Dielectric Materials and Broadband Dielectric Spectroscopy: Introductory Remarks

G. C. Psarras

Department of Materials Science,

School of Natural Sciences,

University of Patras,

Patras 26504, Hellas (Greece)

E-mail: G.C.Psarras@upatras.gr

http://smatlab.upatras.gr/

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Electrical Properties of Materials:

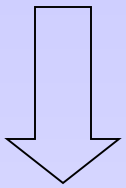
The materials' response to an applied electric field.

Importance of Electrical Properties:

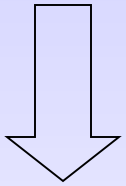
Transfer-distribution of electric power,

Conductors and insulators

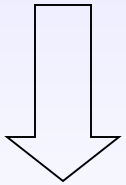
Electrical Properties of Materials



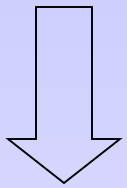
Conductivity



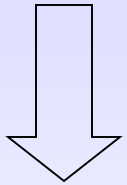
Dielectric behaviour



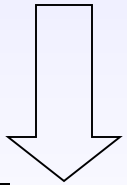
Piezoelectricity
Ferroelectricity



Metals (conductors)



Semi-conductors



Dielectrics (insulators)

Dielectric Materials (Dielectrics) and Insulators

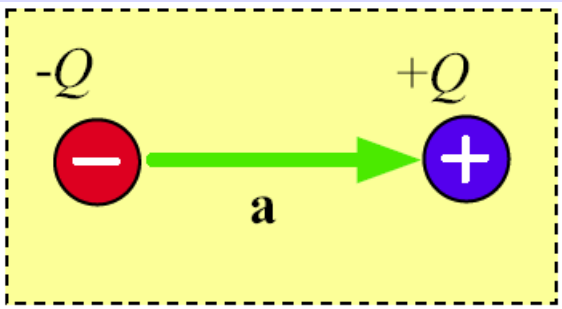
Dielectric material: is a substance whose basic electrical property is the ability to be polarized and in which an electrostatic field can exist, $E \neq 0$.

Insulator or electrical insulating material: a dielectric material used to prevent the leakage of electric charges in electrical engineering devices.

Active dielectrics: are dielectric materials having the ability to vary their polarization and to be polarized in the absence of an electric field.

Dipoles and Polarization

The simplest unit of polarization is a dipole: a distribution of equal positive and negative charges with their centers being apart a small distance.



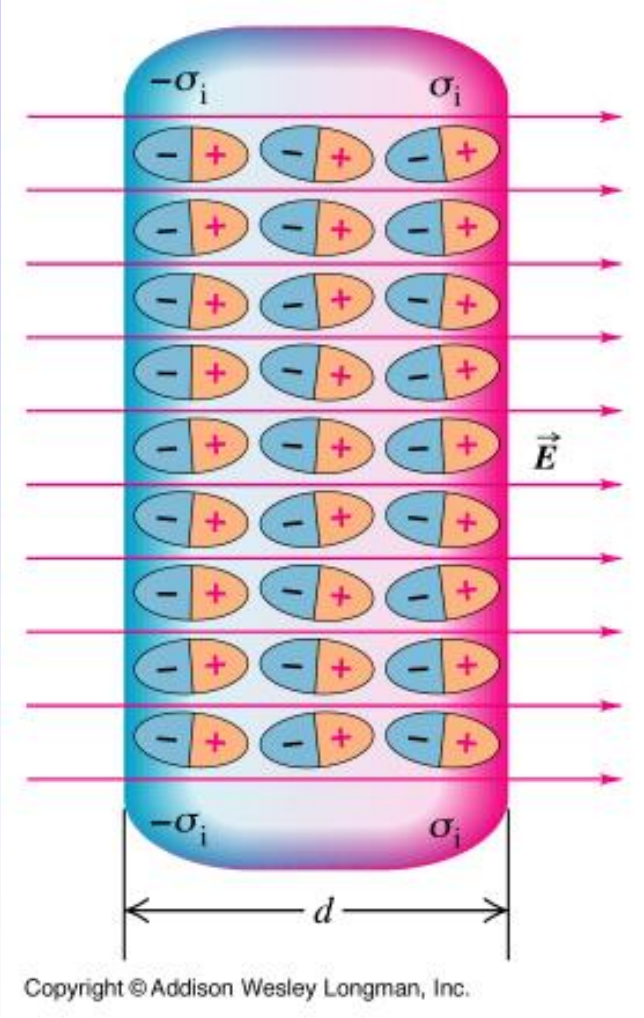
$$Q_{net} = 0$$

$$\mu = Qa$$ Dipole moment

Polarization is the total dipole moment (M) per unit volume (V).

$$P = \frac{M}{V} = \frac{\sum_i Q_i a_i}{V}$$

When a dielectric material is inserted within an electric field, positive charges are forced to the direction of the field while negative too the opposite. Thus the material takes the "form" of a dipole, with zero net charge and equal positive and negative charges at its two edge surfaces. The occurring effect is called **polarization**, and is 100% removed after cutting off the applied field



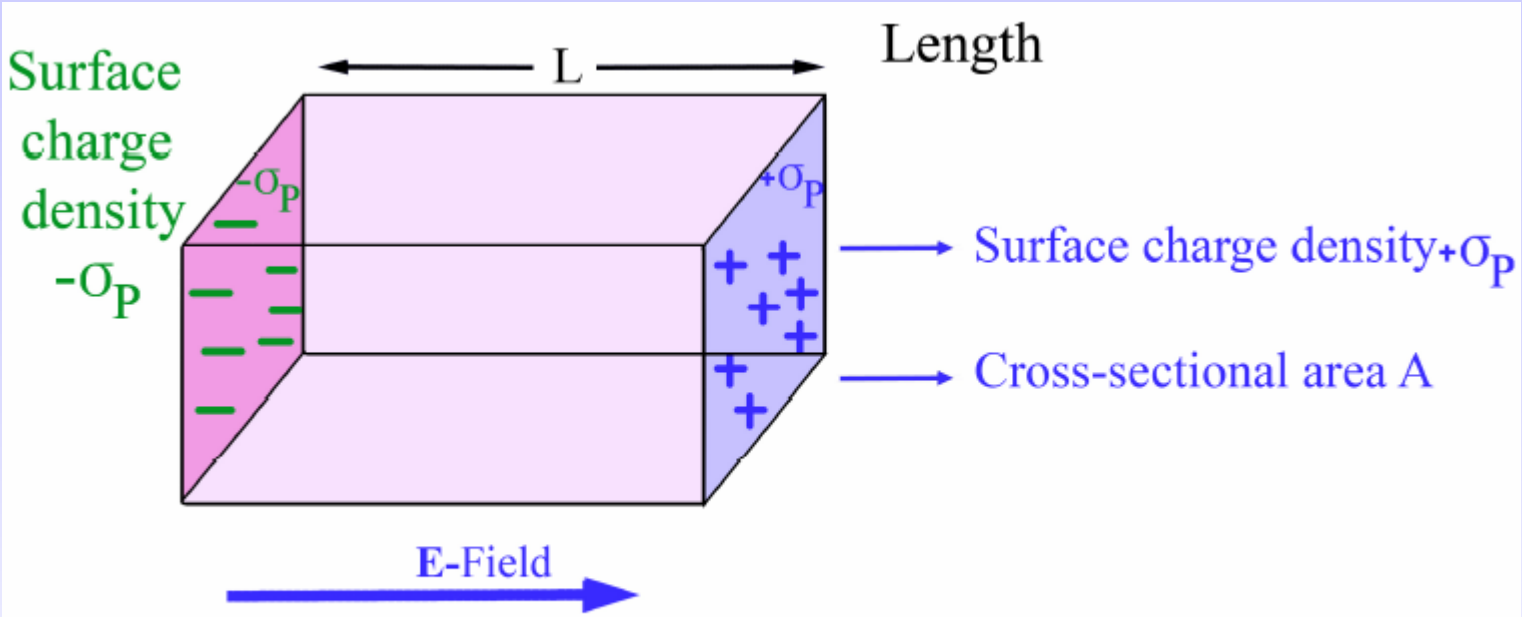


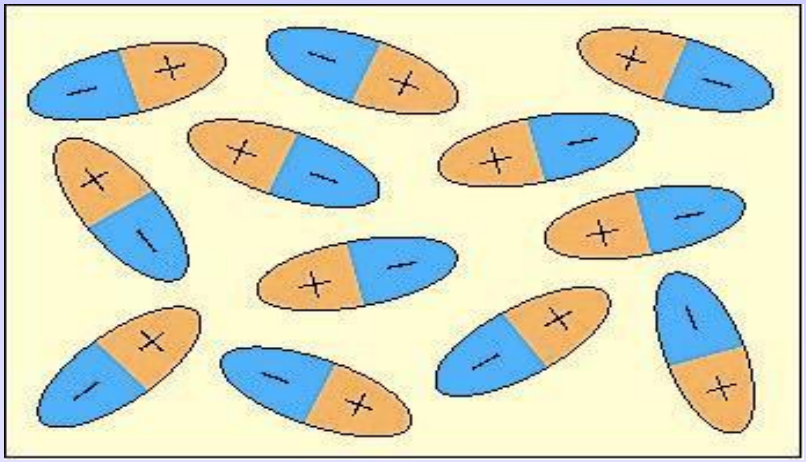
Fig. Surface charge density of a polarized dielectric

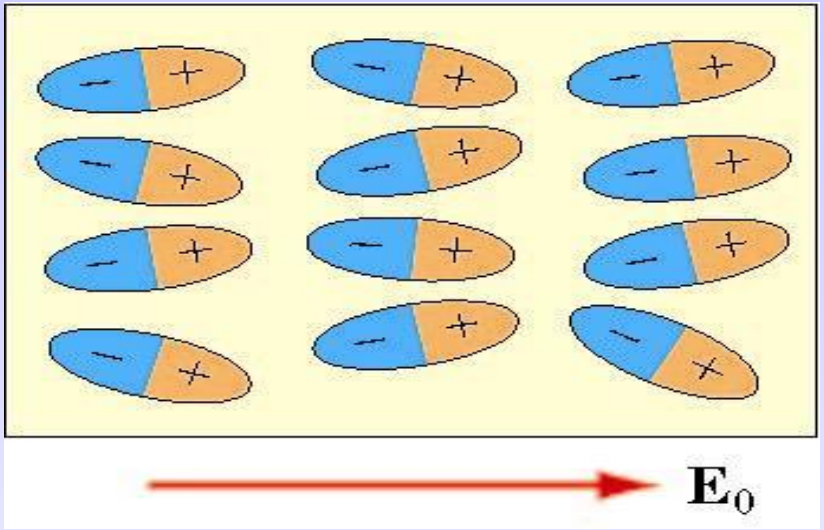
Dielectrics are classified in two categories:

(α) **polar dielectrics**, the molecules of these materials exhibit permanent dipole moment, since the centres of the distribution of positive and negative charges do not coincide, example the water.

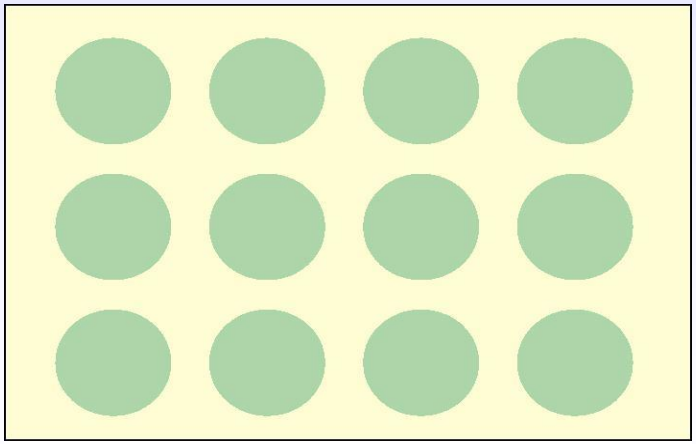
(β) **non-polar dielectrics**, the molecules of these materials do not exhibit permanent dipole moment, since the centers of the distribution of positive and negative charges coincide, example CO_2, CH_4.

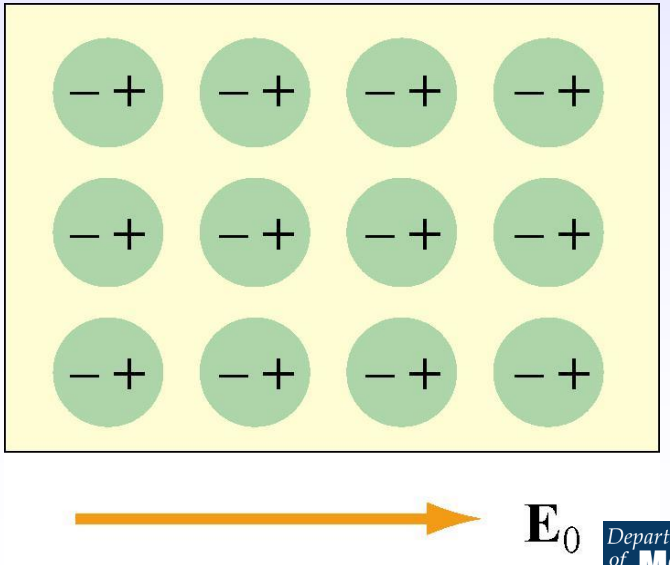
Polar dielectrics



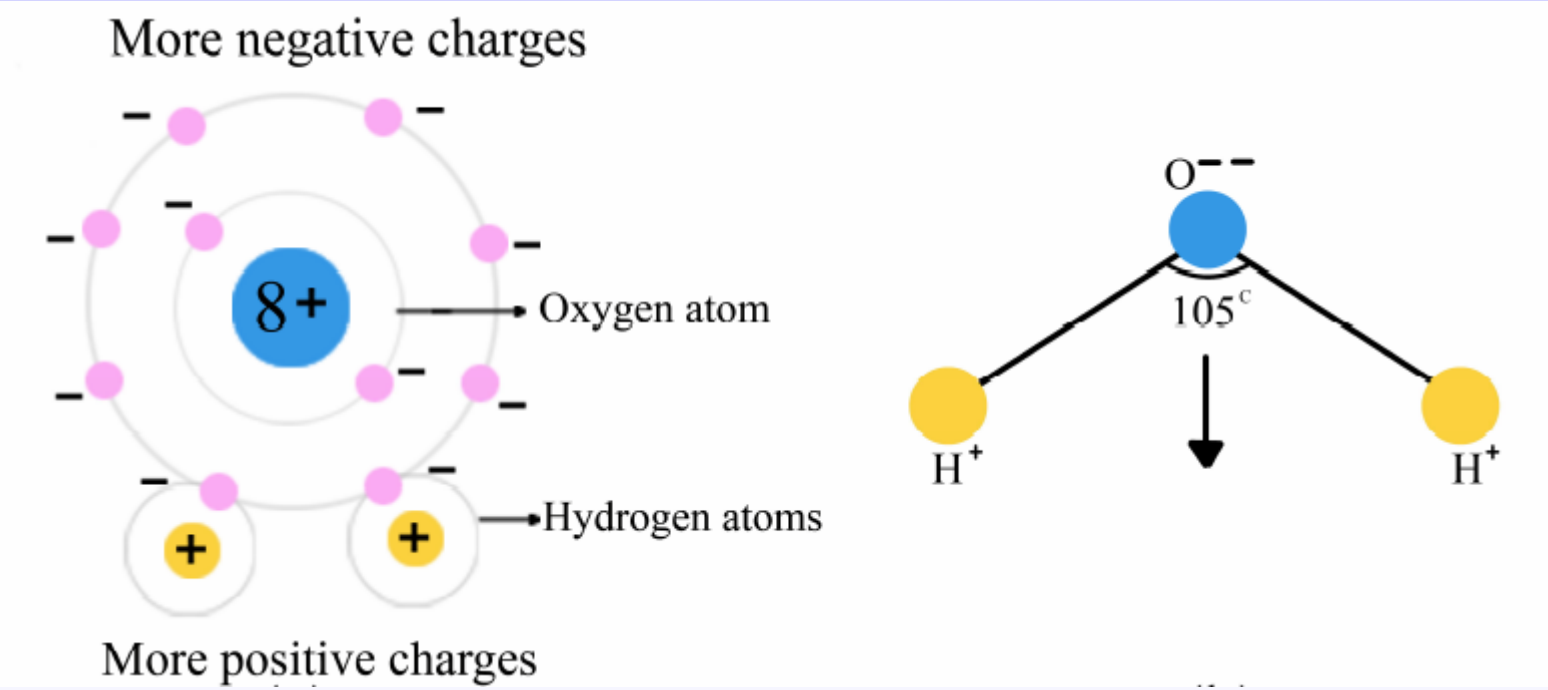


Non-polar dielectrics

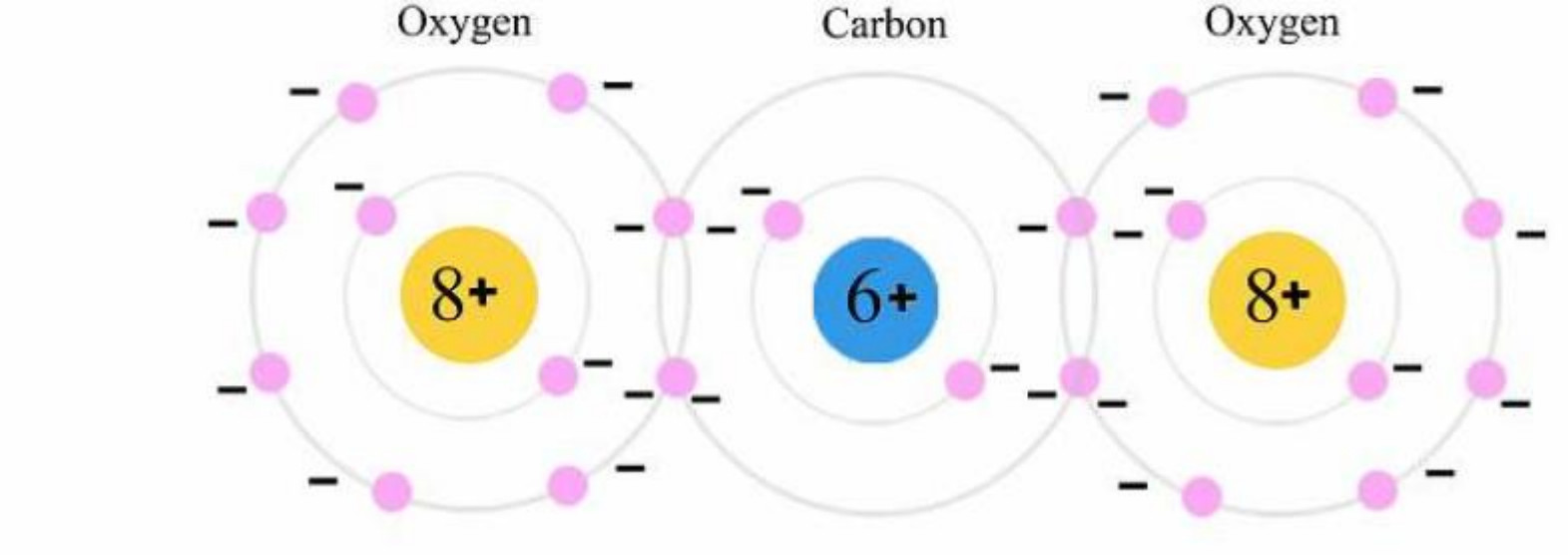




Polar Molecule (H_2O)

