The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
Cultural Organization

IAEA
International Atomic Energy Agency

1996-7

Entrepreneurship for Physicists

17 - 21 March 2008

Success Story

Fernando Galembeck
UNICAMP, Brazil

Opportunities for developing countries in the post-oil era

Fernando Galembeck
Institute of Chemistry
Unicamp, Campinas SP, Brazil

Our context: the Knowledge Society

- Knowledge creates value
  - New products
  - Competitive “commodities”
- Wealth originates from knowledge
  - New resources
  - New jobs
  - Better living
- Neither knowledge or wealth are intrinsically ethical

Innovation in Brazil

- Leader in the production of liquid fuels from renewable sources.
- Competitive in the production of transportation and agricultural equipment, petrochemicals, paper and cellulose, iron and steel and on the agribusiness based on *innovation.*
  - Soybean production does not require nitrogen fertilizers due to the use of seed innoculation techniques.
- Leader in deep-water oil and gas production.

ALL THE EXPORTS ARE STRONGLY DEPENDENT ON SCIENCE, TECHNOLOGY AND INNOVATION

What research, what for, to benefit whom, where?

- To improve our vision of the world
- Creation of opportunities, wealth, jobs
- Strategic value
- Benefits to large populations
- Improvement of the environment
- Pleasant and joyful in the making, debating and learning

The time for non-oil raw materials

- Science and technology in the agribusiness: soybeans, oranges, eucaliptus, chicken, cattle, cotton…
  - Sucrose at US$70/ton in the cane juice
  - Cloned eucaliptus: inexpensive joule of solar energy
  - Prices for natural rubber, castor oil and many others growing faster than oil
- Higher prices for the minerals for industrial applications (clays, calcium carbonate…).

Impact of biofuels

http://br.advfn.com/p.php?pid=qkchart&symbol=NY%5EBG

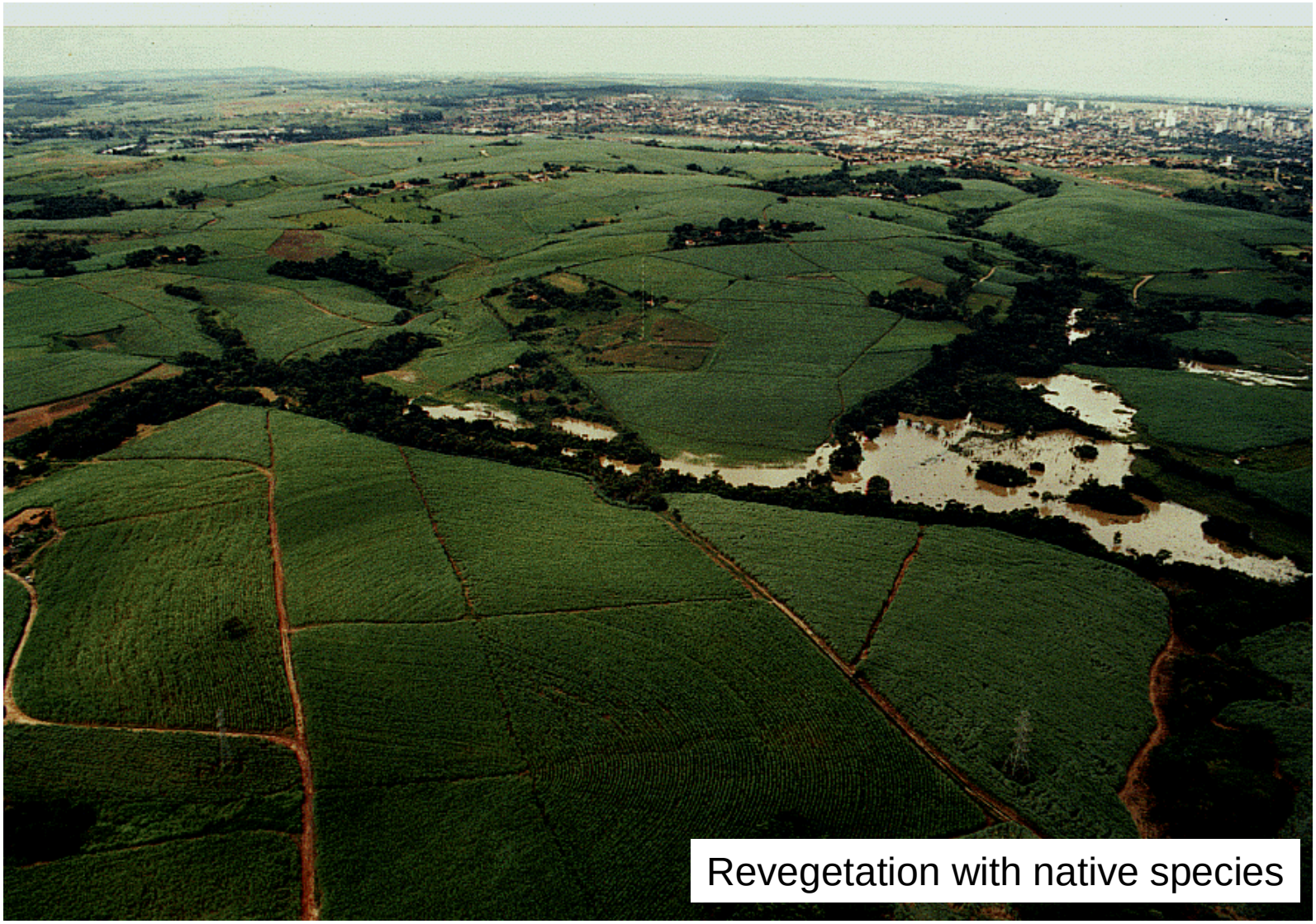
Phosphate fertilizer prices were stagnant from the period high of about $440/t fob Tampa in April of 2007, but as supplies became tighter later in the year in the face of surging wheat and soybean prices began to climb rapidly once more. At the end of November the price of DAP fob Tampa reached $550/t, and indications point towards ending the year at about $580/t.
http://cruonline.crugroup.com/FertilizersChemicals/MarketForecasts/PhosphoricAcidMAPDAPTSPTenYearForecast/tabid/307/Default.aspx

