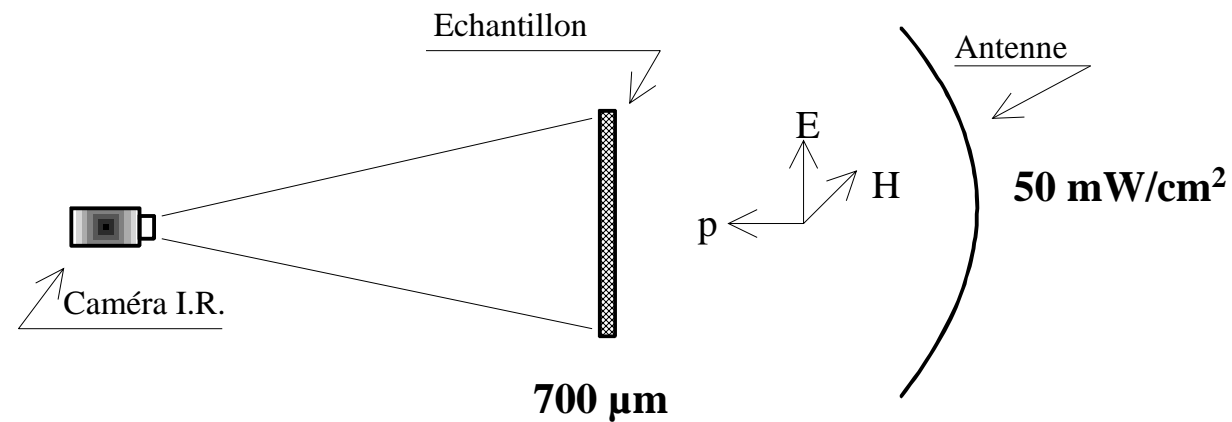
Partículas de carbono na matriz



Aplicações

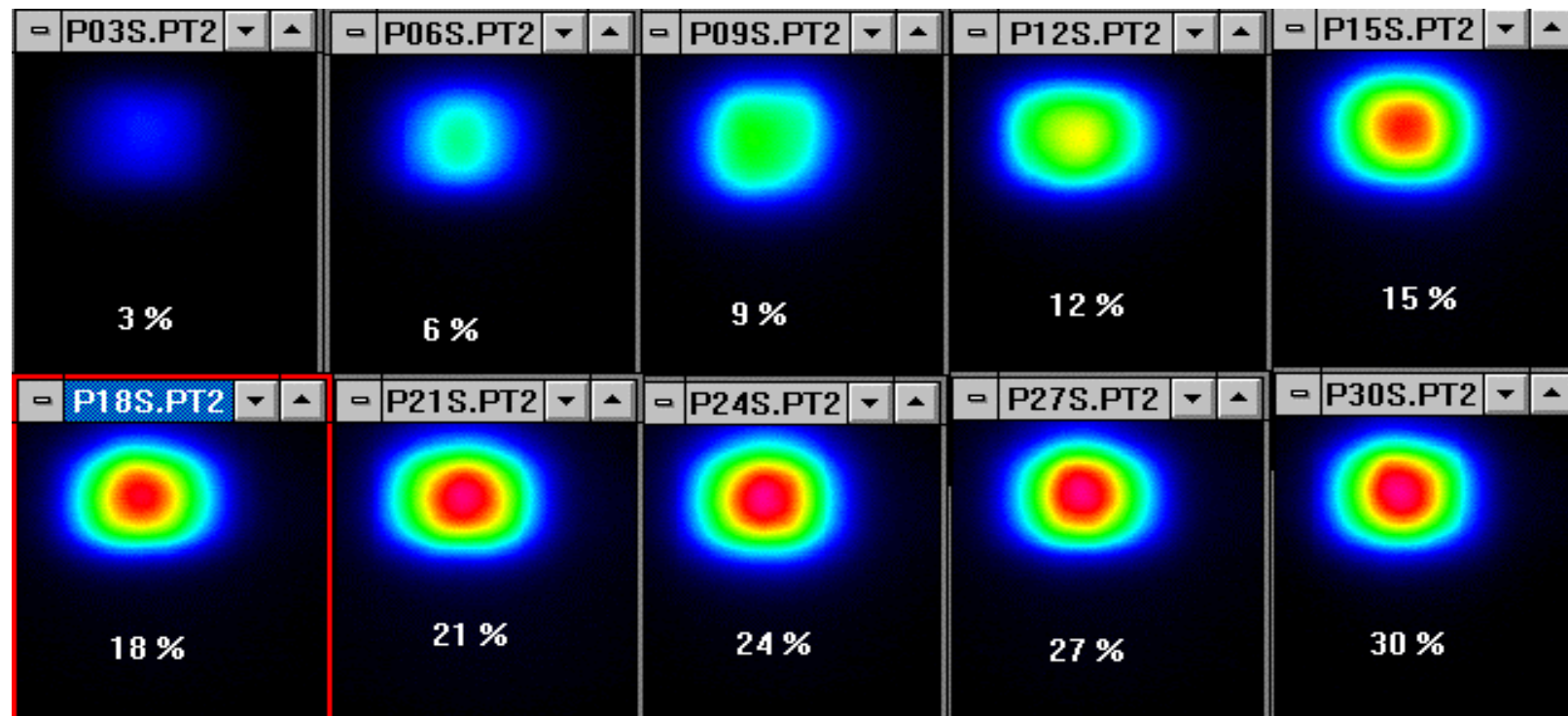
Termografia

$$P_{abs} = \frac{1}{2} \left[(\sigma + \omega \cdot \epsilon'') \cdot E^2 + \omega \cdot \mu'' \cdot H^2 \right]$$