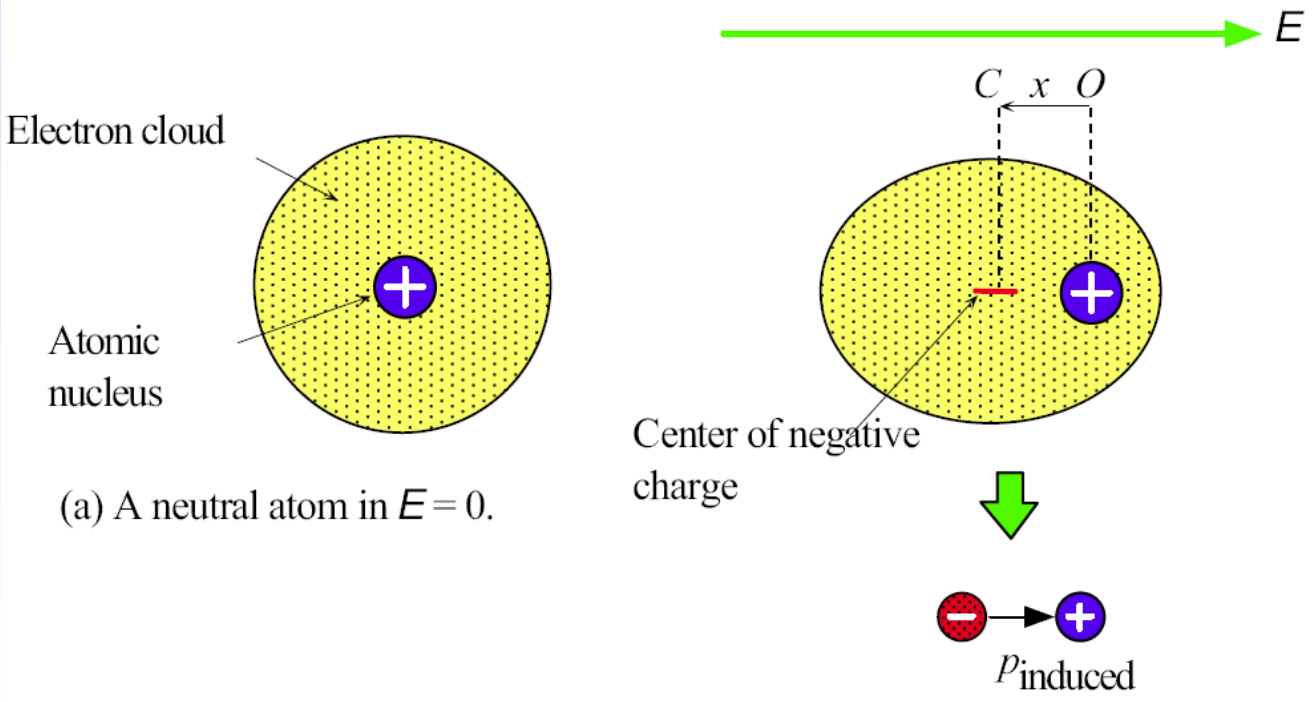


Non-Polar Molecule (CO_2)



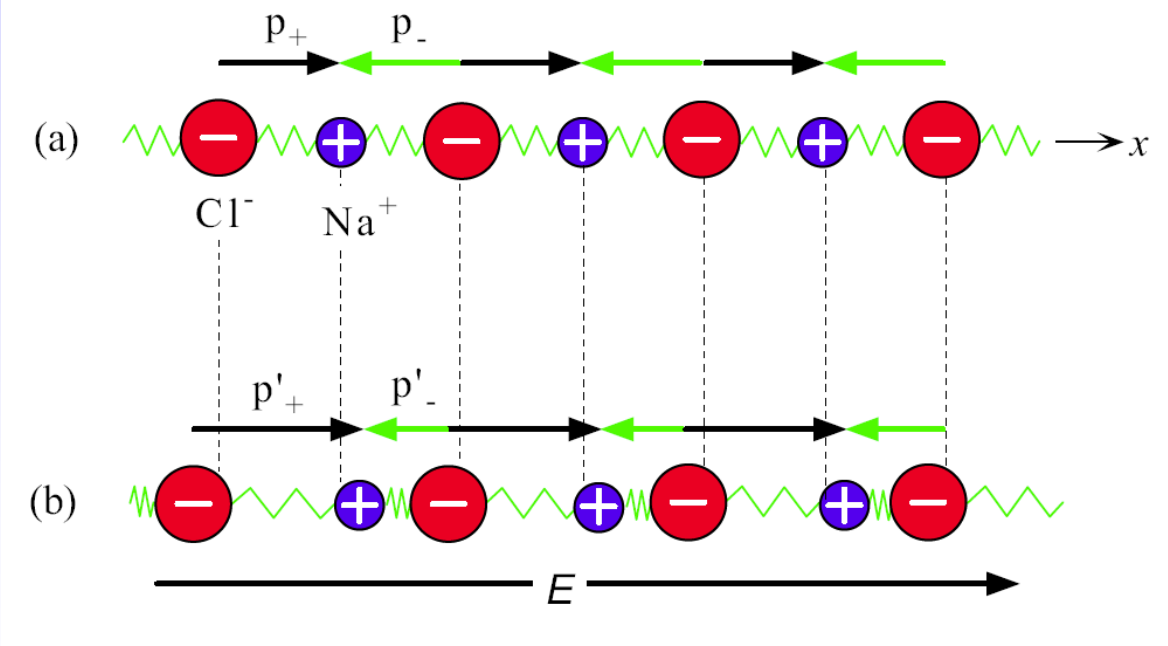
Effect of an electric field on a unpolar atom or molecule:

In an atom or molecule the electron cloud is deformed with respect to the nucleus, which causes an **induced polarization**; this response is fast (psec), because the electrons are light-weight



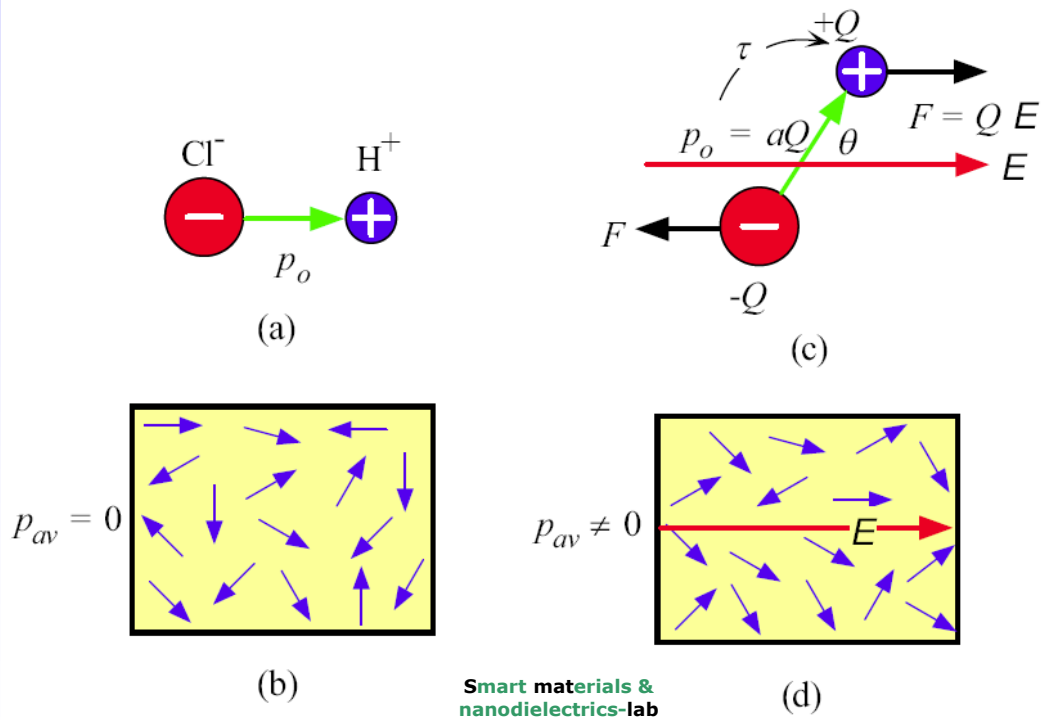
Effect of an electric field on (ionic) charges:

Charges (electronic and ionic) are **displaced** in the direction of the applied field. The latter gives rise to a **resultant polarization** of the sample as a whole.



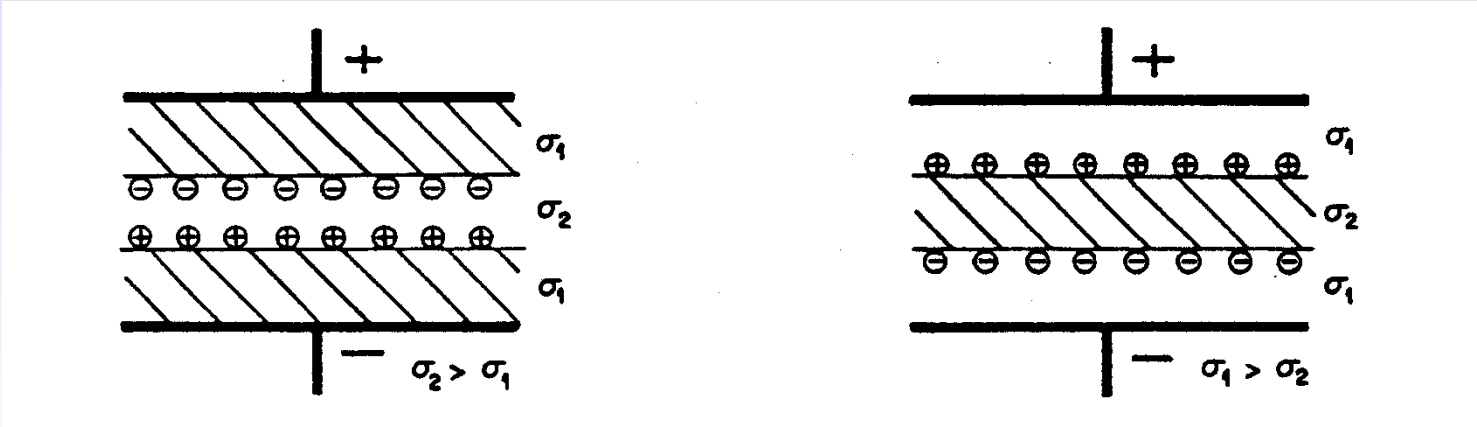
Effect of an electric field on an electric dipole μ:

An electric field tries to orient a dipole with moment μ; but the thermal fluctuations of the surrounding heat bath counteract this effect; as result **orientational polarization** takes place, its time constant is characteristic for the molecular moiety under study and may vary between 10-12s – 1000s and longer.



Interfacial Polarization (space charge)

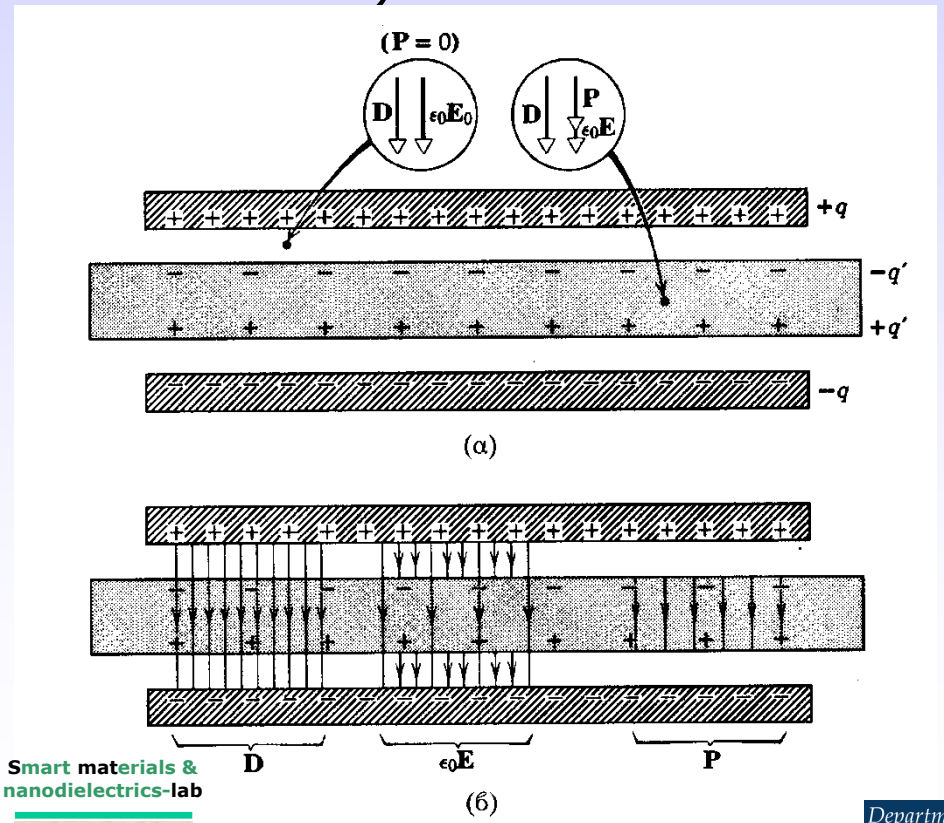
Interfacial polarization is observed in heterogeneous systems (materials) due to the accumulation of unbounded charges at the interfaces of the material's phases.



- The **electric displacement** D is related, only, to the free charges at the plates of the capacitor.
- **Polarization** P is related, only, to the polarization charges (induced).
- The intensity (strength) of the **electric field** E is related to all existing charges (free and induced).

$$D = \varepsilon\varepsilon_0 E$$

$$P = \varepsilon_0(\varepsilon - 1)E$$



Dielectric and Electrical Relaxations of Materials

The interaction of electromagnetic radiation and matter is of fundamental importance in basic and applied science. This interaction is referred as **"spectroscopy"** and reflects how vibrations, rotational and electronic transitions of atoms, molecules or whole materials are related to the IR and UV/visible absorption or emission spectra.

The whole discussion is referred to frequencies higher than $3x10^{11}$ Hz. However, the arising question is "**what is happening at the remaining, 10^{-6} – 10^{11} Hz, frequency spectrum?"**

The answer can be given by studying electrical polarization and conductivity.

What molecular processes take place in the spectral range from (almost) THz to mHz and below?

1. Induced polarization
2. Orientational polarization
3. Charge transport
4. Polarization at interfaces

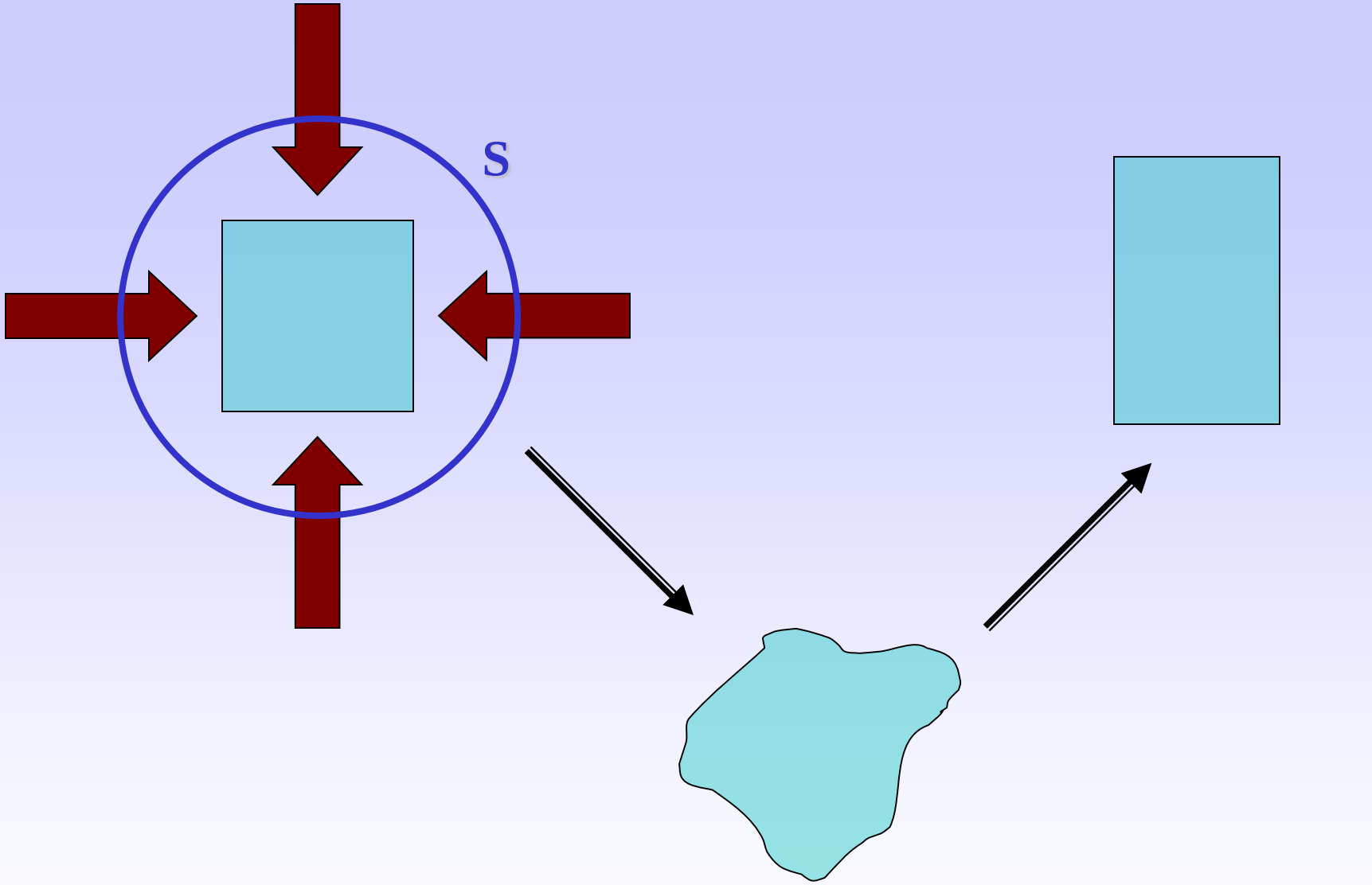
Dielectric relaxations are observed in many materials, such as glasses, polymers, ceramics, liquid crystals, composite materials, and disordered materials.

But what is a relaxation process?

Relaxation is the return of a perturbed system into equilibrium. Each relaxation process can be characterized by a **relaxation time τ**.

What can be derived from studying a system exhibiting relaxation processes?

Relaxation time, activation energy, the influence of variable, such as pressure and temperature, upon the specific process.



Timescale

t

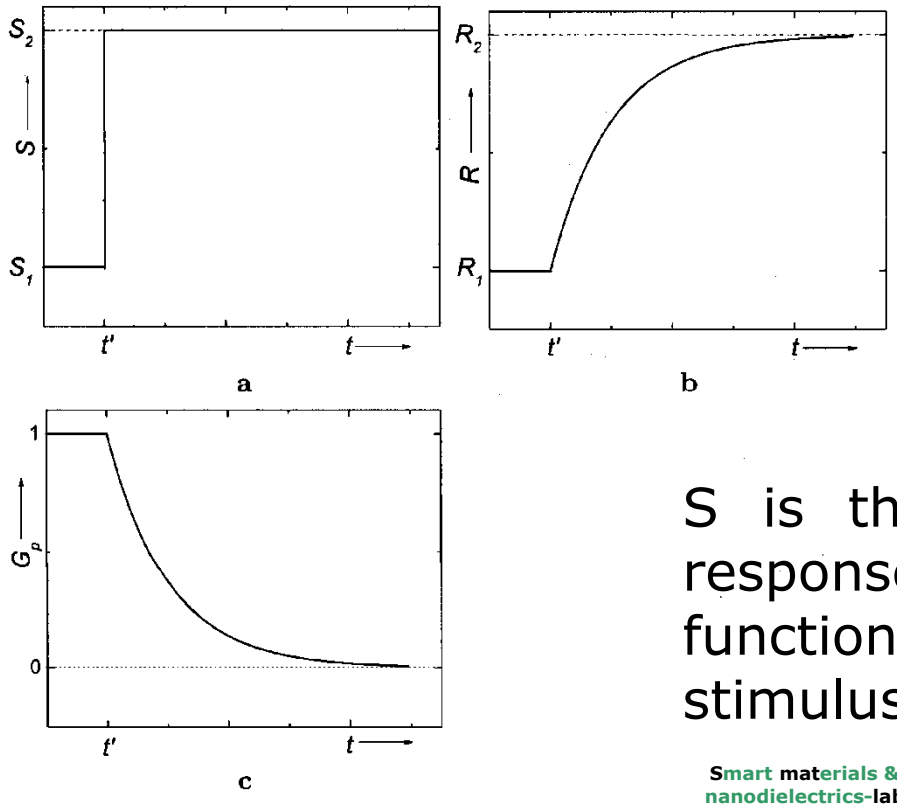
τ

Relaxation Functions:

$$R(t) = R_0(1 - e^{-t/\tau})$$

$$G(t) = G_0 e^{-t/\tau}$$

Relaxation Process



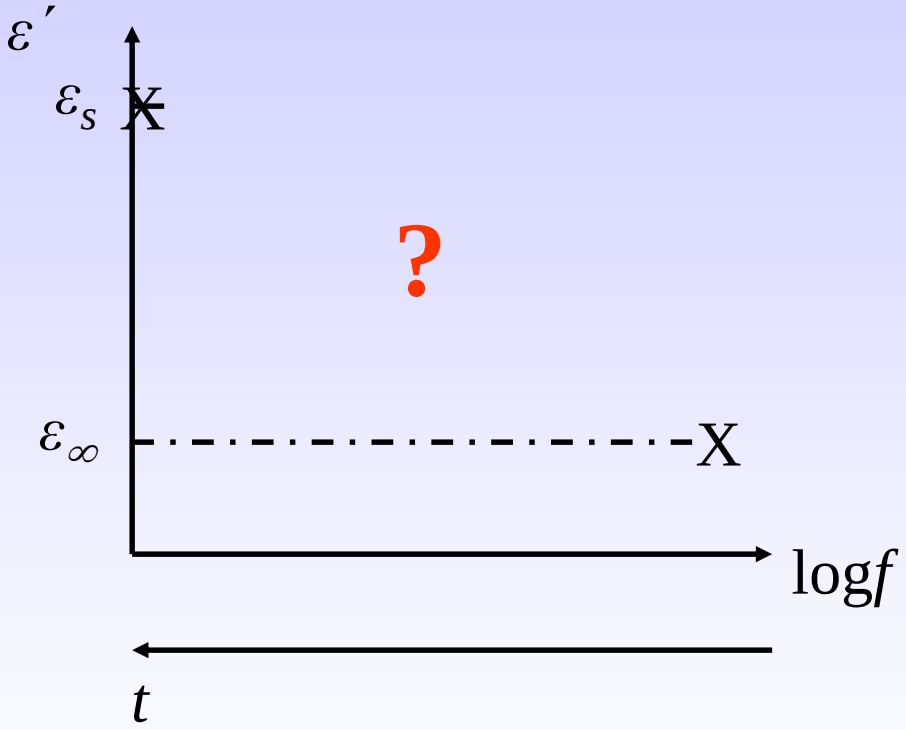
$$F(t - t') = 0, \quad t < t'$$

$$F(t - t') = 1, \quad t > t'$$

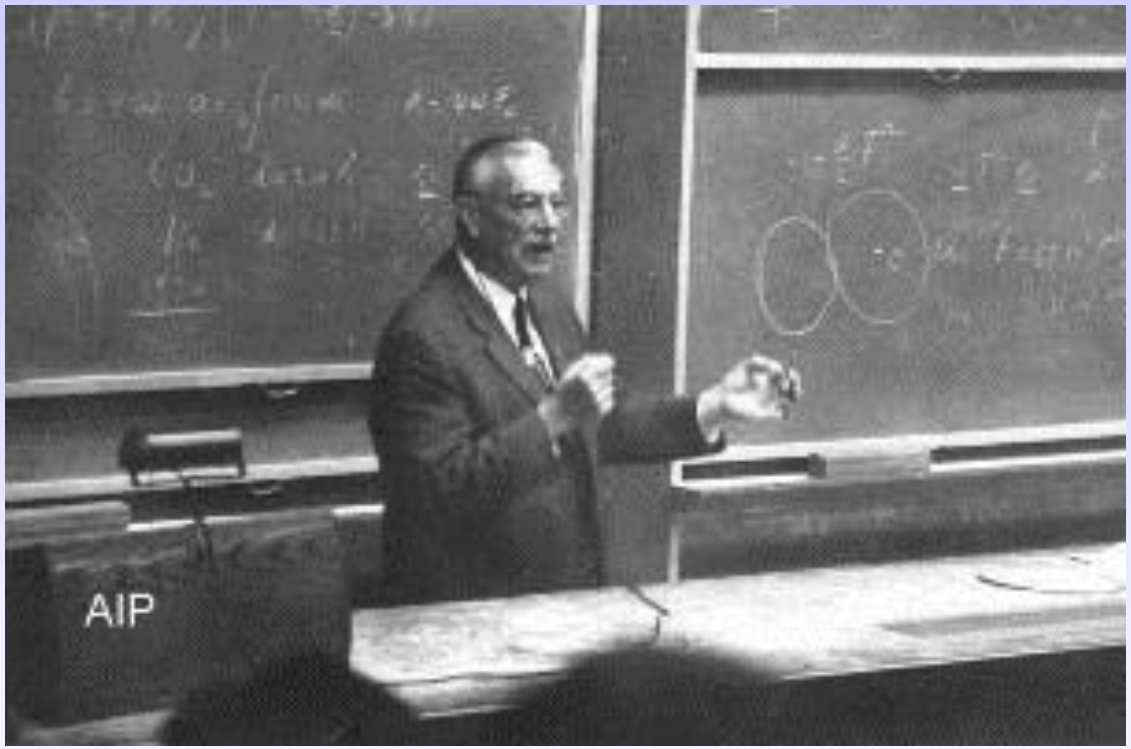
$$S(t) = S_1 + (S_2 - S_1)F(t - t')$$

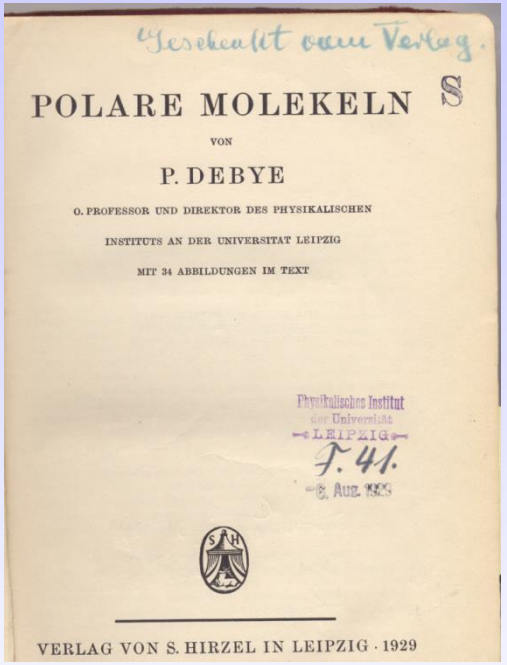
S is the applied stimulus, R the response function and G the decay function after removing the applied stimulus.

Macroscopic Approach – Debye Equations of Dispersion



Peter Josephus Wilhelmus Debye, formed the basic dielectric relaxation theory.




Gesehenkt vom Verlag.

POLARE MOLEKELN

VON

P. DEBYE

O. PROFESSOR UND DIREKTOR DES PHYSIKALISCHEN INSTITUTS AN DER UNIVERSITÄT LEIPZIG

MIT 34 ABBILDUNGEN IM TEXT

Physikalisches Institut der Universität LEIPZIG F. 41.

VERLAG VON S. HIRZEL IN LEIPZIG · 1929

Peter Josephus Wilhelmus Debye (1884 - 1966). He was awarded the **Nobel Prize of Chemistry 1936** *"for his contributions to our knowledge of molecular structure through his investigations on dipole moments and on the diffraction of X-rays and electrons in gases"*.

The orientation of permanent dipoles is a relative slower process, compared to atomic/ionic and electronic polarization.

Only after a sufficient interval of time, from the application of the electric field, the system will equilibrate and the polarization of the material will attain its maximum value, which corresponds the maximum value of dielectric permittivity (dielectric constant).

- **Static value of dielectric permittivity**

  ε_s when $t \to \infty$, $f \to 0$ (maximum value of polarization)

- **Dielectric permittivity at very high (optical) frequencies**

  ε_∞ when $t \to 0$, $f \to \infty$ (minimum value of polarization)

$$\tau \frac{\mathrm{d}D(t)}{\mathrm{d}t} + D(t) = \tau \varepsilon_0 \varepsilon_\infty \frac{\mathrm{d}E(t)}{\mathrm{d}t} + \varepsilon_0 \varepsilon_s E(t)$$

Suppose that a time depending electric field $E(t)$ is applied on a dielectric:

$$E(t) = E_0 e^{i\omega t}$$

Then the electric displacement will be:

$$D(t) = D_0 e^{(i\omega t - \delta)}$$

After substituting in the differential equation we have:

$$\frac{D(t)}{\varepsilon_0 E(t)} = \frac{\varepsilon_s + \varepsilon_\infty (i\omega t)}{1 + i\omega t}$$

$$\frac{D(t)}{\varepsilon_0 E(t)} = \frac{\varepsilon_s + \varepsilon_\infty (i\omega t)}{1 + i\omega t}$$

using the relation:

$$\varepsilon^* = \frac{D(t)}{\varepsilon_0 E(t)}$$

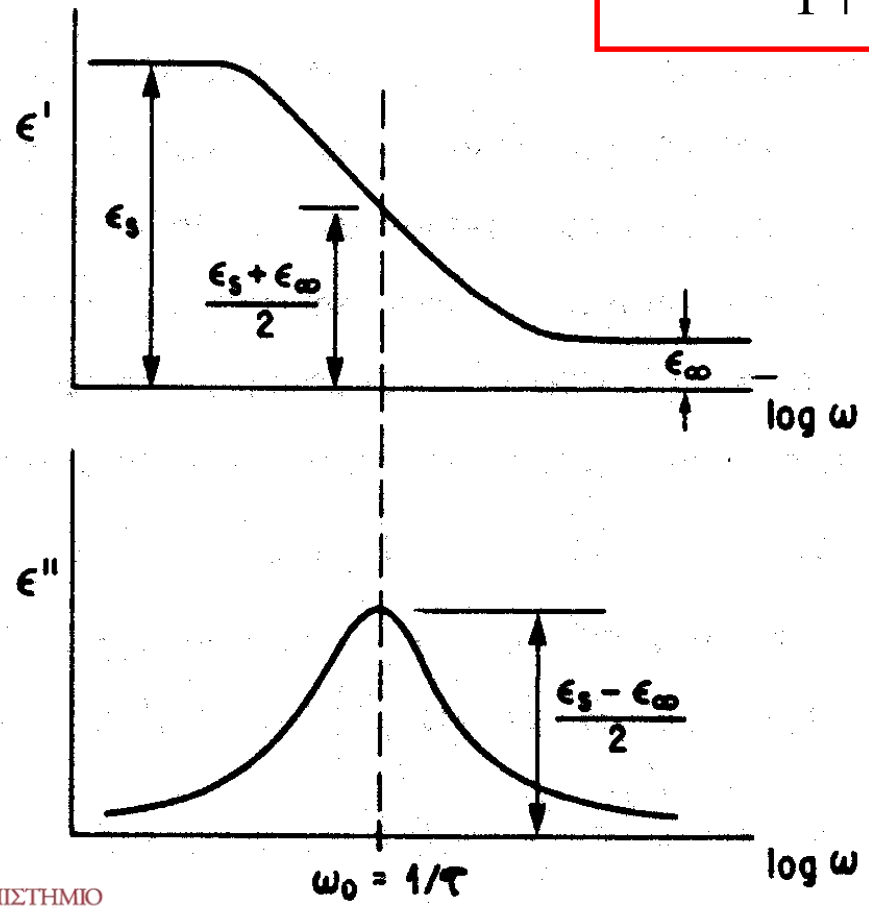
the Debye's equation of dispersion is derived:

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

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

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

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

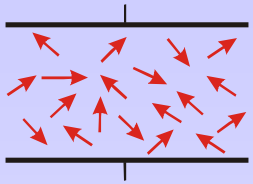


$$\omega_0 = 1/\tau$$

$$\varepsilon'_{\omega_0} = \frac{\varepsilon_s + \varepsilon_\infty}{2}$$

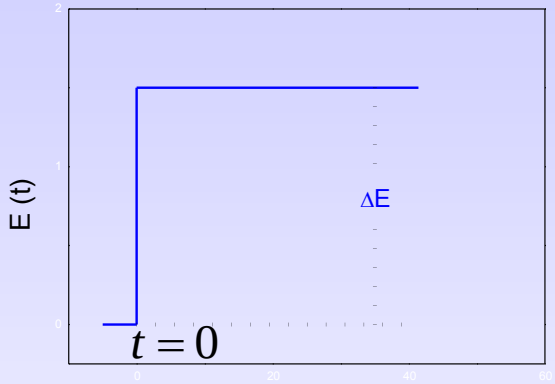
$$\varepsilon''_{\omega_0} = \frac{\varepsilon_s - \varepsilon_\infty}{2}$$

Orientational Polarization as a Relaxation Process



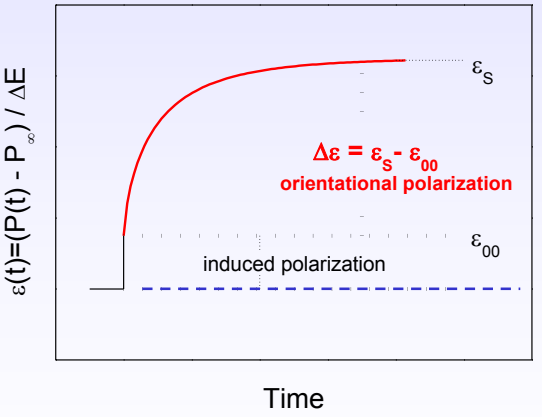
Capacitor with a dielectric containing N dipoles, dipole Moment μ

Debye type relaxation: complex dielectric function ε* = f(ω, T)



$$E(t) = E_0 \qquad E(t) = E_0 e^{i\omega t}$$

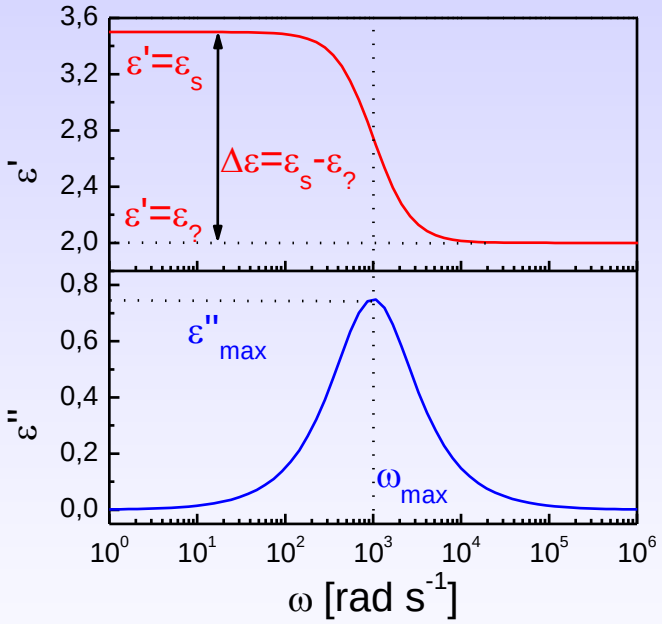
$$P(\omega) = \varepsilon_0[\varepsilon^*(\omega,T) - 1]E(\omega)$$



$$P_s = (\varepsilon_s - 1)\varepsilon_0 E$$

$$P(t) = P_s\left[1 - \exp\left(-\frac{t}{\tau}\right)\right]$$

$$P_\infty = (\varepsilon_\infty - 1)\varepsilon_0 E$$



$$\varepsilon(t) = [\varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)(1 - e^{-t/\tau})]$$

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

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

Electrical Properties of Dielectrics (Polymers and Polymer Matrix Composites)

- **Dielectric behaviour** (variation of dielectric permittivity and loss with frequency and temperature)
- **Conductivity or Resistivity**
- **Dielectric Strength** (maximum applied voltage or time – at constant voltage- before breakdown)

Polymers differ form simple crystalline solids and ordinary liquids, since the length scale of their molecules is much larger than the atomic dimensions.

The structure of a polymer is a long chain where one or more "chemical units" are repeated.

The majority of the skeletal bonds allow rotations, leading thus to an incredible high number of possible configurations in space.

Polymers and polymer matrix composites are basically **electrical insulators**, since their concentration of free charge carriers is very low.

Under this point of view their electrical properties are primarily refer to **dielectric relaxation *phenomena*** occurring under the influence of ac field.

Revealed relaxation processes are related to dipolar orientation effects of **permanent or induced dipoles** and in some cases to **space charge** migration.

Amorphous and semi-crystalline polymers exhibit electrical relaxations associated with glass/rubber transition, segmental mobility of polar groups, interfacial effects and crystallization processes.

Experimental Techniques and Data Analysis

The electrical behaviour of these systems can be experimentally investigated by means of Dielectric Spectroscopy (DS) and dc conductivity measurements.

The obtained (DS) data can be analysed in different formalisms:

- in terms of dielectric permittivity
- in terms of a.c. conductivity
- in terms of electric modulus

Dielectric Spectroscopy

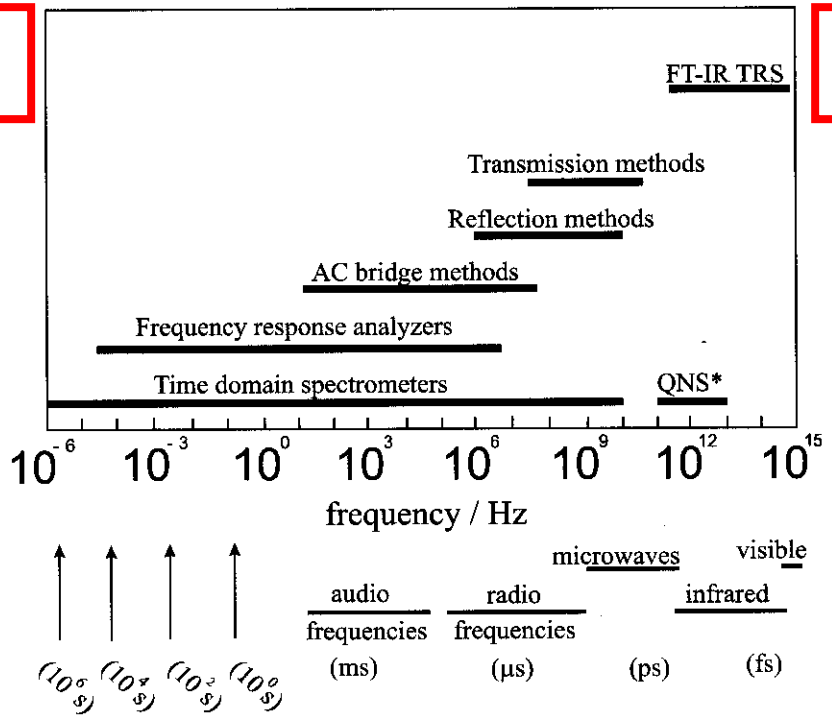
Broadband Dielectric Spectroscopy (BDS) is a powerful tool for the investigation of molecular mobility, phase changes, conductivity mechanisms and interfacial effects in polymers and complex systems

$$\varepsilon' = F(\theta, f)$$

$$\varepsilon'' = F(\theta, f)$$

$$M' = F(\theta, f)$$

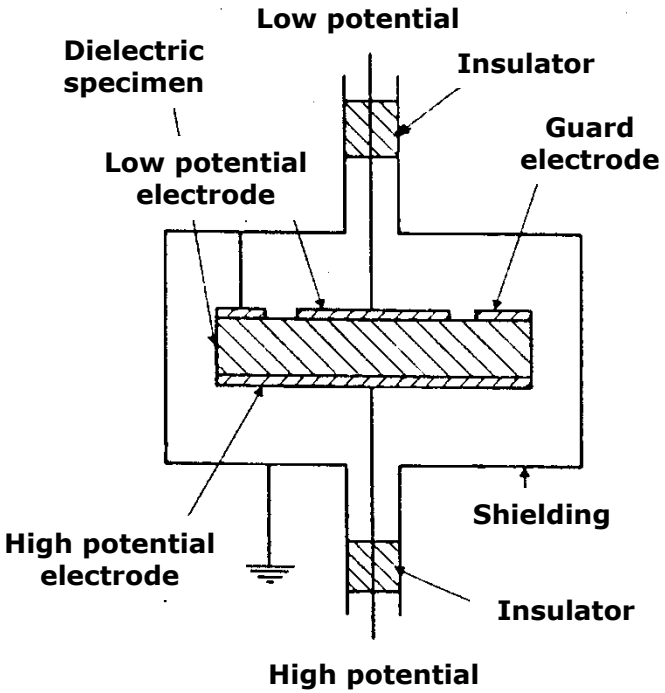
$$M'' = F(\theta, f)$$

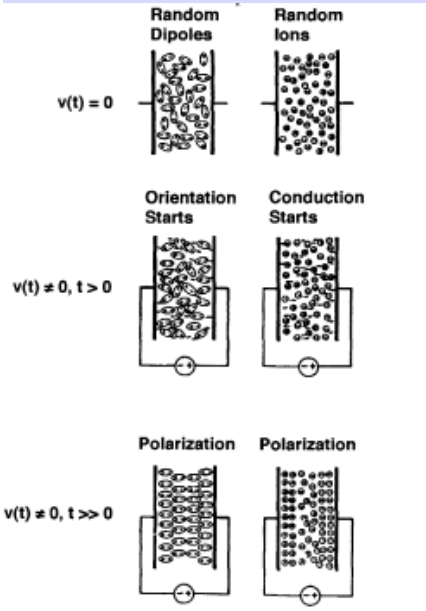


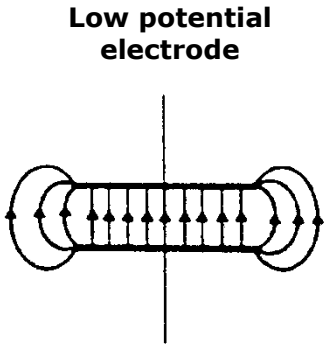
Experimental Set Up
Three Terminal Guarded Test Cell

(ASTM D150-98 re-approved 2004)