Today: above $1,000/t

Fertilizers

- Potassium (KCl) and urea lead the list of imports
  - 2005: 1 US$ Bi KCl
- Multiple solutions are required for the K, N and P needs
  - Loss reduction and improved use
  - Diversification of sources including reuse and recycling
- Oligoelements

- From the plantation: Ajinomoto makes 72 ktons of lysine/year in Valparaiso, SP, and another 60 ktons/y in Pederneiras, SP, using raw materials derived from sugar cane. Part is used to make betaine surfactants.



Nanoscience and nanotechnology for creating value

- Modern chemists, screaming to high heaven that they have nothing to do with alchemy, have fulfilled the alchemist's dream — transmuting sickness into health and, with superb ingenuity, changing mud (the raw materials of organic synthesis) into gold (what pharmaceutical companies sell).

Roald Hoffmann, American Scientist 92 (2004) 312

White pigments

- The **albedo** or "whitening" was seen by many alchemists as the climax of their work. As Jung put it: "From the darkness of the unconscious comes the light of illumination, the *albedo*."
- It is a time of cleansing, purifying, sifting and sorting; a bit like wiping away the muck that prevents clear-sightedness.

http://alch3my.tribe.net/

Albedo today

- Energy savings
  - Improved lighting
  - Lower heating from the roofs
    - Less air-conditioning
- Decreased heat trapping in cities

White pigments, 2008

- World markets are dominated by titanium dioxide
- Strong backscattering due to
  - High refractive index
  - Adequate particle sizes
    - Following Mie theory

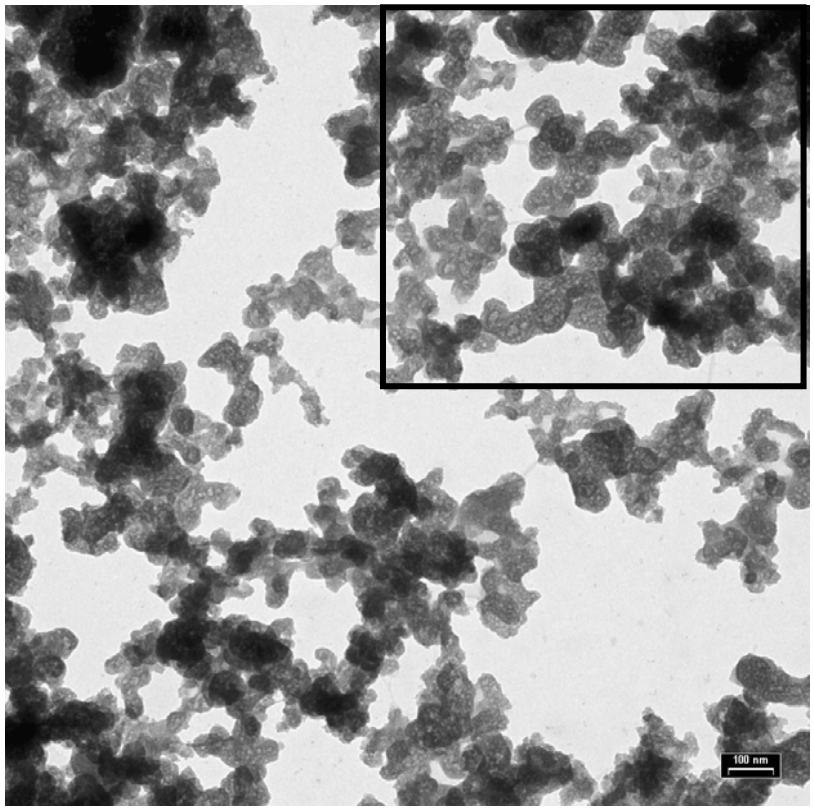
Can we make a white pigment out of other materials?