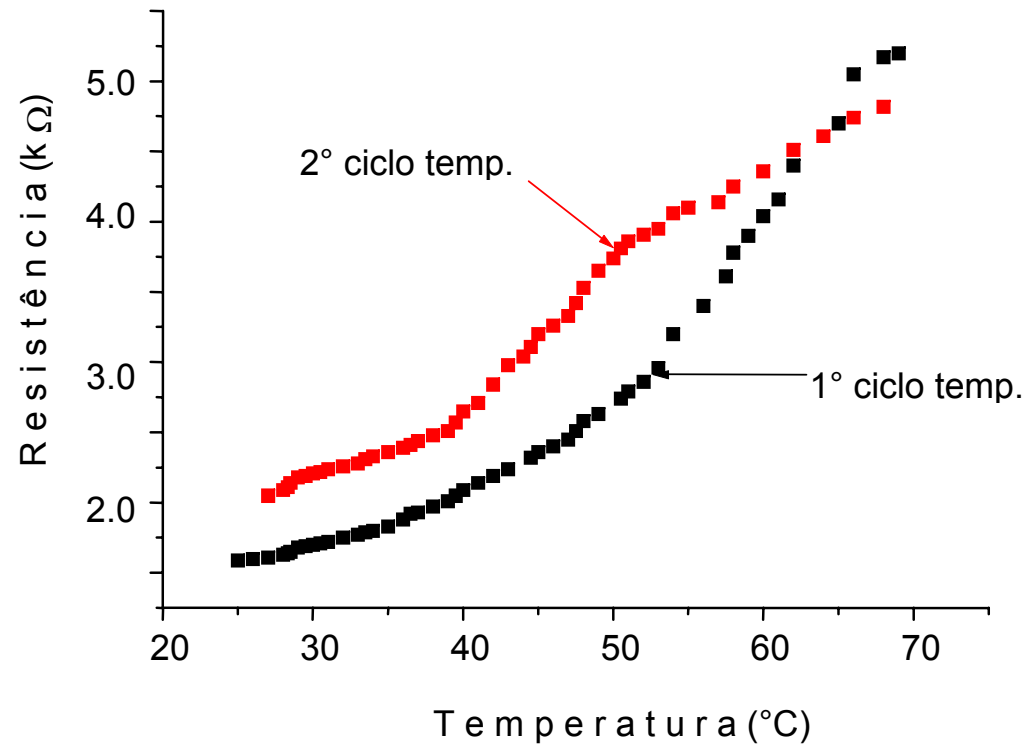
Aplicações

Termografia



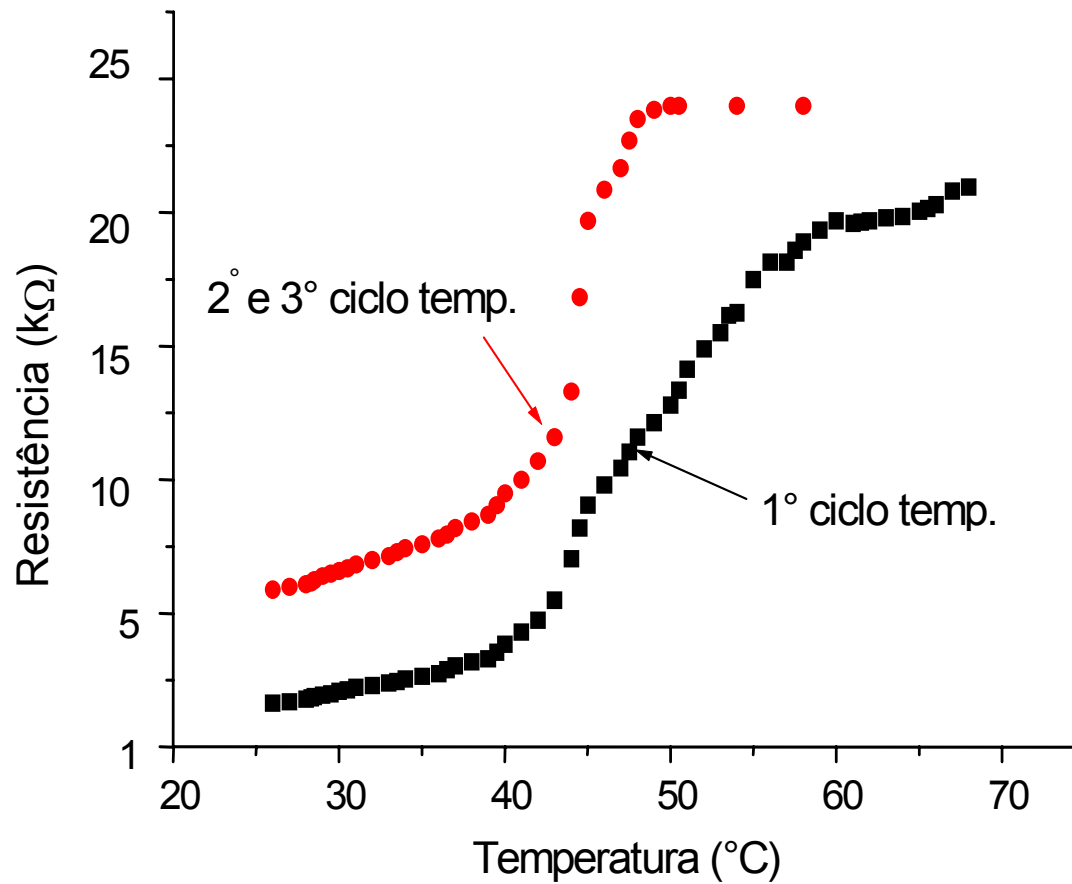
Aplicações

Com 30% de tetracosano encapsulado



Aplicações

Com 44% de tetracosano encapsulado



Conclusões

- O método apresentado revela-se útil para produzir compósitos com efeito PTCR.
- É necessário a sua otimização de modo a obter uma reprodutibilidade do efeito em sucessivos ciclos térmicos, e sobretudo aumentar o salto na resistência num menor intervalo de temperatura.
- Poderá conseguir-se, encapsulando as partículas de tetracosano no estado líquido, isto é, quando possuem um maior volume.
- Dispositivos auto reguladores e de segurança.

Thanks for your attention!