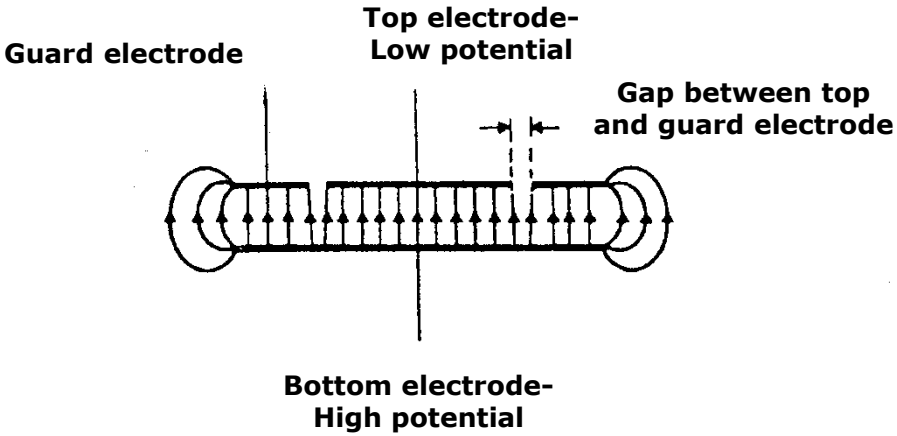
Alpha-N Analyser
10^{-6} – 10^{7} Hz





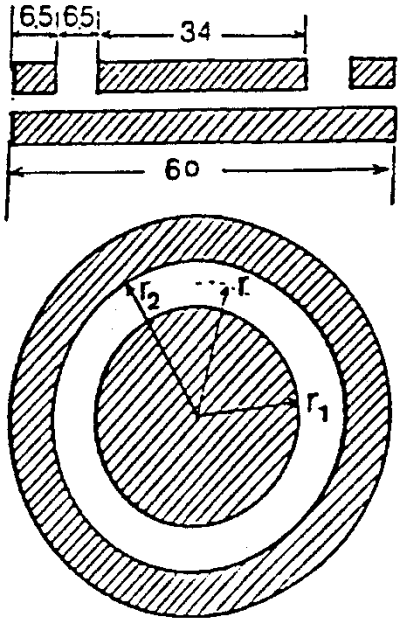


(α)



(β)

Measuring of stray capacitances should be avoided



$$\varepsilon' = \frac{C}{C_0(1+D^2)}$$

$$\varepsilon'' = \frac{C \cdot D}{C_0(1+D^2)} = \varepsilon' D$$

$$D = \tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

$$C_0 = \varepsilon_0 \frac{S}{l} \qquad \varepsilon_0 = 8.854 \times 10^{-12}\,\mathrm{Fm}^{-1}$$

$$S = \pi r^2$$

$$r = r_1 + \frac{g}{2} - \delta \qquad g = r_1 - r_2$$

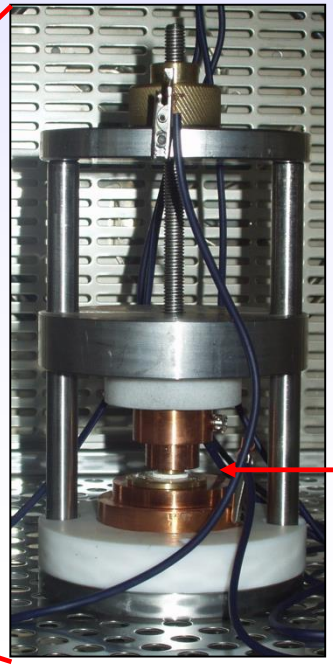
$$\frac{\delta}{l} = \frac{2}{\pi}\ln\left(\cosh\frac{\pi g}{4l}\right)$$

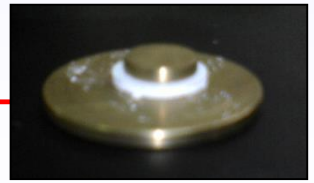
ASTM D150

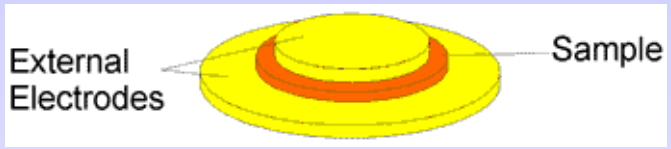
where *l* is the thickness of the specimen

Two Electrodes Test Cells

BDS
1200







Complex Dielectric Permittivity

When a dielectric is subjected to an external ac electrical field its response depends on a number of parameters, including:

- the amplitude and the frequency of the field
- temperature
- molecular structure of the material

$$\varepsilon^* = \varepsilon' - i\varepsilon'' \qquad \tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

The Electric Modulus Formalism

Complex modulus, electric modulus or inverse complex permittivity, M* is defined by the following equation

$$M^* = \frac{1}{\varepsilon^*} = \frac{1}{\varepsilon' - j\varepsilon''} = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} + j\frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} = M' + jM''$$

AC Conductivity

Alternating current conductivity sums all dissipative effects including an actual ohmic conductivity, caused by migrating charge carriers on isolated or adjacent conductive sites or clusters, as well as a frequency dielectric dispersion (*A. von Hippel, Dielectrics and Waves, Arttech, Boston, 1995*).

The ac conductivity of all samples has been calculated from the dielectric loss according to the relation:

$$\sigma^*(\omega) = j\varepsilon_0\omega\varepsilon^*(\omega) = j\varepsilon_0\omega(\varepsilon' - j\varepsilon'') = \varepsilon_0\omega\varepsilon'' + j\varepsilon_0\omega\varepsilon'$$

The real part of $\sigma^*(\omega)$ is given by:

$$\sigma_{ac} = \varepsilon_0\omega\varepsilon''$$

where, ε_0 = 8.85 x 10^{-12} Fm^{-1} is the permittivity of free space and $\omega = 2\pi f$ the angular frequency.

Debye

Dielectric Permittivity

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

Electric Modulus

$$M' = M_\infty M_s \frac{M_\infty + M_s\omega^2\tau^2}{\mathrm{M}_\infty^2 + \mathrm{M}_s^2\omega^2\tau^2} \qquad M'' = M_\infty M_s \frac{(M_\infty - M_s)\omega\tau}{\mathrm{M}_\infty^2 + \mathrm{M}_s^2\omega^2\tau^2}$$

G. M. Tsangaris, G. C. Psarras, N. Kouloumbi,
Journal of Materials Science, 33(8), 2027-2037, 1998.

Cole-Cole

Dielectric Permittivity

$$\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)\left[1 + (\omega\tau)^{1-\alpha}\sin\frac{\alpha\pi}{2}\right]}{1 + (\omega\tau)^{2(1-\alpha)} + 2(\omega\tau)^{1-\alpha}\sin\frac{\alpha\pi}{2}}$$

$$\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_\infty)(\omega\tau)^{1-\alpha}\cos\frac{\alpha\pi}{2}}{1 + (\omega\tau)^{2(1-\alpha)} + 2(\omega\tau)^{1-\alpha}\sin\frac{\alpha\pi}{2}}$$

Electric Modulus

$$M' = M_\infty M_s \frac{[M_s \mathrm{A} + (M_\infty - M_s)\cos\phi]\mathrm{A}}{M_s^2\mathrm{A}^2 + 2\mathrm{A}(M_\infty - M_s)\mathrm{M}_s\cos\phi + (M_\infty - M_s)^2}$$

$$M'' = M_\infty M_s \frac{[(M_\infty - M_s)\sin\phi]\mathrm{A}}{M_s^2\mathrm{A}^2 + 2\mathrm{A}(M_\infty - M_s)\mathrm{M}_s\cos\phi + (M_\infty - M_s)^2}$$

$0 \leq \alpha < 1$, $\alpha = 0$ Debye

$$\mathrm{A} = \left\{1 + 2(\omega\tau)^{1-\alpha}\sin\frac{\pi\alpha}{2} + (\omega\tau)^{2(1-\alpha)}\right\}^{1/2}$$

$$\phi = \alpha rctg\left\{(\omega\tau)^{1-\alpha}\cos\frac{\alpha\pi}{2} \Big/ 1 + (\omega\tau)^{(1-\alpha)}\sin\frac{\alpha\pi}{2}\right\}$$

G. M. Tsangaris, G. C. Psarras, N. Kouloumbi,
Journal of Materials Science, 33(8), 2027-2037, 1998.

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Cole-Davidson

Dielectric Permittivity

$$\varepsilon' = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)(\cos\phi)^\gamma \cos\gamma\phi$$

$$\varepsilon'' = (\varepsilon_s - \varepsilon_\infty)(\cos\phi)^\gamma \sin\gamma\phi$$

Electric Modulus

$$tg\phi = \omega\tau$$

$$\omega_{\max}\tau = tg\left(\frac{1}{\gamma+1}\cdot\frac{\pi}{2}\right)$$

$$M' = \frac{M_\infty M_s\left[M_s + (M_\infty - M_s)(\cos\phi)^\gamma \cos\gamma\phi\right]}{M_s^2 + (M_\infty - M_s)(\cos\phi)^\gamma\left[2M_s\cos\gamma\phi + (M_\infty - M_s)(\cos\phi)^\gamma\right]}$$

$$M'' = \frac{M_\infty M_s (M_\infty - M_s)(\cos\phi)^\gamma \sin\gamma\phi}{M_s^2 + (M_\infty - M_s)(\cos\phi)^\gamma\left[2M_s\cos\gamma\phi + (M_\infty - M_s)(\cos\phi)^\gamma\right]}$$

$0<\gamma\leq 1$, $\gamma = 1$ Debye

G. M. Tsangaris, G. C. Psarras, N. Kouloumbi,
Journal of Materials Science, 33(8), 2027-2037, 1998.

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Havriliak-Negami

Dielectric Permittivity

$$\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)\cos\gamma\phi}{\left[1+(\omega\tau)^{2(1-\alpha)} + 2(\omega\tau)^{1-\alpha}\sin\frac{\alpha\pi}{2}\right]^{\gamma/2}}$$

$$\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_\infty)\sin\gamma\phi}{\left[1+(\omega\tau)^{2(1-\alpha)} + 2(\omega\tau)^{1-\alpha}\sin\frac{\alpha\pi}{2}\right]^{\gamma/2}}$$

$$\omega_0 = \frac{1}{\tau}\left[\sin\frac{(1-\alpha)\pi}{2+2\gamma}\right]^{1/\gamma}\left[\sin\frac{(1-\alpha)\gamma\pi}{2[1+(1-\alpha)]}\right]^{-1/(1-\alpha)}$$

Electric Modulus

$$M' = M_\infty M_s \frac{\left[M_s A^\gamma + (M_\infty - M_s)\cos\gamma\phi\right]A^\gamma}{M_s^2 A^{2\gamma} + 2A^\gamma (M_\infty - M_s)M_s\cos\gamma\phi + (M_\infty - M_s)^2}$$

$$M'' = M_\infty M_s \frac{\left[(M_\infty - M_s)\sin\gamma\phi\right]A^\gamma}{M_s^2 A^{2\gamma} + 2A^\gamma (M_\infty - M_s)M_s\cos\gamma\phi + (M_\infty - M_s)^2}$$

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G. M. Tsangaris, G. C. Psarras, N. Kouloumbi,
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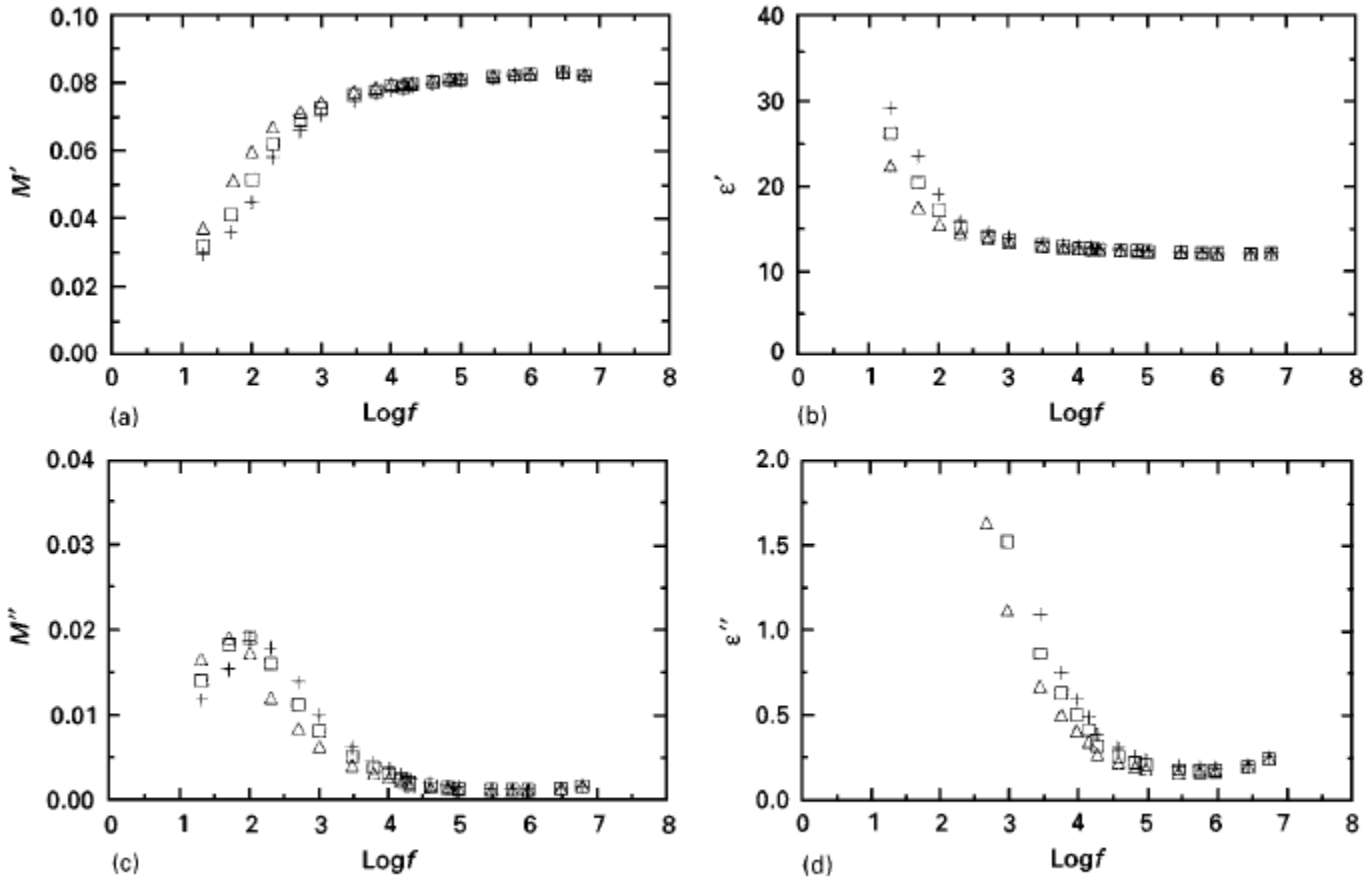
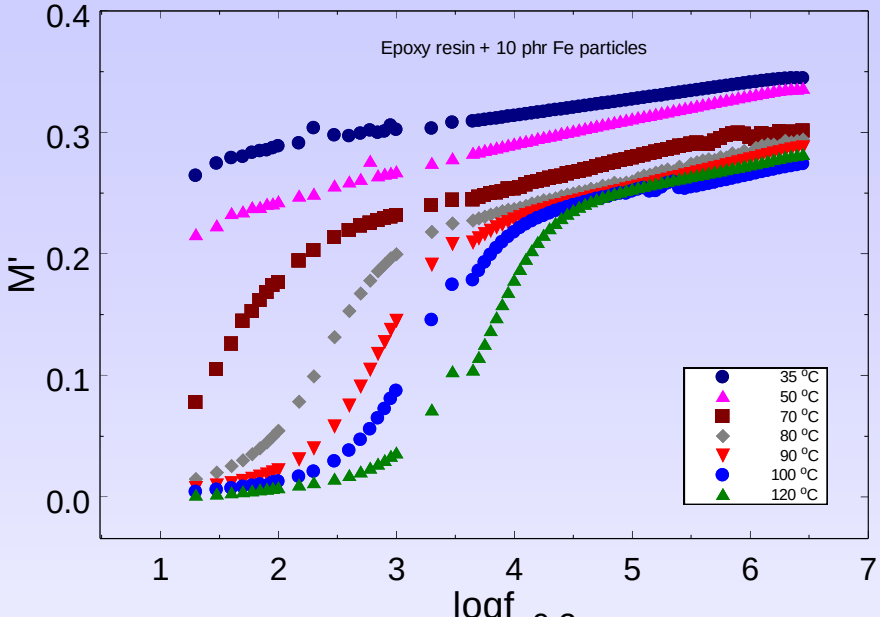


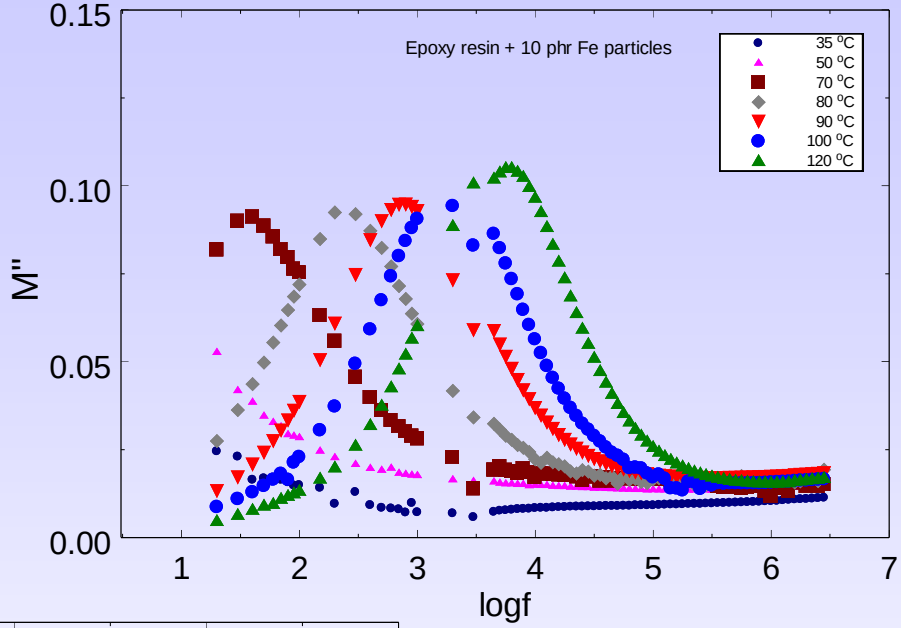
Figure 2 (a, b) Real M', ε' and (c, d) imaginary M'', ε'' parts of electric modulus and dielectric permittivity versus frequency for various temperatures of the composite with 25 p.h.r. in Al and 0.5 p.h.r. in Kevlar fibres. (△) 140 °C, (□) 145 °C, (+) 150 °C.

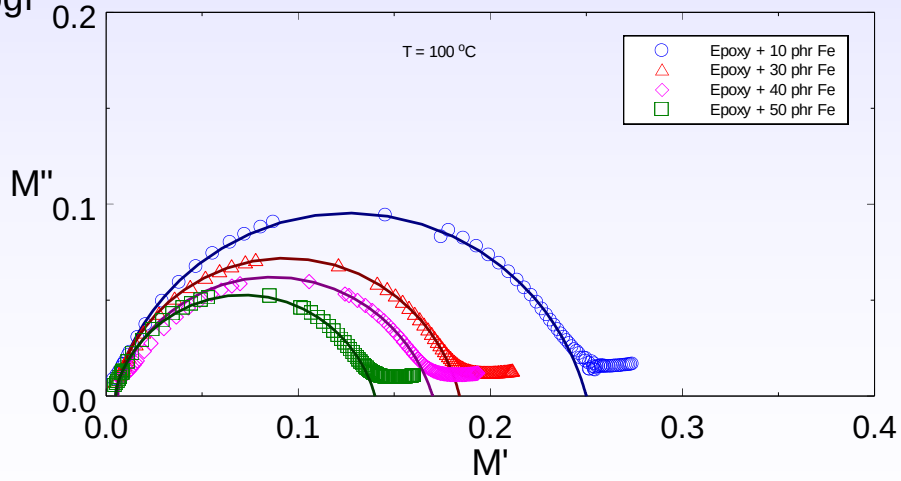
G. M. Tsangaris, G. C. Psarras, N. Kouloumbi,

Journal of Materials Science, 33(8), 2027-2037, 1998.