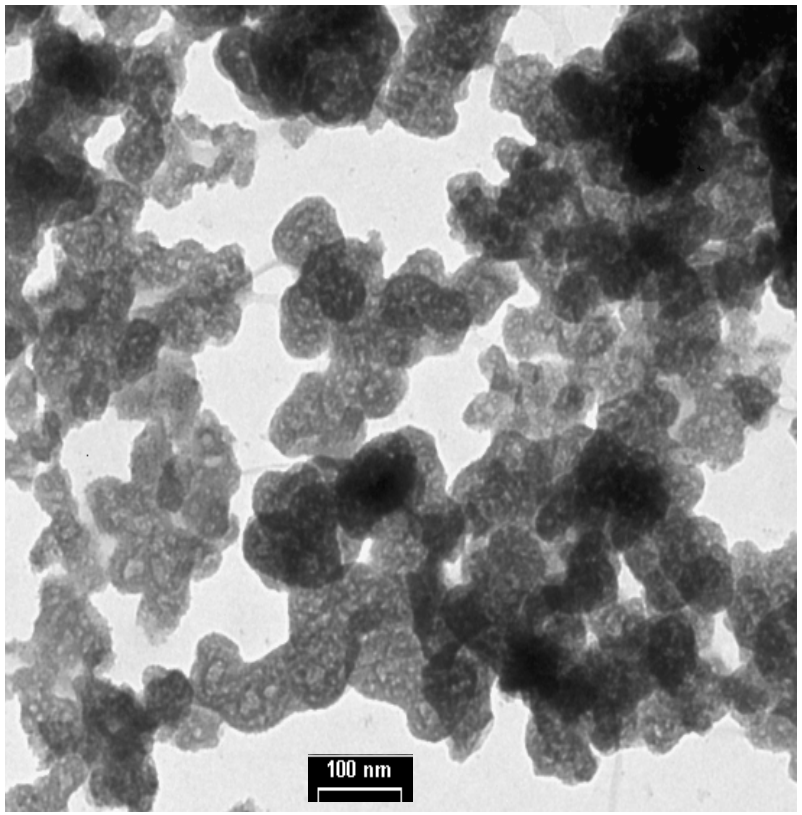
- **Yes, based on the formation of voids in the paint.**
- **Voids can be**
  - **Intrinsic to particles**
  - **Formed during paint drying**
    - **An emergent property**
  - **Due to rare processes of formation of organized nano-structures**

Aluminum phosphate white pigment

- **Biphor, a new white pigment**
  - **Created, patented and published in Unicamp, in the 90s**
    - **Poster received a prize in ICSCS (Compiègne, 1991)**
    - **Contract with the Serrana Company in 1995**
  - **Presented by Bunge Fertilizantes in the Abrafati congress in 9/2005, www.biphorpigments.com**
  - **Presentation in the International Coatings Expo (New Orleans) in 11/2006**