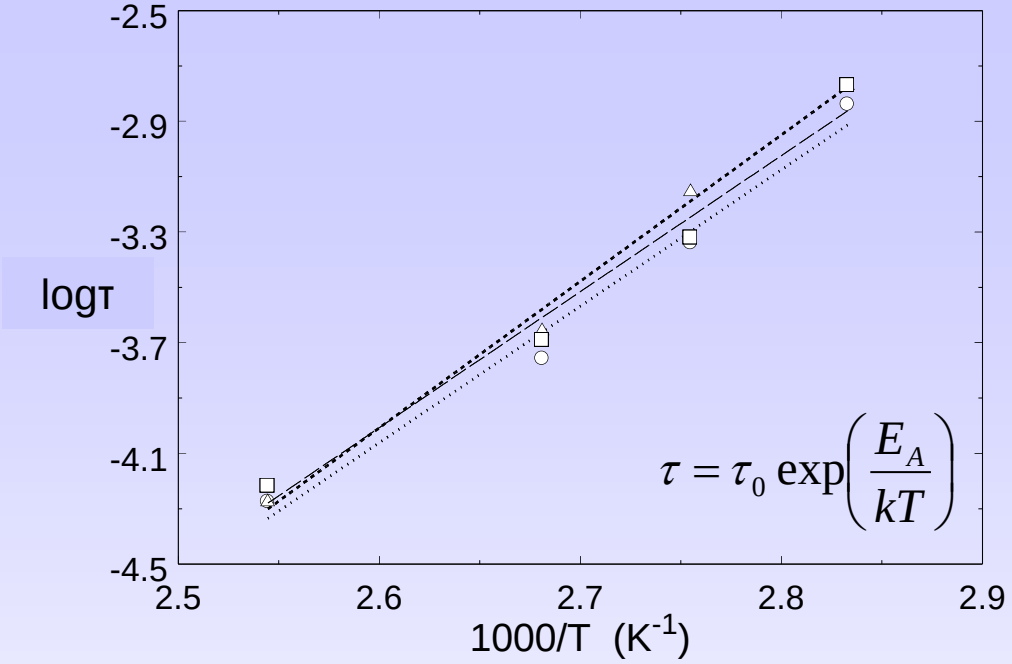
Epoxy Resin – Iron Particles







G. C. Psarras, E. Manolakaki, G. M. Tsangaris, Composites Part A, 34(12), 1187-1198 2003.

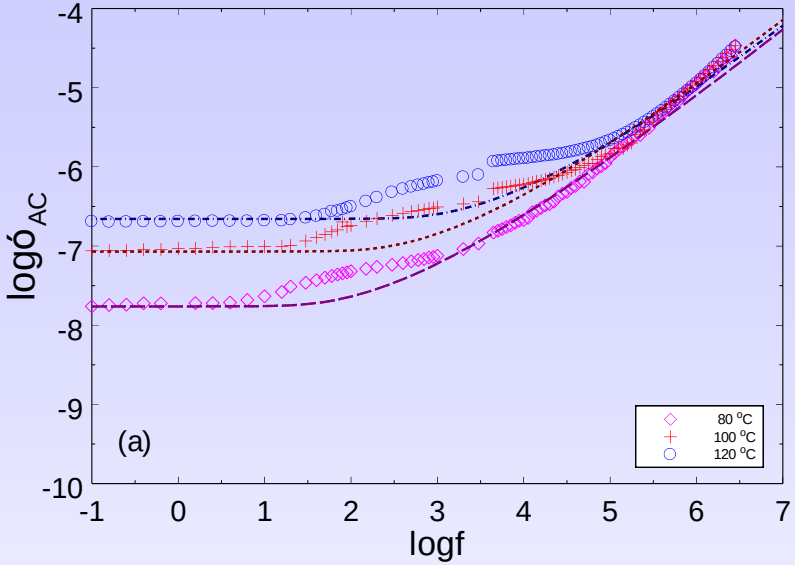


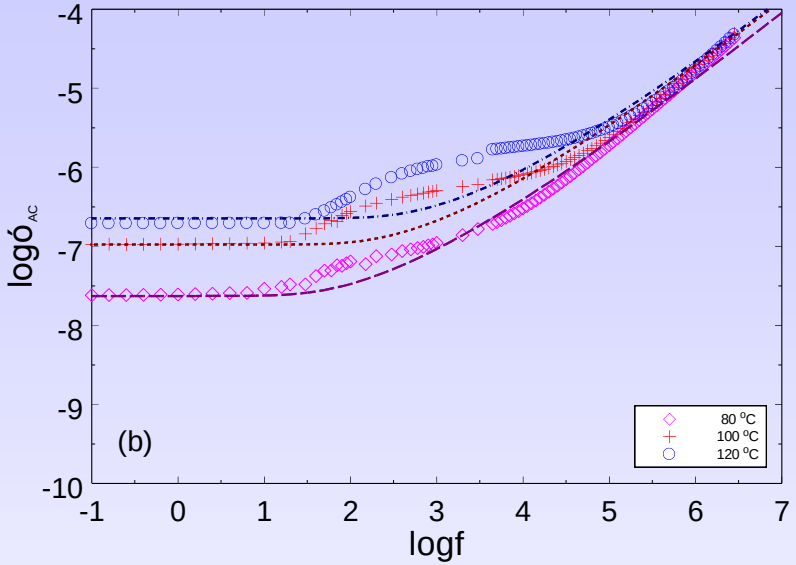
10 phr

θ (°C)	M_s	M_∞	τ_M (s)	γ	E_A (eV)
80	0.004	0.242	1.45×10^{-3}	0.828	0.978
90	0.004	0.247	4.58×10^{-4}	0.831	
100	0.005	0.250	1.75×10^{-4}	0.835	
120	0.004	0.260	5.32×10^{-5}	0.867	

G. C. Psarras, E. Manolakaki, G. M. Tsangaris, Composites Part A, 34(12), 1187-1198 2003.

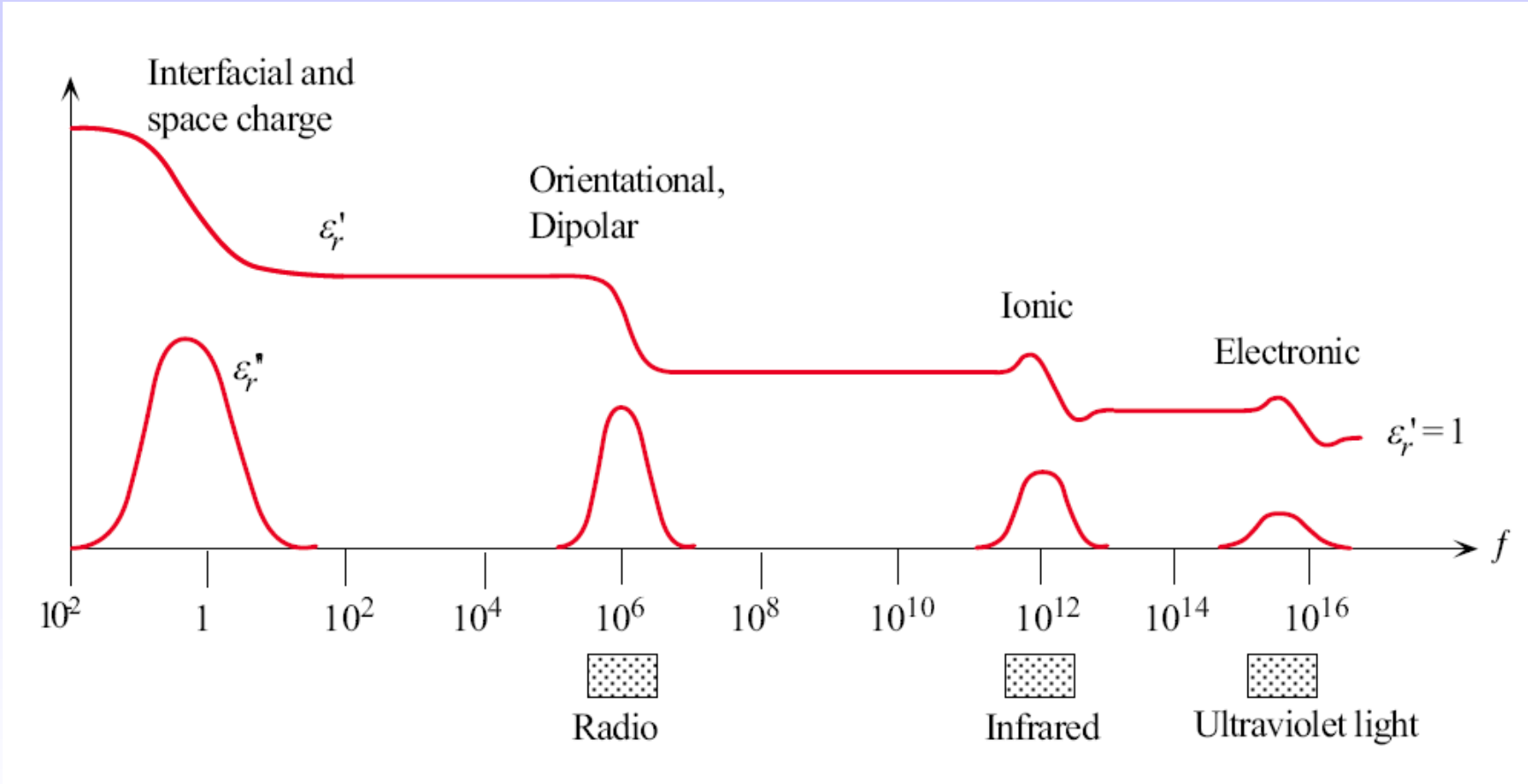
AC Conductivity versus log*f*





(a) 10 and (b) 50 phr in Fe content. (◊) 80°C, (+) 100°C, (O) 120°C. Dashed lines are produced by the **random free-energy barrier model**, the used values of dc conductivity were measured and found to be (a) 1.7×10^{-8}, 8.5×10^{-8} and 2.2×10^{-7} $(\Omega\text{-m})^{-1}$ and (b) 2.4×10^{-8}, 1.1×10^{-7} and 2.3×10^{-7} $(\Omega\text{-m})^{-1}$ respectively to each of the examined temperatures.

Broadband Dielectric Spectrum



Polymers and polymer matrix composites are basically **electrical insulators**, since their concentration of free charge carriers is very low.

Under this point of view their electrical properties are primarily refer to **dielectric relaxation *phenomena*** occurring under the influence of ac field.

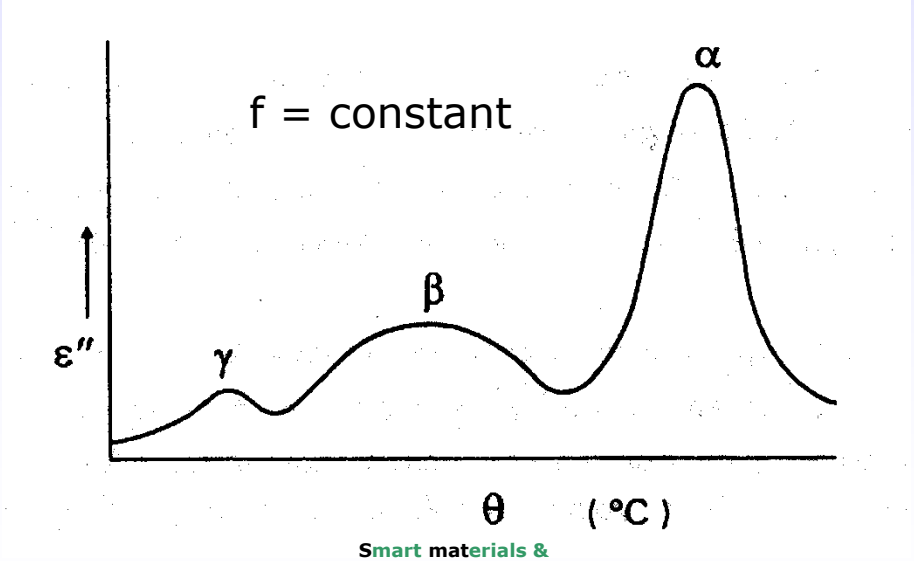
Revealed relaxation processes are related to dipolar orientation effects of **permanent or induced dipoles** and in some cases to **space charge** migration.

Amorphous and semi-crystalline polymers exhibit electrical relaxations associated with glass/rubber transition, segmental mobility of polar groups, interfacial effects and crystallization processes.

Typically, the dielectric loss peaks of a polymer are labeled with the small letters of the Greek alphabet, starting with α- for the process, which is recorded at the higher temperature at constant frequency scan.

Usually, **α-mode** is related to **glass/rubber transition** of the amorphous part of the polymer and the occurring rearrangement of large parts of the polymer chains.

β and γ-mode are broader, less intensive and attributed to **local motions or re-orientations of polar side groups and small segments of the polymer chain**, respectively.



Polymer Matrix Composites

Polymer Matrix Composites are basically insulators and their electrical performance is directly related to:

- the permittivities and conductivities of their constituents
- the volume fraction of the filler
- the size and shape of the inclusions
- the adhesion between the hosted medium and the matrix
- the method of processing
- possible interactions between the conductive and the non conductive phase

Polymer Matrix Particulate Composites

Particulate reinforcement is present even from the earliest days of the commercial uses of polymers.

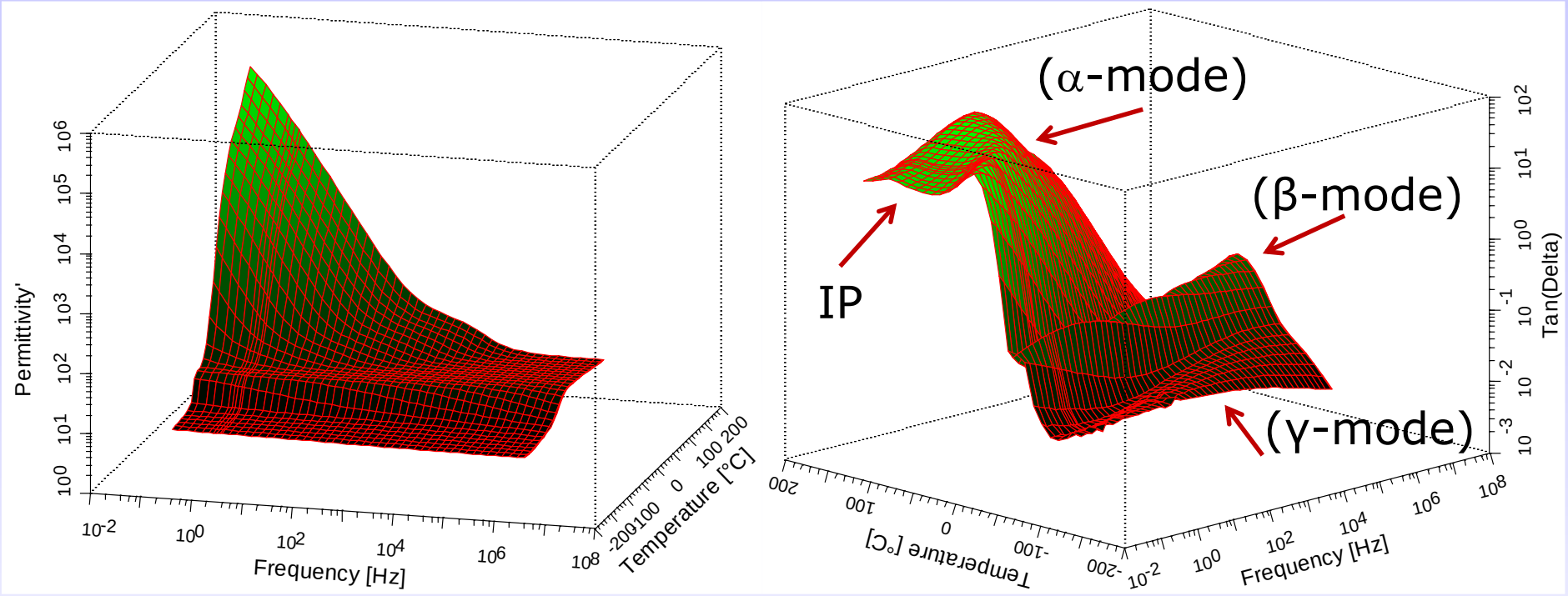
Originally, they were mainly seen as cheap diluents, hence the name filler.

However, their ability to beneficially modify many properties, of the resulting composite system, was soon realized and in our days are used for many purposes.

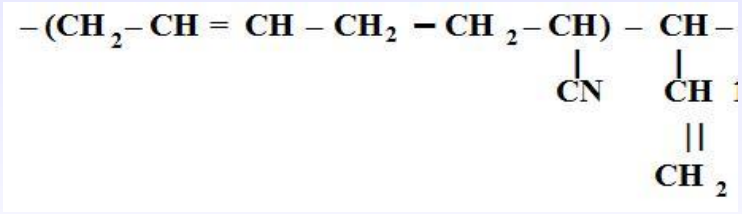
The main reasons for using particulate fillers are:

- Cost reduction
- Improved processing
- Density control
- Optical effects, such as translucency
- Thermal conductivity
- Control of thermal expansion
- **Electrical properties**
- Magnetic properties
- Flame retardancy
- Improved mechanical properties, notably hardness, stiffness, abrasion and tear resistance.

Of course, there is no unique filler providing all these benefits.



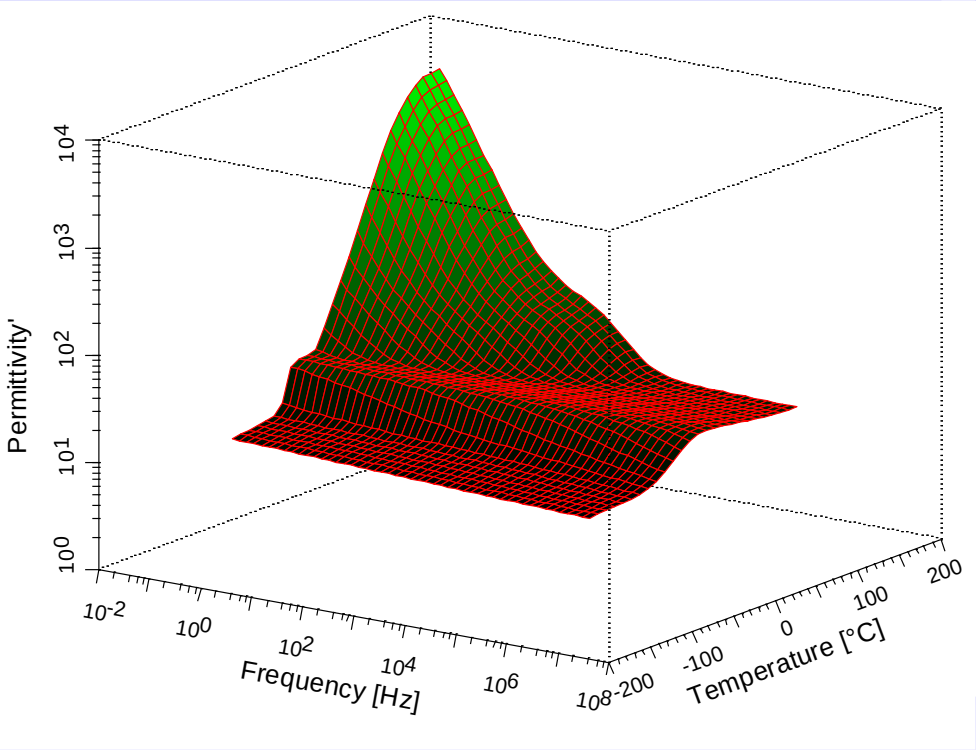
(a)

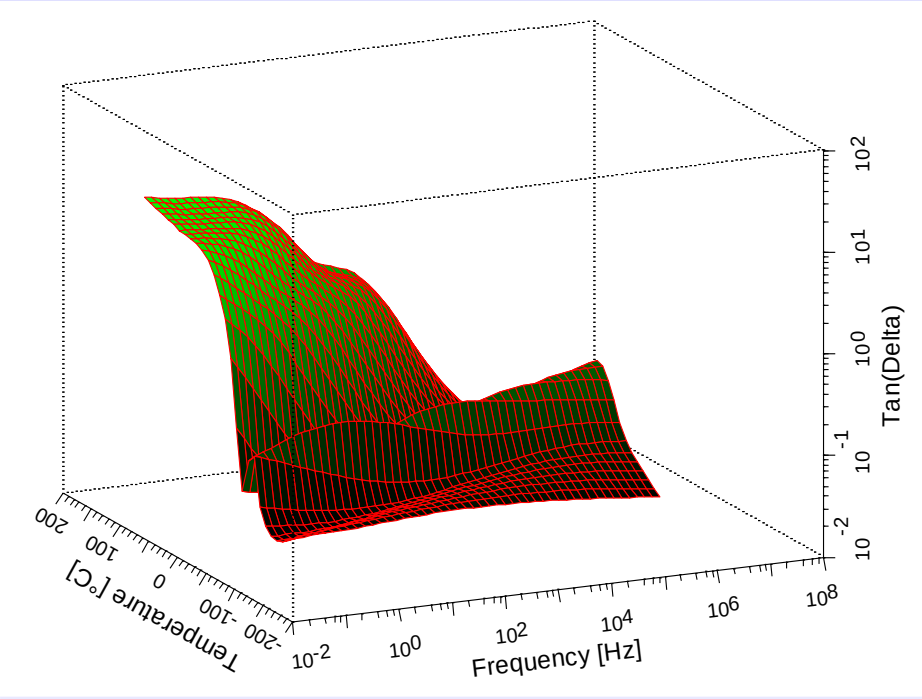


(b)

Variation of (a) real part of permittivity and (b) loss tangent, with temperature and frequency for unfilled Hydrogenated Acrylonitrile Butadiene Rubber (HNBR).

G. C. Psarras, G. A. Sofos, A. Vradis, D. L. Anastassopoulos, S. N. Georga, C. A. Krontiras, J. Karger-Kocsis, European Polymer Journal, 54, 190-199, 2014.





Variation of (a) real part of permittivity and (b) loss tangent, with temperature and frequency for filled Hydrogenated Acrylonitrile Butadiene Rubber (HNBR)with 10 phr MWCNTs.

G. C. Psarras, G. A. Sofos, A. Vradis, D. L. Anastassopoulos, S. N. Georga, C. A. Krontiras, J. Karger-Kocsis, European Polymer Journal, 54, 190-199, 2014.

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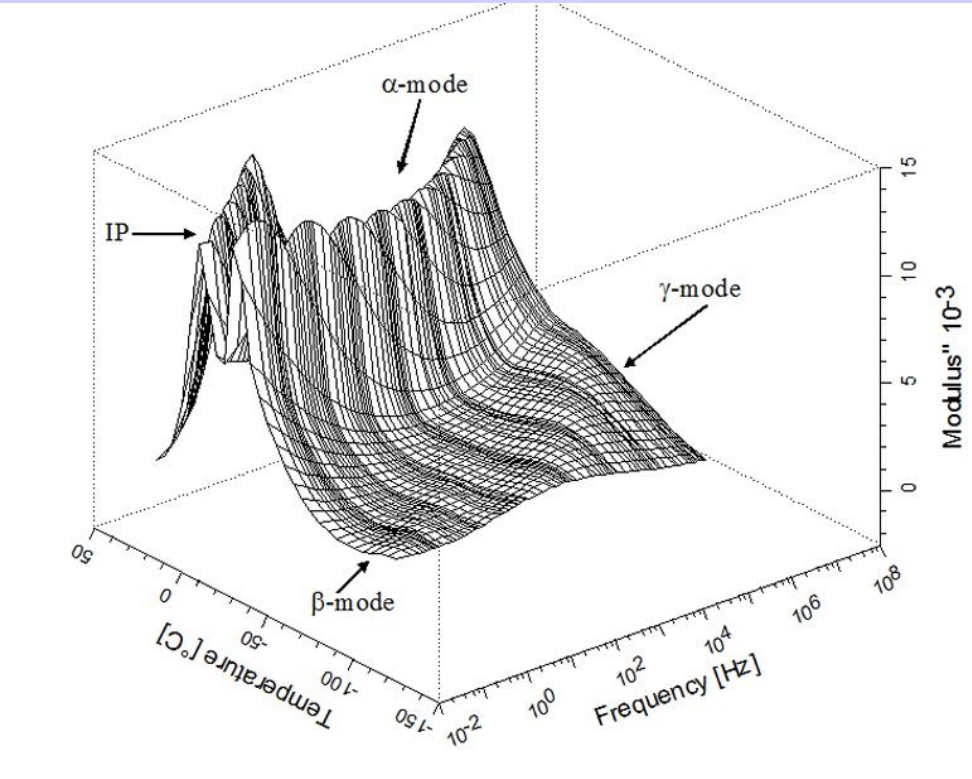
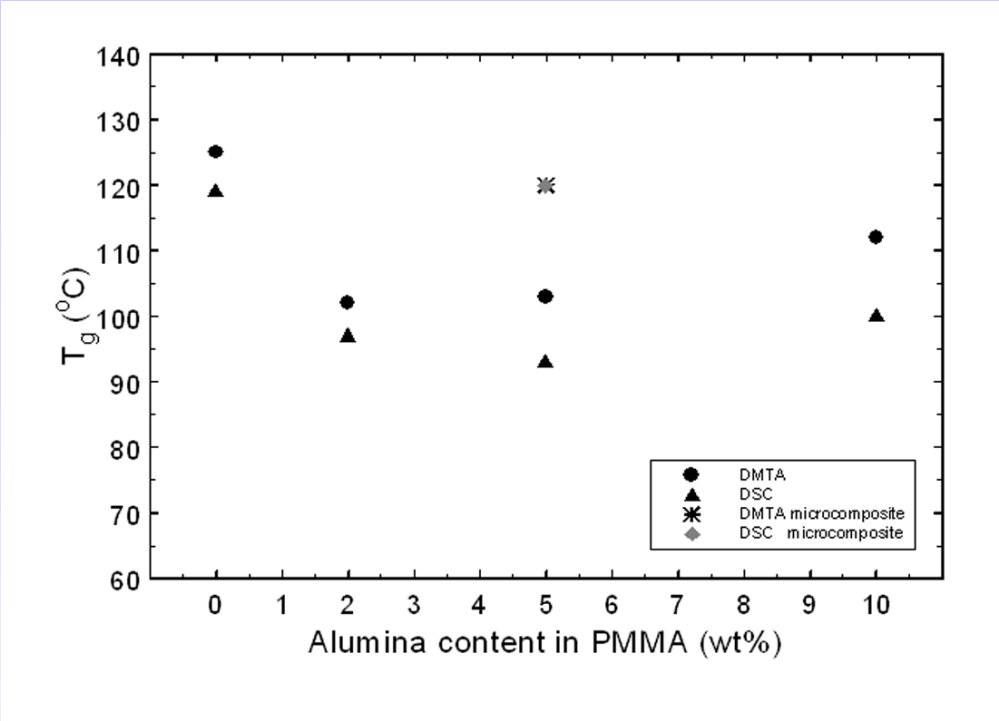
Dielectric Relaxations in Polymer Nanocomposites



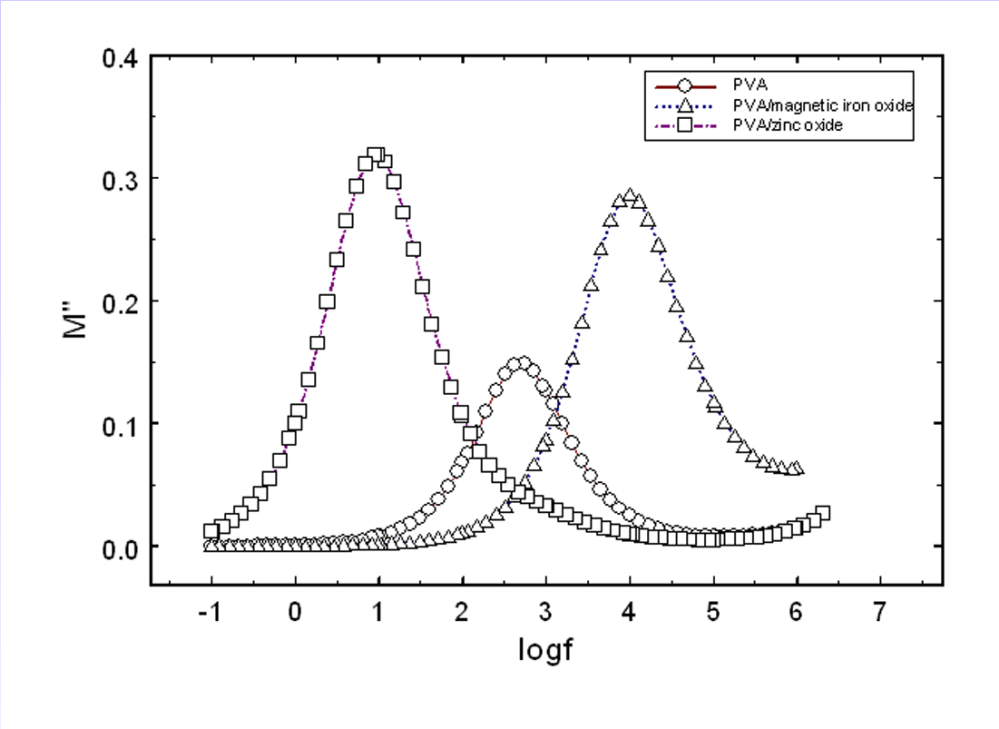
Imaginary part of electric modulus vs frequency and temperature, for a polyurethane/alumina nanocomposite. The concentration of alumina nanoparticles is 10phr and their mean diameter is 25nm.

Relaxation phenomena in elastomeric nanocomposites, G. C. Psarras and K. G. Gatos, p. 89-118, in "Recent advances in elastomeric nanocomposites", edited by V. Mittal, J. K. Kim and K. Pal, Springer-Verlag, Berlin-Heidelberg, 2011.



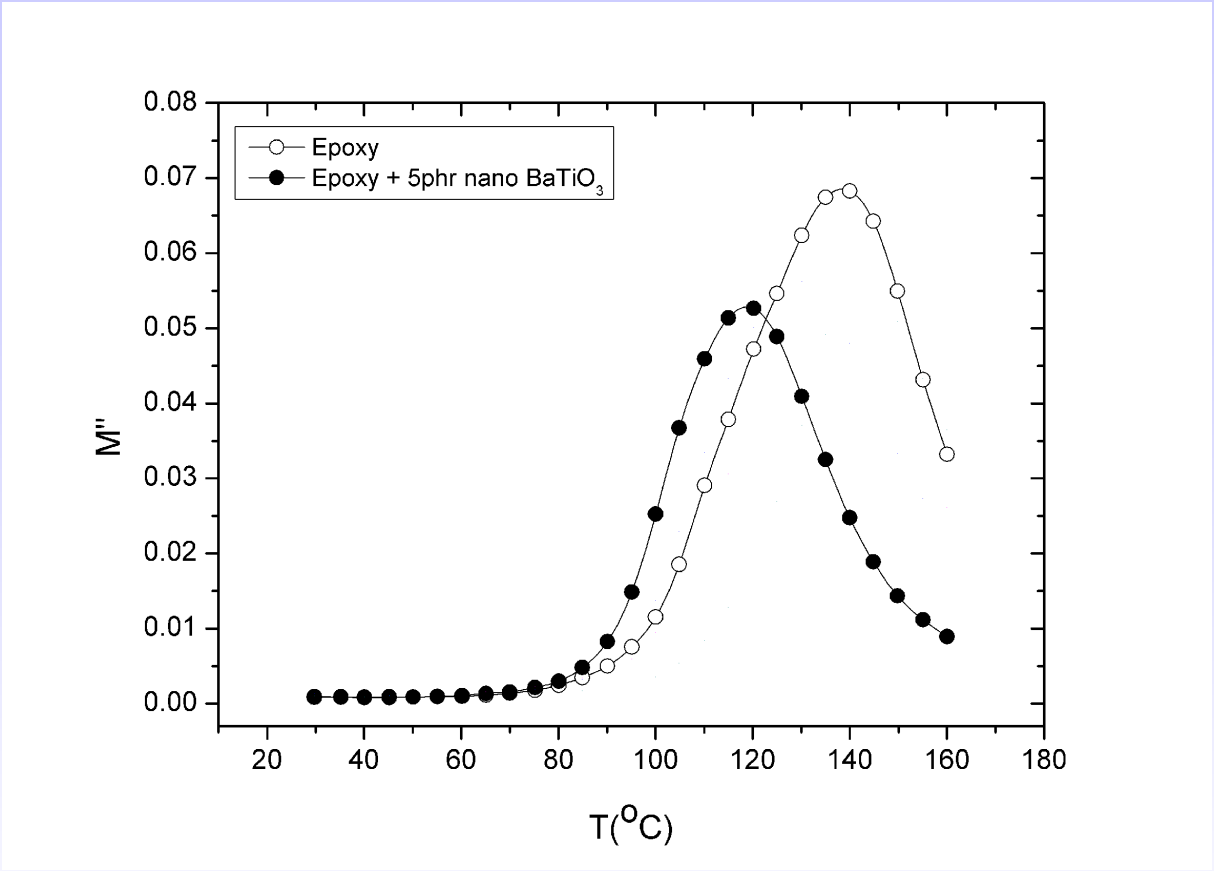
Variation of glass transition temperature of PMMA/alumina nanocomposites, as determined by DMTA and DSC, as a function of the alumina nanoparticles content.

Conductivity and dielectric characterization of polymer nanocomposites, G. C. Psarras, p. 31-69, in "Polymer nanocomposites: Physical properties and applications", ed. by S. C. Tjong and Y.-M. Mai, Woodhead Publishing Limited, Cambridge, 2010.



Electric modulus loss index versus frequency for the α-mode of pure PVA and PVA/magnetic iron oxide, PVA/zinc oxide nanocomposites. Concentration of both nanofillers is 10wt%.

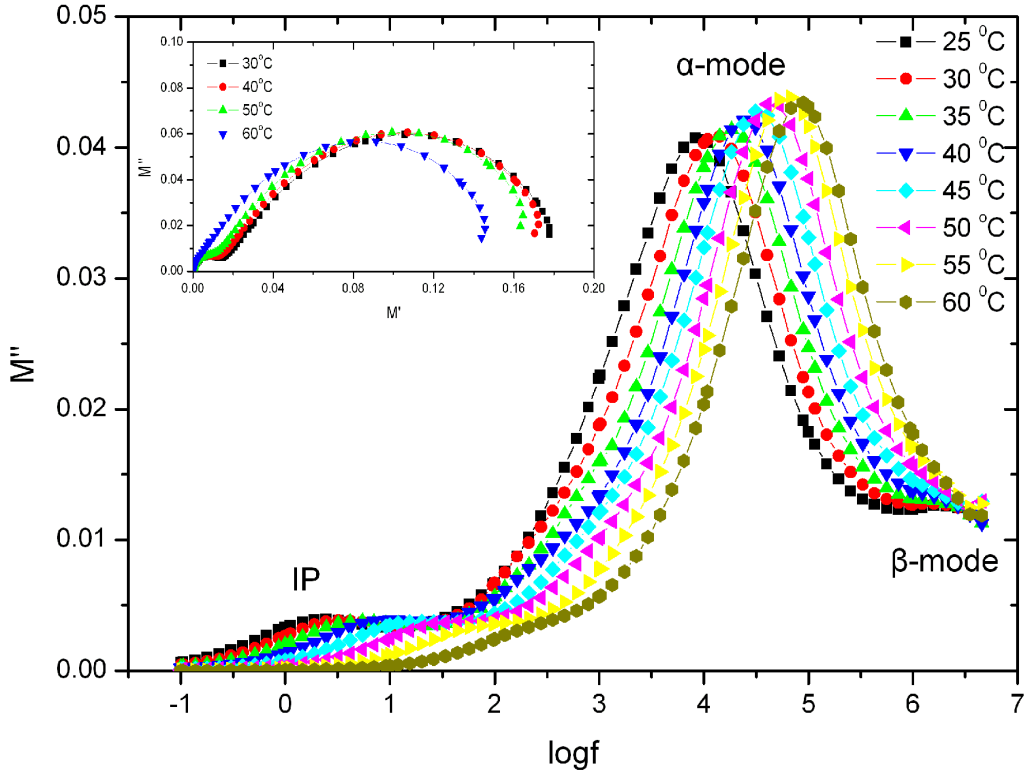
Conductivity and dielectric characterization of polymer nanocomposites, G. C. Psarras, p. 31-69, in "Polymer nanocomposites: Physical properties and applications", ed. by S. C. Tjong and Y.-M. Mai, Woodhead Publishing Limited, Cambridge, 2010.



Imaginary part of electric modulus as a function of temperature for the α-mode of an unfilled epoxy resin and for the corresponding epoxy/$BaTiO_3$ particulate nanocomposite at f=1Hz.

Conductivity and dielectric characterization of polymer nanocomposites, G. C. Psarras, p. 31-69, in "Polymer nanocomposites: Physical properties and applications", ed. by S. C. Tjong and Y.-M. Mai, Woodhead Publishing Limited, Cambridge, 2010.

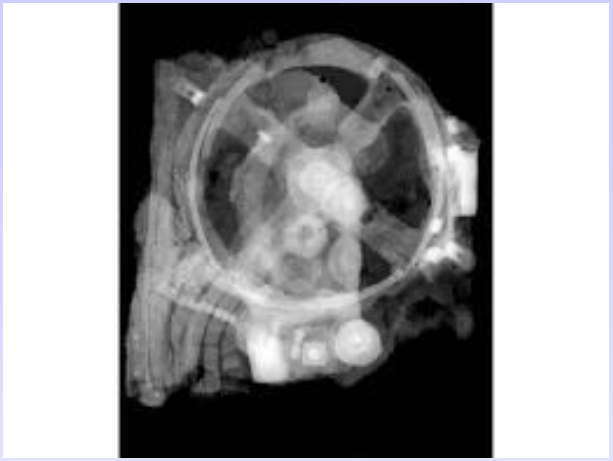
Poly(ethylene oxide)/MWCNT Nanocomposites

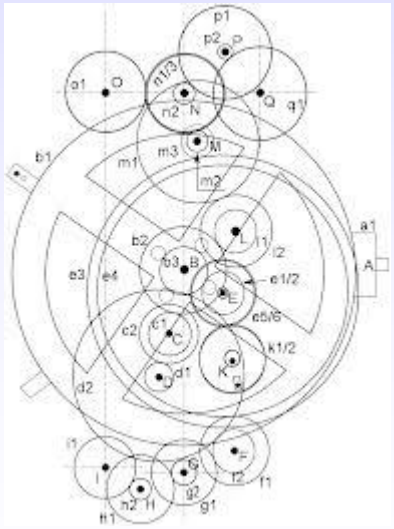


Variation of modulus loss index with frequency, at various temperatures, for the PEO/(0.25wt%) modified-MWCNT nanocomposite. Inset depicts Cole-Cole plots at various temperatures.

Conductivity and dielectric characterization of polymer nanocomposites, G. C. Psarras, p. 31-69, in "Polymer nanocomposites: Physical properties and applications", ed. by S. C. Tjong and Y.-M. Mai, Woodhead Publishing Limited, Cambridge, 2010.

Antikythera Mechanism



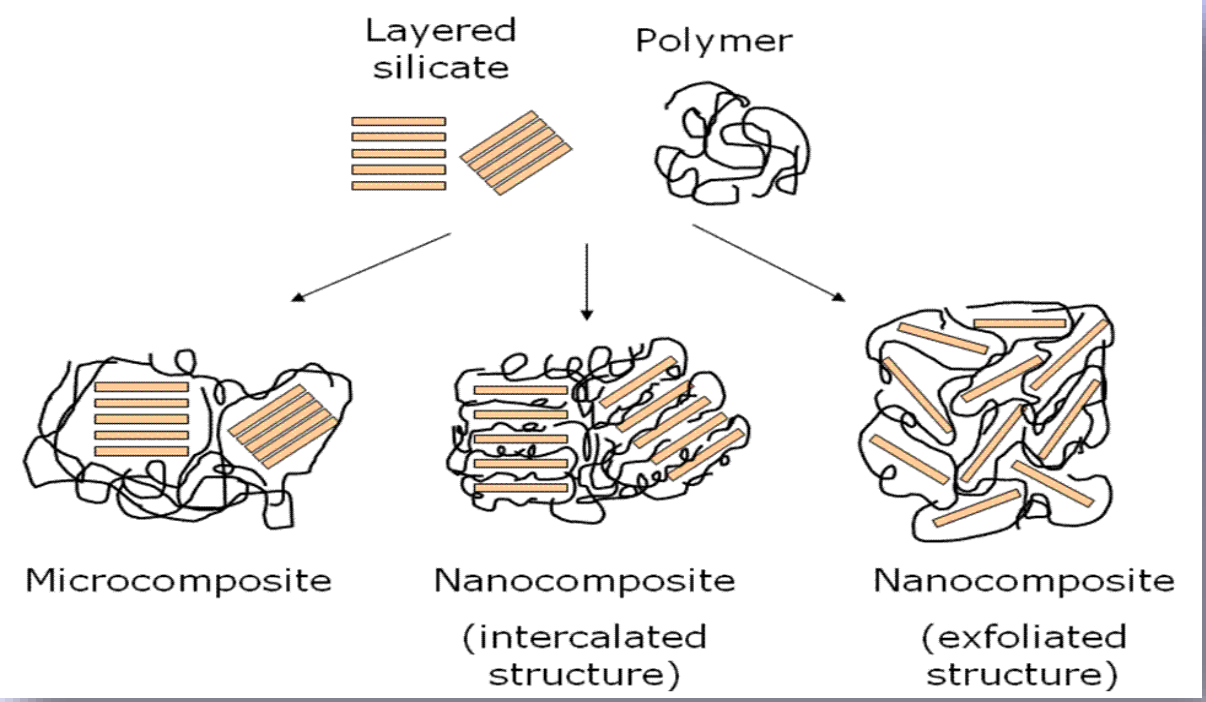


The **Antikythera mechanism** is an ancient analog computer designed to predict astronomical positions and eclipses. It was recovered in 1900–01 from the Antikythera wreck, a shipwreck of the Greek island of Antikythera. The computer's construction has been attributed to the Greeks and dated to the early 1st century BC. Technological artifacts approaching its complexity and workmanship did not appear again until 14th century, when mechanical astronomical clocks began to be built in Western Europe.