TEM

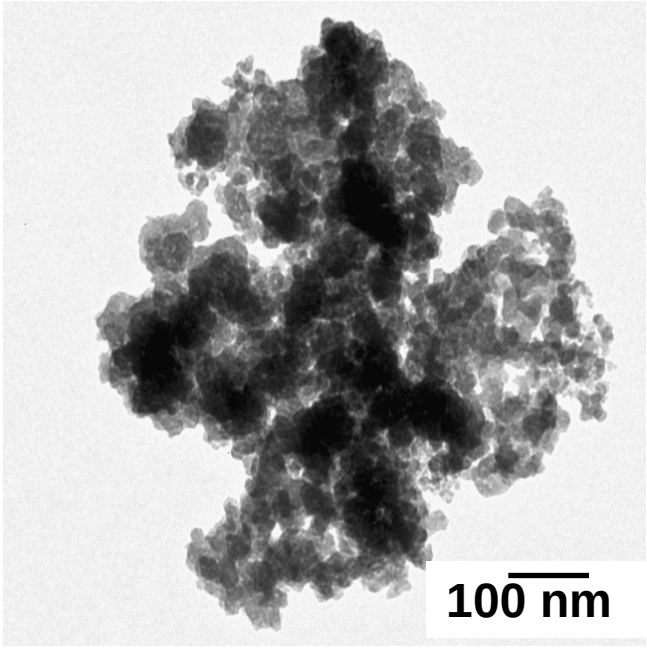


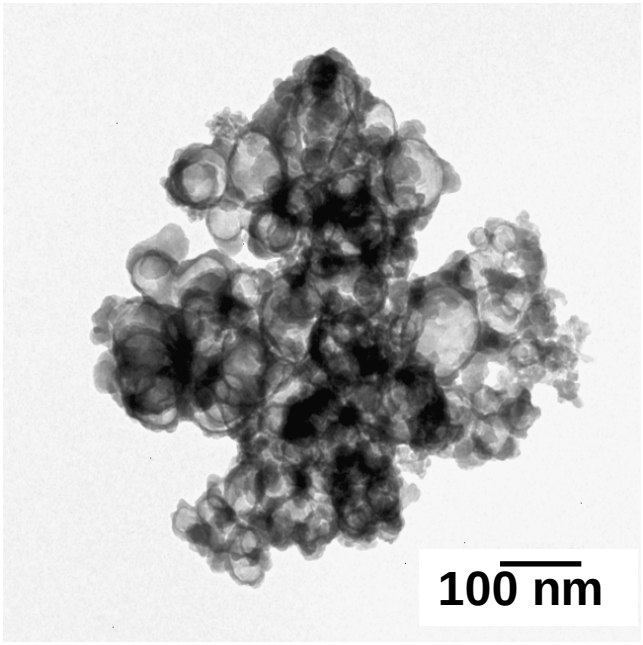


Particles with voids

Core-shell nanostructure

- Particles under the electron beam loose material from their interior but the overall perimeter shows little change.
- Plastic interior, rigid walls.





Free from environmental and toxicity problems

- Wet chemistry under mild conditions
- No effluents
- Residues are safely discarded
  - composting

Current stage

- **Plant in Cajati: 1 ton/batch**
- **New plant for local market**
- **September 2007: conclusion of basic project for large scale plants**
- **Also, some problems**
- **Further information:**
  - ***GALEMBECK, F. ; SILVA, M. C. V. M. ; ROSSETO, R. ; PINHEIRO, G. O. ; BRITO, J. DE . Biphor - nanotechnology for waterborne paint improvement. Paint & Coatings Industry, v. 1, p. 56-62, 2006.***
  - ***ROSSETO, R. ; SANTOS, A. C. M. A. ; GALEMBECK, F. . Hydrous non-crystalline phosphates: structure, function and a new white pigment. Journal of the Brazilian Chemical Society, v. 17, p. 1465-1472, 2006.***

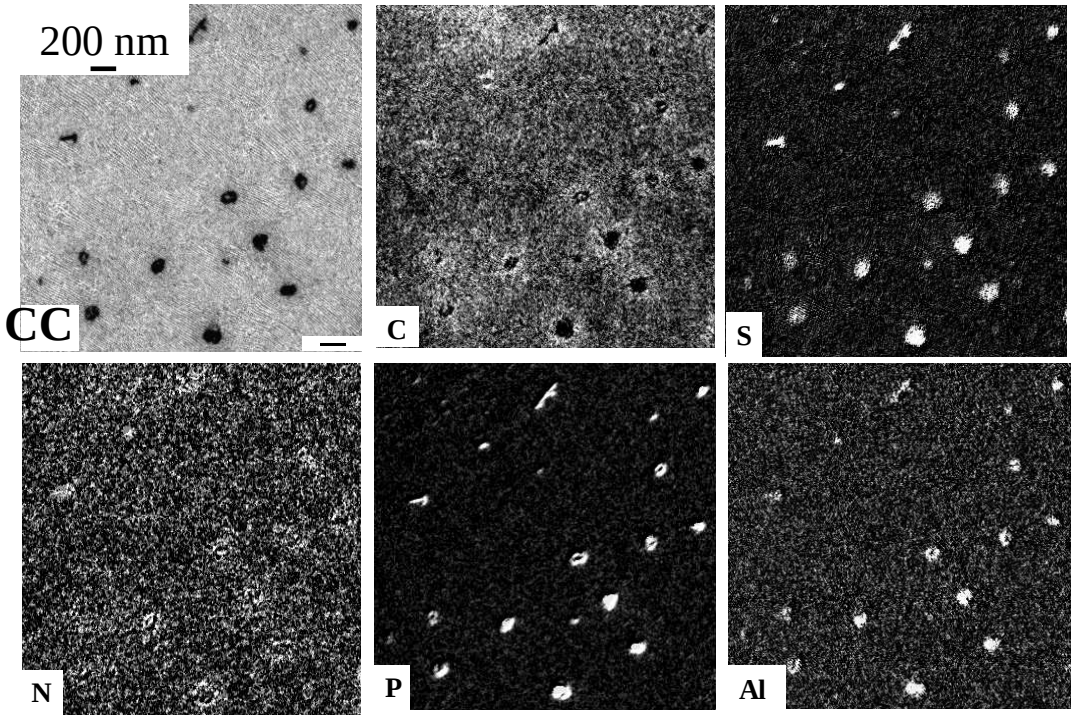

13 15:30

The “mistery of natural rubber”

- Still irreplaceable in many products
  - Tires, adhesives
- Why can’t poly(cis-isoprene) show the same properties as natural rubber?
- Which is the role of the inorganic constituents, proteins and phospholipids in natural rubber properties?

- Ph.D. Thesis of Márcia Maria Rippel
- Found that natural rubber has a complex nanostructure, with many participating elements.
- Capes Prize: best thesis in Chemistry in Brazil, in 2005.
- Publications, patent.
- Where does the rubber-particle compatibility come from?

Coleta de látex no IAC



Electrostatic Adhesion in Nanocomposite Materials

Fernando Galembeck
Universidade Estadual de Campinas
Millennium Institute for Complex Materials

Invited lecture at ICAM/IUMRS, Bangalore 2007

Nanocomposites

Great improvements over usual polymer composites.

Mechanical, solvent resistance, permeation and other properties are drastically changed.

Achievement of new properties depends on the combination of adequate morphology and strong surface interactions.

Pinnavaia, T. J. and Beall, G. W. *Polymer-Clay Nanocomposites* Wiley, London, **2000**.
Okada, A. and Usuki, A. *Macromol. Mater. Eng.* **2006**, 291, 1449.
Okamoto, M. *Mater. Sci. Technol.* **2006**, 22, 756.

Who holds patents?

- Eastman Kodak, AMCOL International, Eastman Chemical, Dow Chemical, BASF, Bekaert, Sumimoto Special Metals, Rohm and Haas, Exxonmobil Chemical Patents and Matsushita Electric...

- University of South Carolina Research Foundation, Korea Advanced Institute of Science and Technology (KAIST), Industrial Technology Research Institute de Taiwan, University of Chicago, University of Massachusetts, Cornell Research Foundation, Kawamura Institute of Chemical Research and MIT (Massachusetts Institute of Technology)…

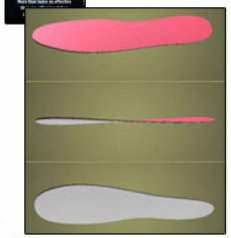
Nanotech products

More From Forbes.com

Forbes.com Top Ten Nanotech Products

slower | stop | faster | next >

Footwarmers (Shock Doctor/Aerogel Hotbeds)



Northborough, Mass.-based Aspen Aerogels launched a nanotechnology-based footwarmer in March of 2004, which is now used by the 2004 winner of the North Pole Marathon, the Canadian Ski Team and the U.S. Military's Elite Special Forces. Aspen's Pyrogel AR5401 utilizes highly-insulative nanoporous-aerogel technology, providing 3-to-20 times more thermal performance at a given thickness when compared to existing materials. Plymouth, Minn.-based Shock Doctor has developed a product called Hotbeds, which is being used in military boots for improving the level of comfort in cold weather operations. Since the Pyrogel AR5401 is so efficient, the Hotbeds are only 2.5mm thick.

More From Forbes.com

Forbes.com Top Ten Nanotech Products

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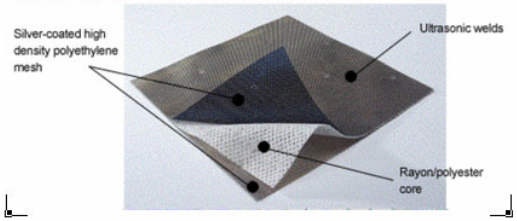
Nanosilver Wound Dressing For Burn Victims

Used on Navy submarines, cruise ships, aircrafts and healthcare facilities, San Jose, Calif.-based EnviroSystems' EcoTru nanoemulsive disinfectant cleaner cleans and disinfects in one step. In the post SARS virus scares of 2003, Boeing recommended EcoTru for use on airplanes, which helped EnviroSystems attract 30 airlines as customers. Currently, EcoTru is the only EPA-registered Tox Category IV disinfectant product in the U.S. This means there are no harmful dermal (skin), ocular (eyes), inhalation (breathing) or ingestion (swallowing) effects.



More From Forbes.com

Forbes.com Top Nano Products of 2005

< previous | slower | stop | faster | next >

7. Stink-Proof Nano Soxs - ARC Outdoors, ArcticShield Socks

Another nano-improved apparel application made our list: Military PX stores stateside and abroad are now selling ArcticShield polyester socks from ARC Outdoors in Broken Arrow, Okla. They incorporate 19-nanometer silver particles within their fibers. Long known for its antimicrobial properties, silver has been used previously to provide protection against odor and fungus in socks. The material never bonded well with polymers, however, and needed to be applied as a spray, or woven directly into the fabric as an uncomfortable metal thread. NanoHorizons developed a proprietary process that solved this silver-to-polymer bonding problem. Now sold as E47 Polyester Master Compound, it helps to make a comfortable synthetic fiber sock with permanent resistance to odor and fungus.

Forbes.com

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AFX News Limited

Solvay JV launches new vinyl nanocomposite 'smart material'

11.27.2006, 03:04 AM

Forbes.com LEADERSHIP NEWS

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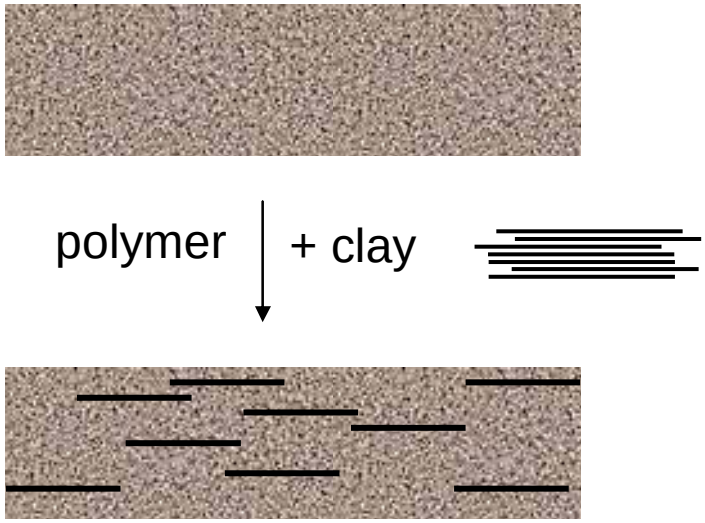
BRUSSELS (AFX) - Belgian chemical group Solvay SA said it will launch a new vinyl nanocomposite through its vinyls joint venture with BASF AG in Europe, SolVin.