Rubber/Layered Silicates Nanocomposites

The impact of nanostructured materials is very high due to their potential applications (thermo-mechanical resistance, flame resistance, electrical properties etc.)

Rubber/ Layered Silicates nanocomposites are attracting increased scientific and technological attention, due to the high reinforcing efficiency of the LS, even at very low loading.



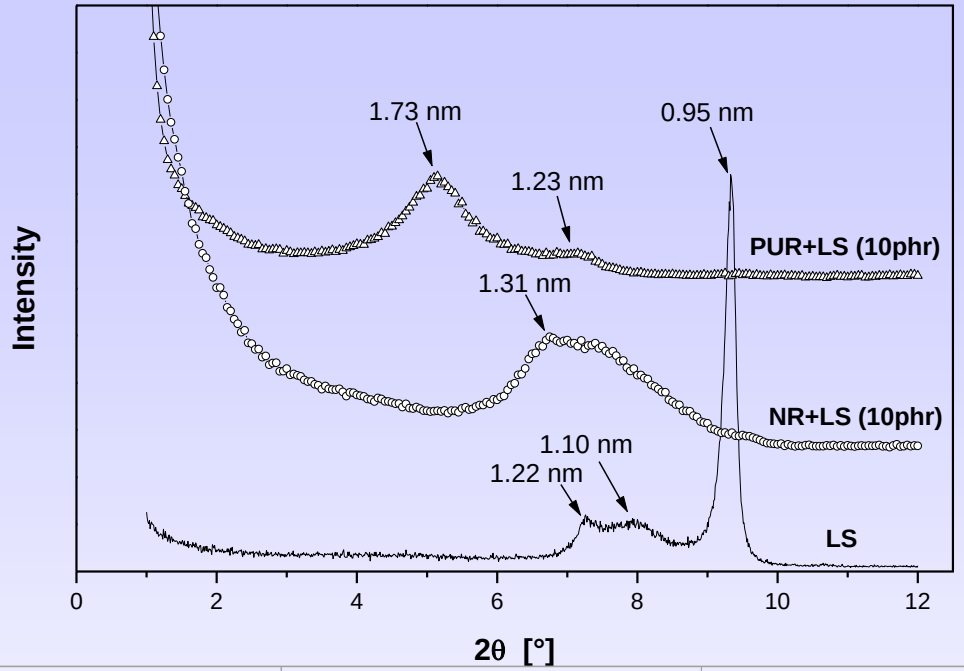
Polymer matrix/LS nanocomposites exhibit three different configurations:

(a) microphase separated composites, where polymer matrix and layered silicates remain immiscible,

(b) intercalated structures, where polymer molecules are inserted between the silicate layers, and

(c) exfoliated structures, where individual silicate layers are dispersed in the polymer matrix

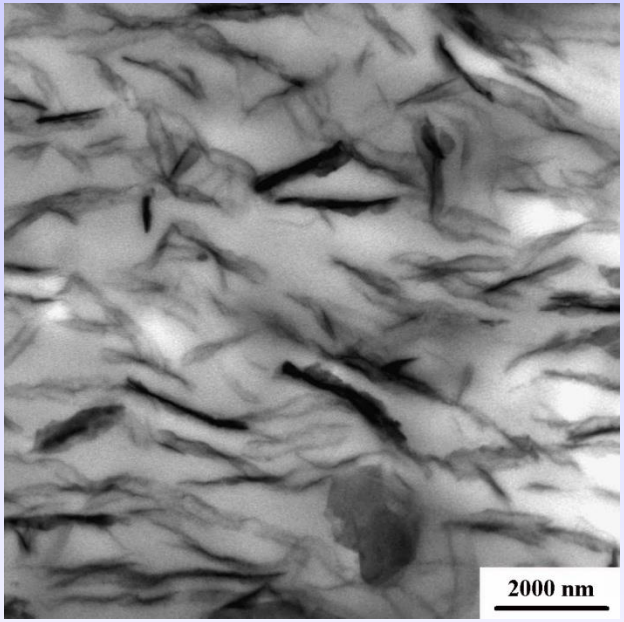
Morphology - XRD

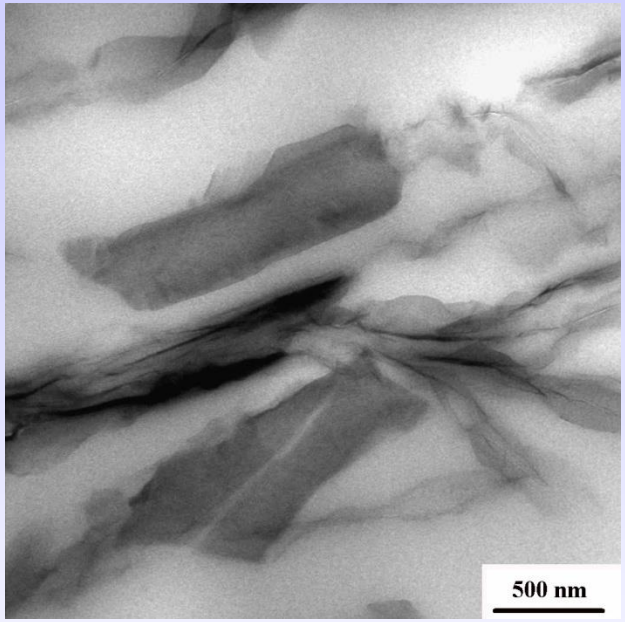


	Peak position (2θ/°)	Interlayer distance (nm)
LS	7.25 / 8.04 / 9.31	0.95 / 1.10 / 1.22
NR + 10phr LS	6.75 / 7.43	1.19 / 1.31
PUR/NR + 10phr LS	4.23 / 6.75	1.31 / 2.09
PUR + 10phr LS	5.11 / 7.19	1.23 / 1.73

XRD spectra of the layered silicate (LS) reinforced latex nanocomposites of various compositions, *S. Varghese et al JAPS, 92, 543-551, 2004.*

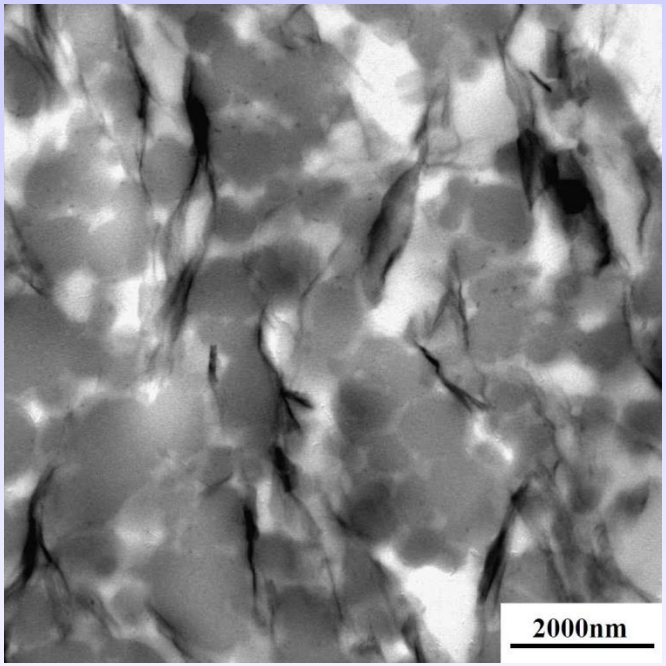
Morphology - TEM

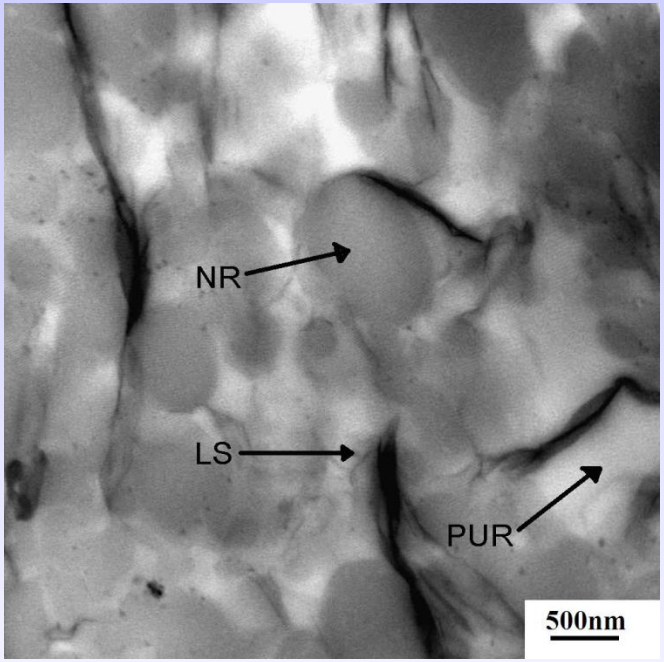




TEM images at two magnifications for the PUR + 10 phr LS nanocomposite.

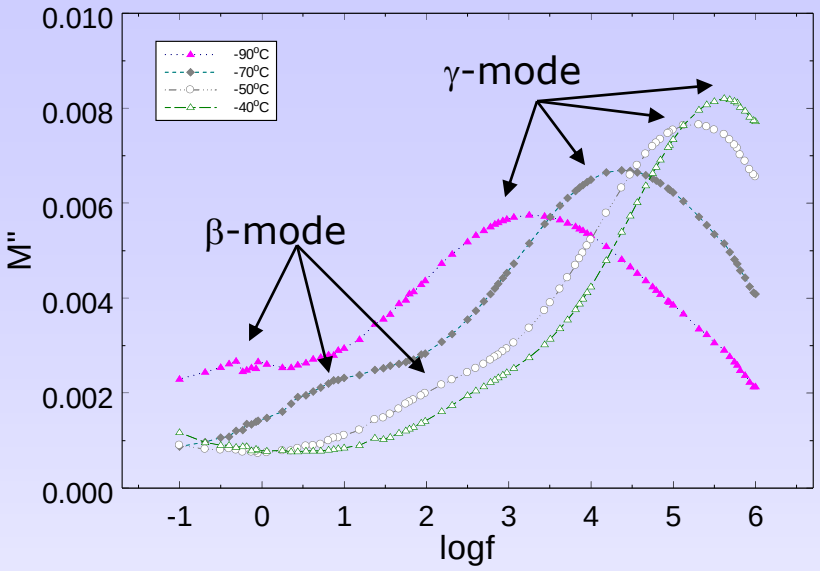
Morphology - TEM

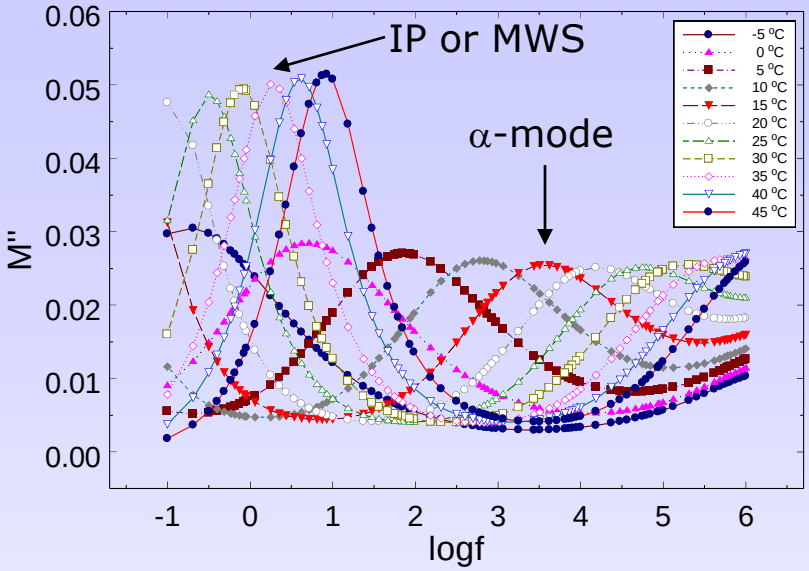




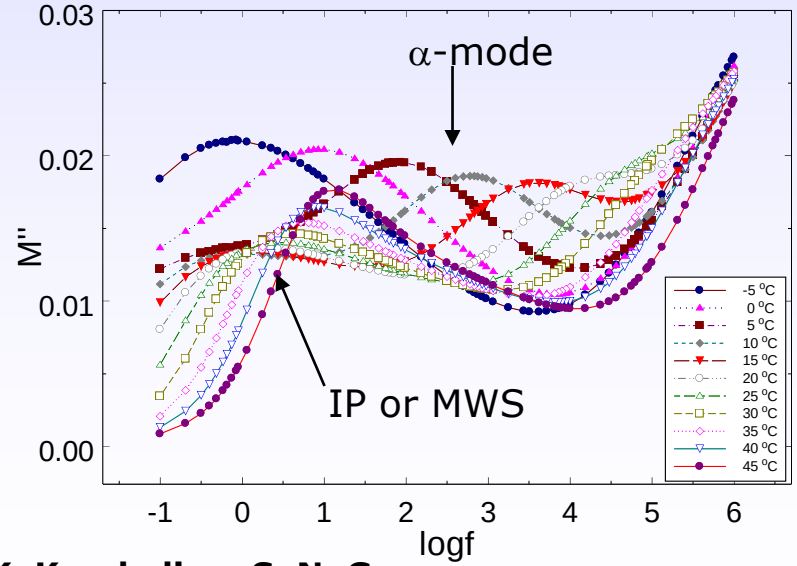
TEM images at two magnifications for the PUR/NR + 10 phr LS nanocomposite. Note: the vulcanised more or less spherical NR particles are well resolved.

PUR





PUR + 10 phr LS →



G. C. Psarras, K. G. Gatos, P. K. Karahaliou, S. N. Georga, C. A. Krontiras, J. Karger-Kocsis, Express Polymer Letters, 1(12), 837-845, 2007.

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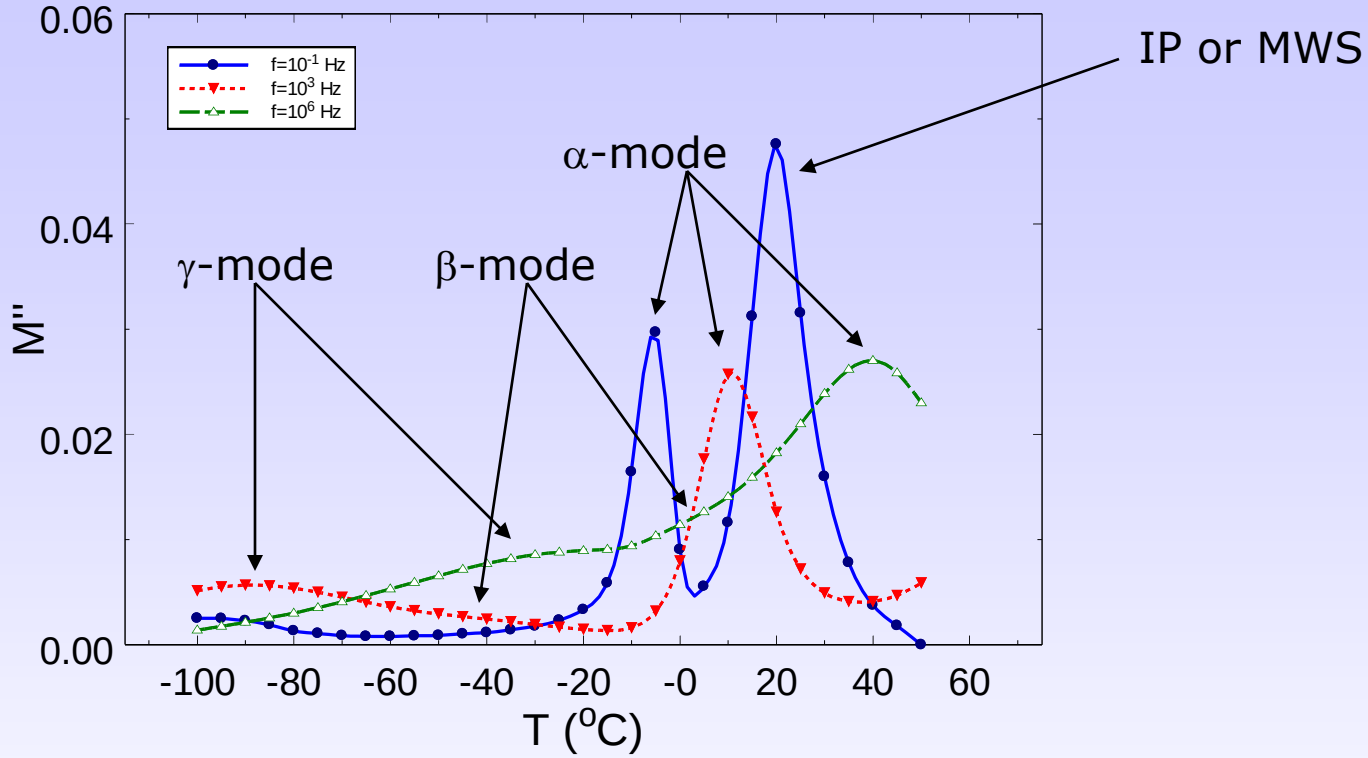
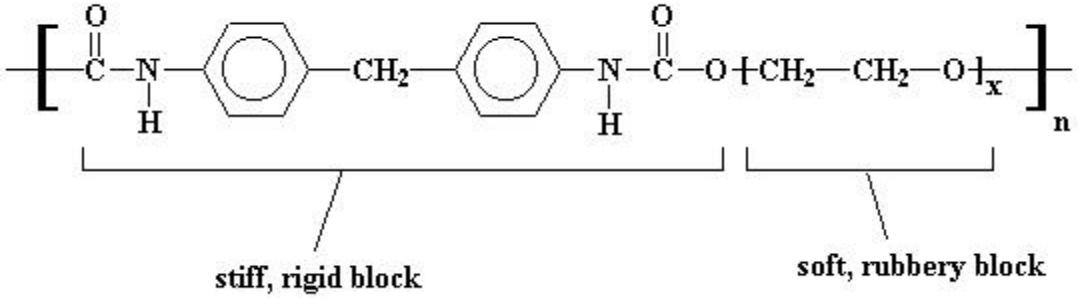
PUR





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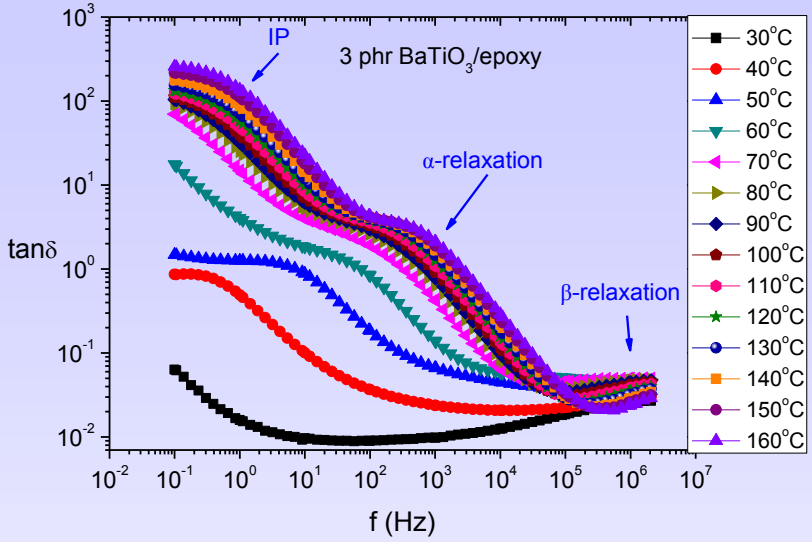
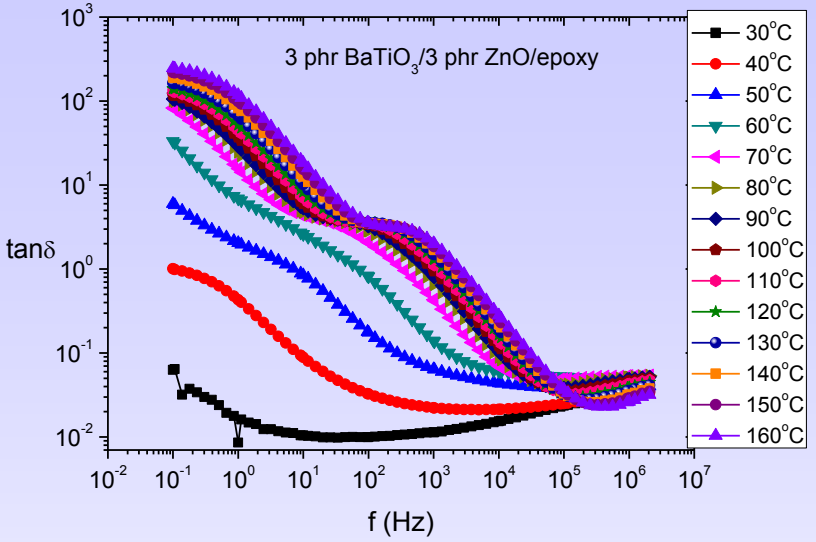
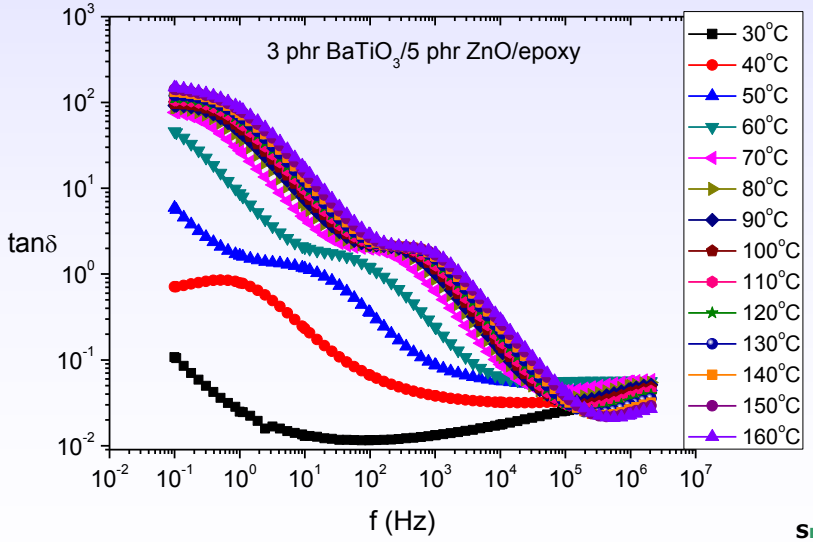
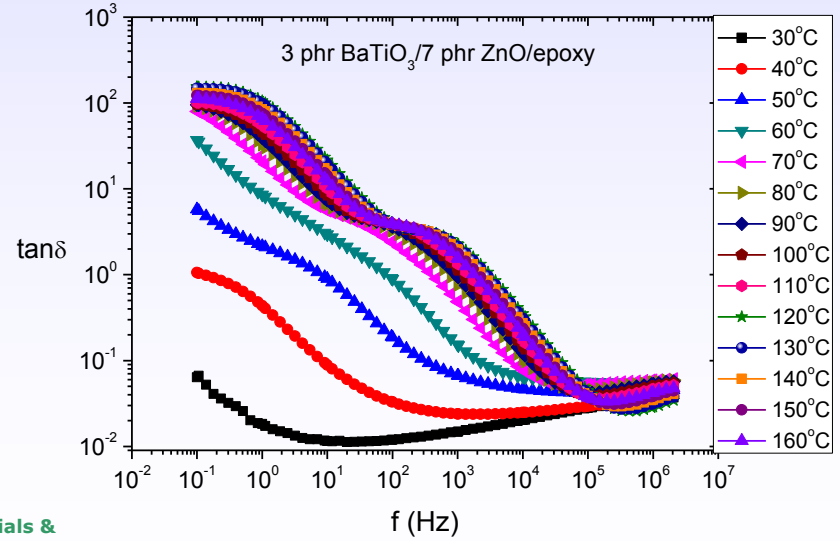
$BaTiO_3$/ZnO/Epoxy: tanδ vs f



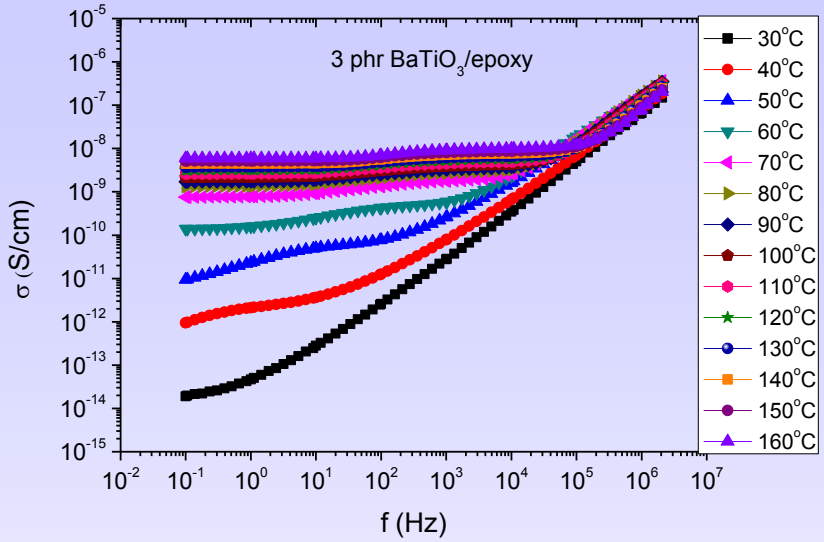


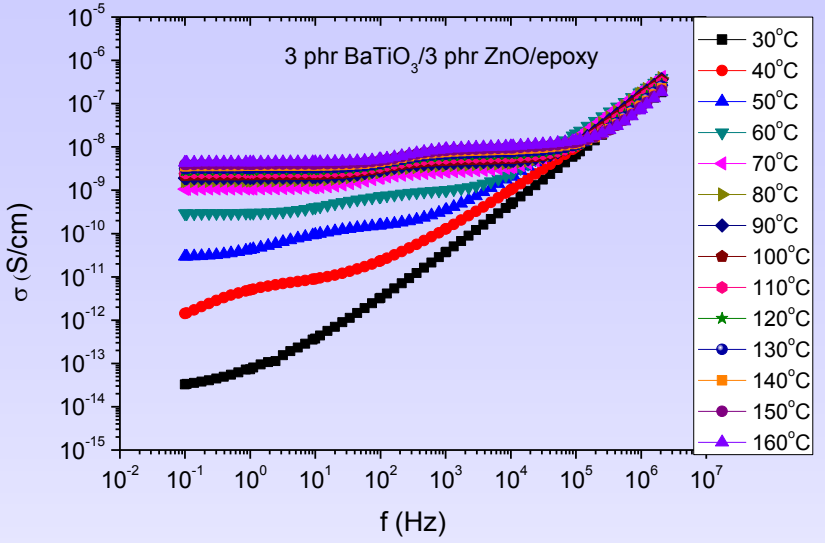


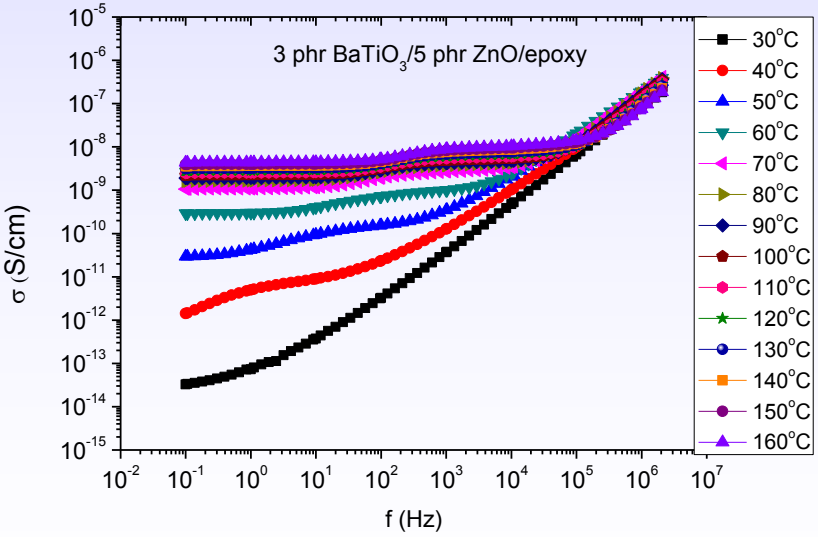
γ-mode

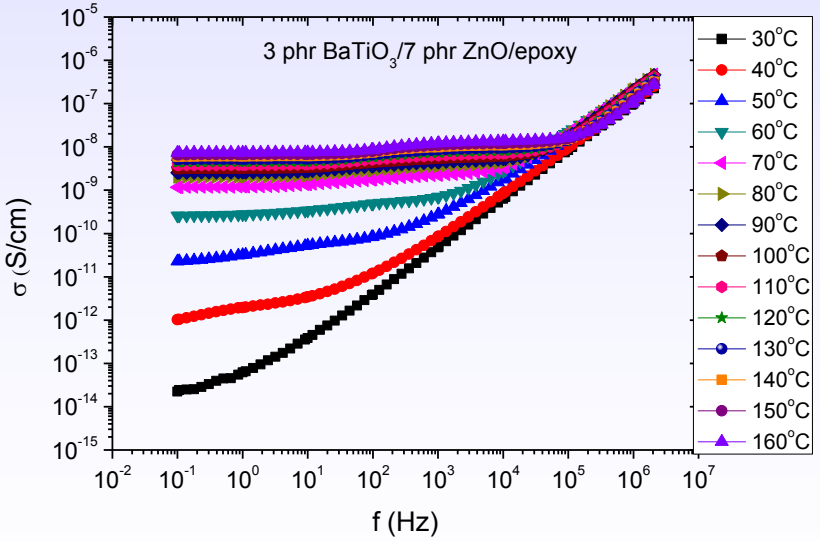


$BaTiO_3$/ZnO/Epoxy: AC Conductivity



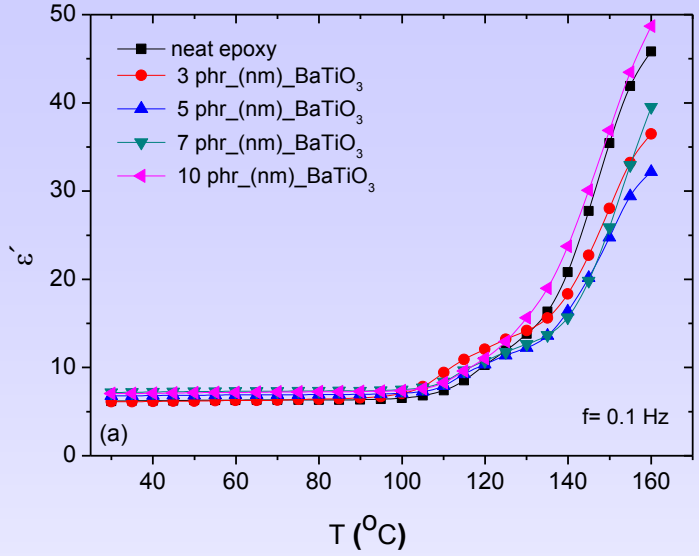


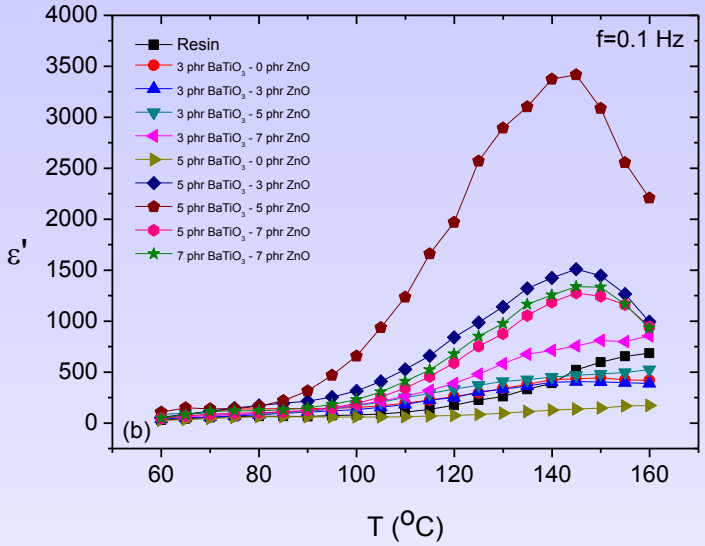


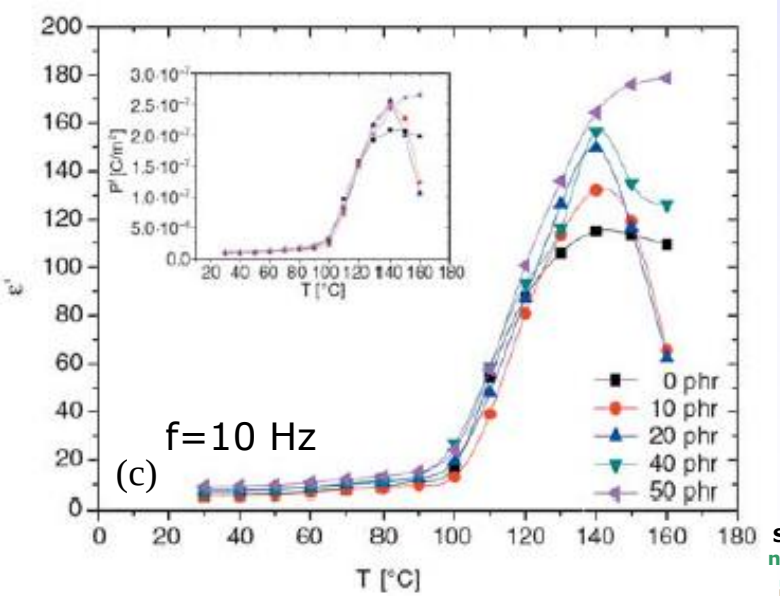


$$\sigma_{AC} = \sigma_{DC} + A\omega^{s}$$

Variable Polarization and Functionality

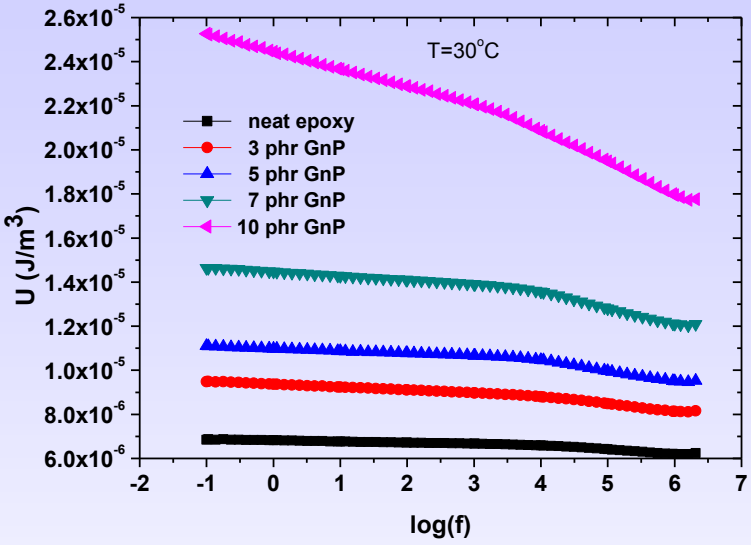


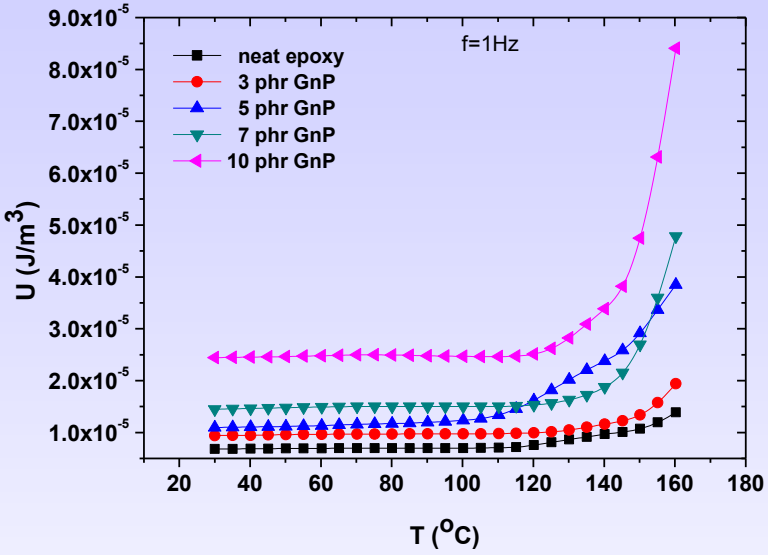




Effect of $BaTiO_3$ particles' size:
(a)30-50 nm
(b) < 100 nm
(c) ~ 2 μm.

Energy Density: GNP Composites





$$U = \int E \cdot dD \Rightarrow U = \frac{1}{2}\varepsilon_0 \varepsilon' E^2$$

Material property

Applied field E = 0.5 kV/m

A. C. Patsidis, K. Kalaitzidou, G. C. Psarras, Journal of Thermal Analysis and Calorimetry, 116, 41-49, 2014.

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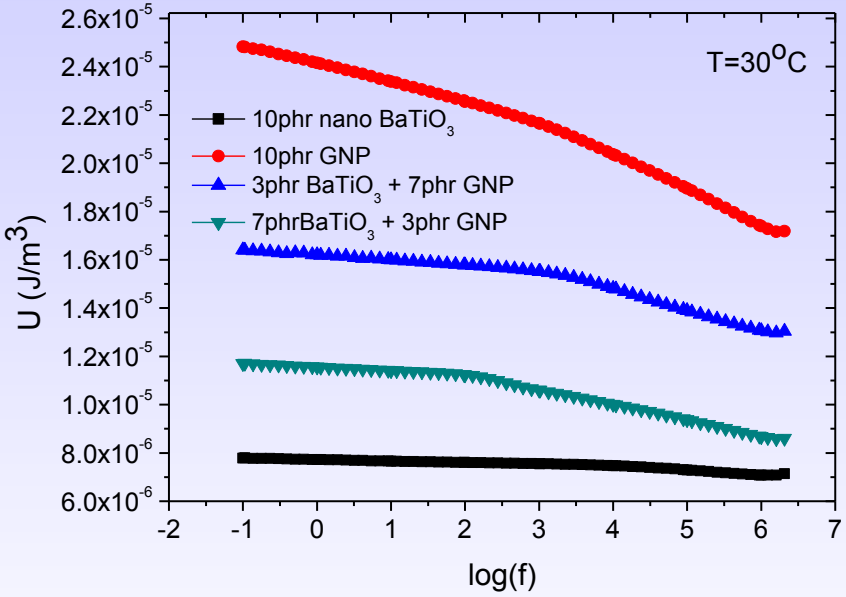
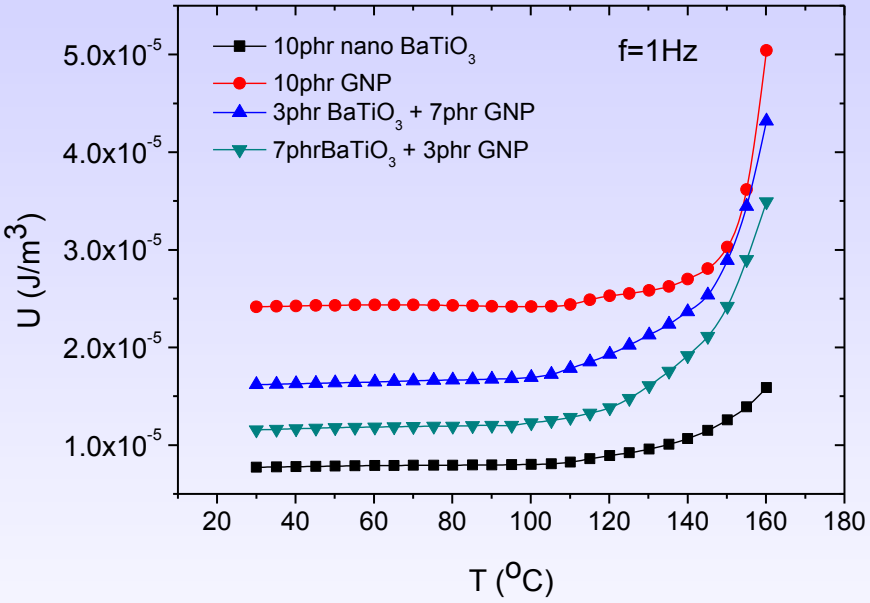
Energy Density: GNP vs $BaTiO_3$ vs Hybrid /Composites





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Conclusions

Dielectric spectroscopy can provide useful information with respect to:

- Relaxation phenomena,
- Interfacial effects,
- Molecular mobility,
- Conductivity mechanisms,
- Phase changes, in polymers and polymer matrix composites.

The electric modulus formalism offers some advantages in interpreting relaxation processes, since difficulties like electrode polarization and space charge injection phenomena can be resolved or even ignored.

Dielectric data should be interpreted in all three (or four) formalisms.

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