NanoVin is a nanocomposite which combines polyvinyl chloride (PVC) and nanoparticles of clay. Classified as a specialty product, the material offers improved plasticity, viscosity and flow, and will be used for bodywork in the automotive industry as well as thick coatings, such as artificial leather.

SolVin has operations in France, Germany, Spain and the Benelux countries and a total annual production capacity of 1.3 million tons of PVC, with nearly 2,000 employees. Solvay owns 75 pct of SolVin and BASF the remaining 25 pct.

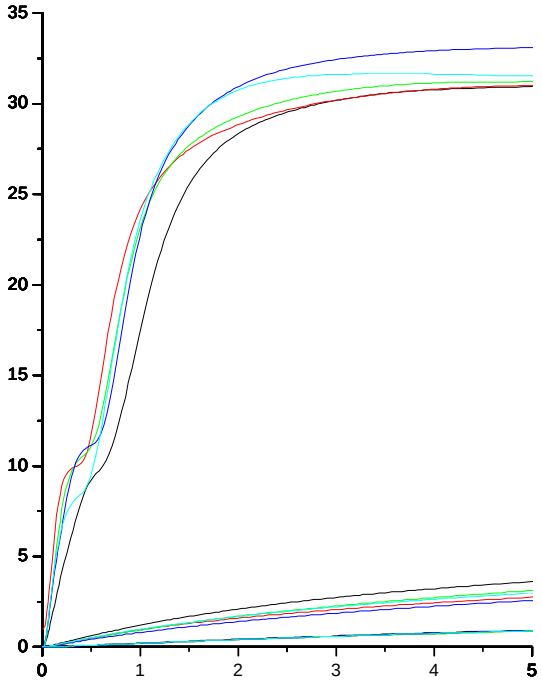
http://www.forbes.com/investmentnewsletters/2005/01/12/cz_jw_0112soapbox.html
http://www.forbes.com/investmentnewsletters/2006/01/10/apple-nano-in_jw_0109soapbox.inl.html
http://www.forbes.com/afxnewslimited/feeds/afx/2006/11/27/afx3204478.html

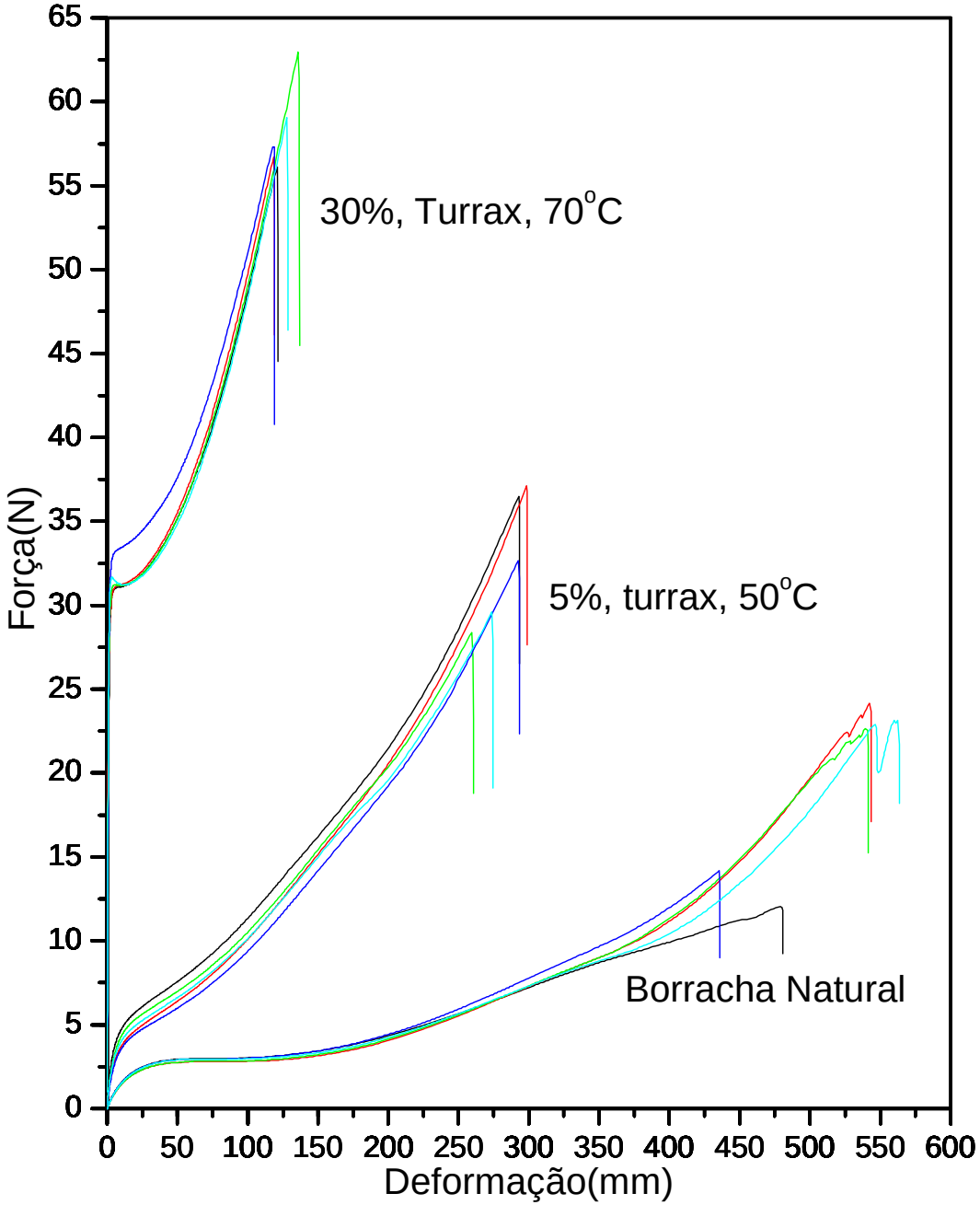
Design of a nanocomposite

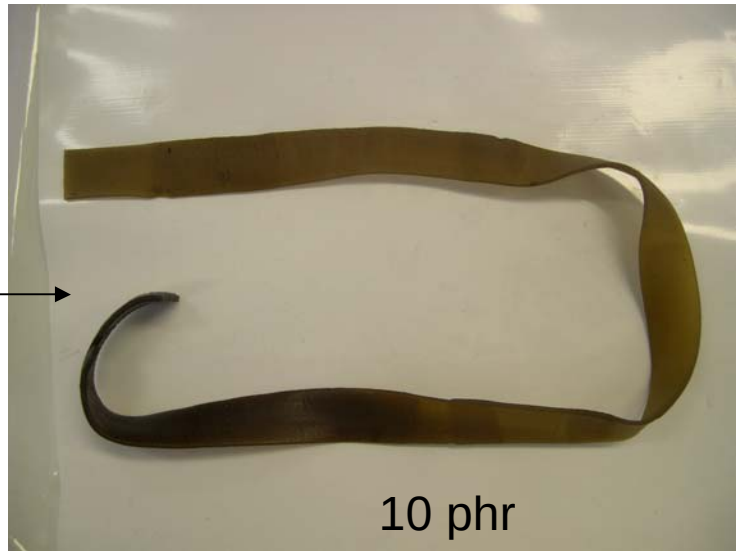


- Silicate lamellae exfoliation.
  - Not a spontaneous process
- Gas permeability can be drastically reduced.
- Elastic moduli increase.
- Ceiling use temperature increases.

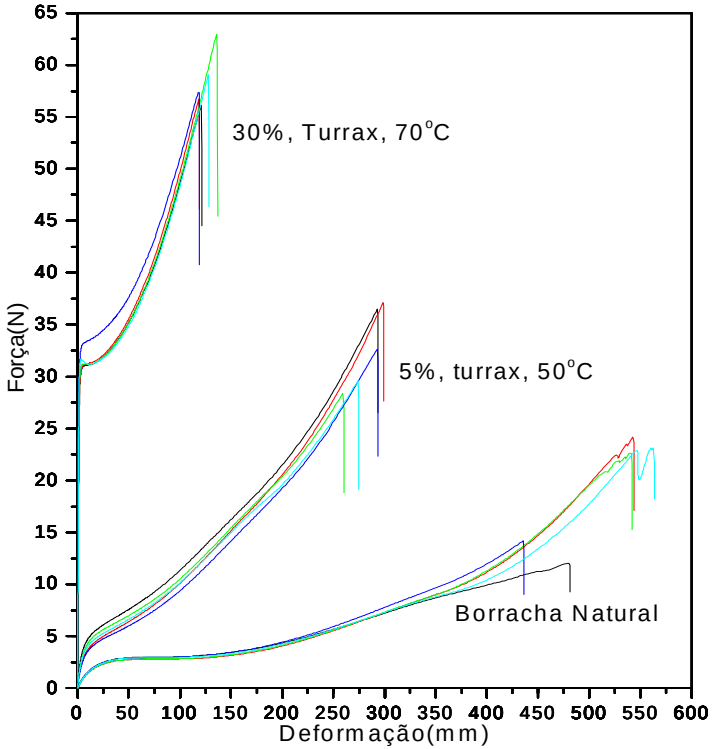
Natural rubber-clay nanocomposites: unmatched properties for non-vulcanized rubber







A prospective application: an elastomeric thermoplastic out of any rubber (target: recyclable tires)



Current situation

- Patent license to a materials development company (Orbys)
  - Funding from Finep
- Project with Oxiteno
  - Network with UFCG and UFSCar
- In 2007: new patents
- Started in 2001 due to a request from Rhodia-Ster (currently M&G)
  - PCT

Hypothesis:
Electrostatic adhesion

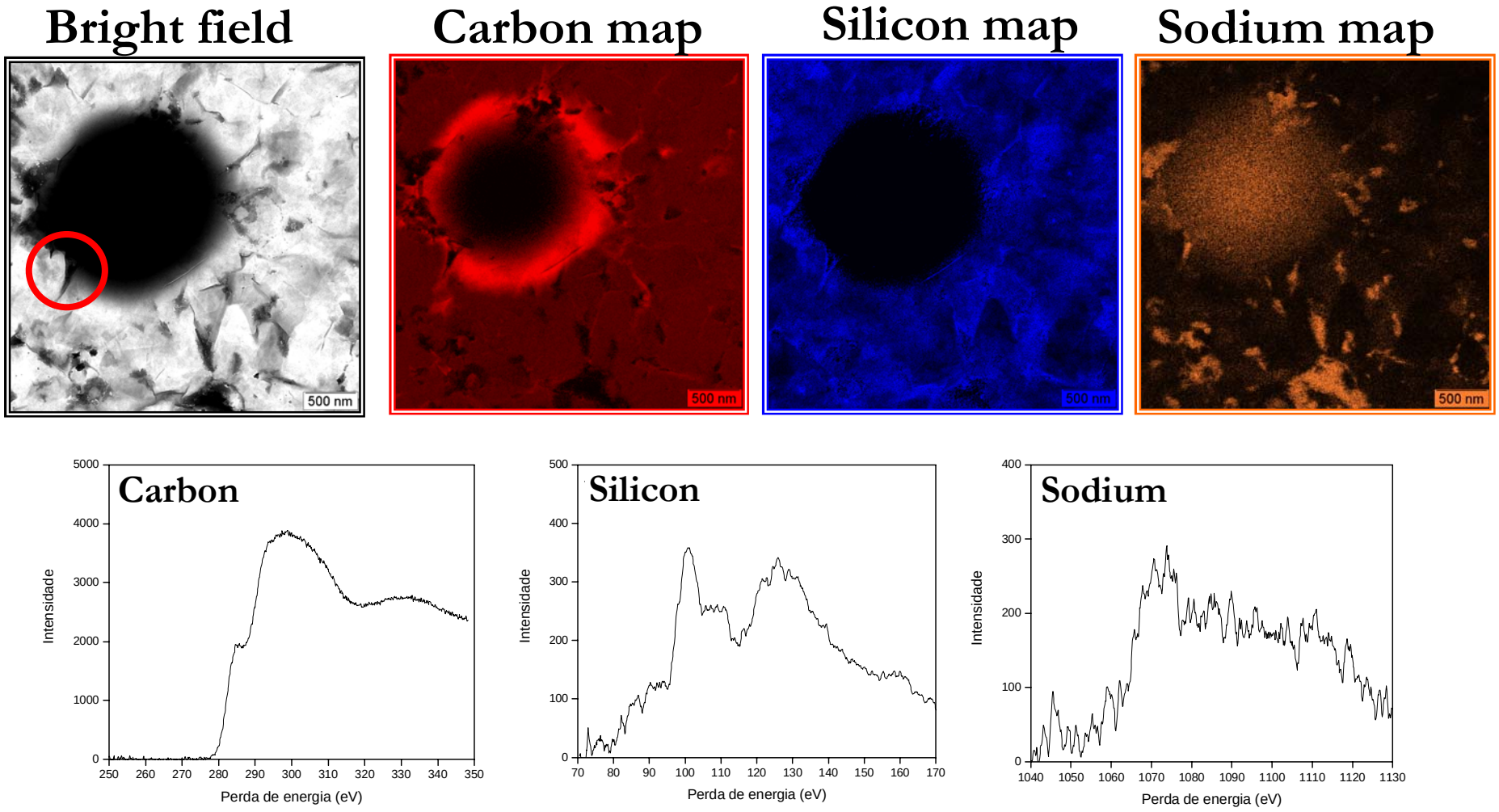
- **Polymer latex particles AND clay lamellae have negative surface charges in aqueous media.**
- **Latex and clay particles adhere to each other.**
- **Clay counterions should act as ionic bridges thus influencing mechanical and morphological properties of the clay-latex nanocomposite.**
- **Nanocomposite properties depend on clay counter-ions.**

Ion-exchanged clays

	Sodium (mequiv/100g)	Calcium (mequiv/100g)	Lithium (mequiv/100g)	Potassium (mequiv/100g)
Na-MMT	**117.3**	**1.9**	**0**	**0**
Ca-MMT	**1.3**	**89.8**	**0**	**0**
Li-MMT	**17.0**	**0.9**	**58.0**	**0**
K-MMT	**3.8**	**0**	**0**	**71.6**

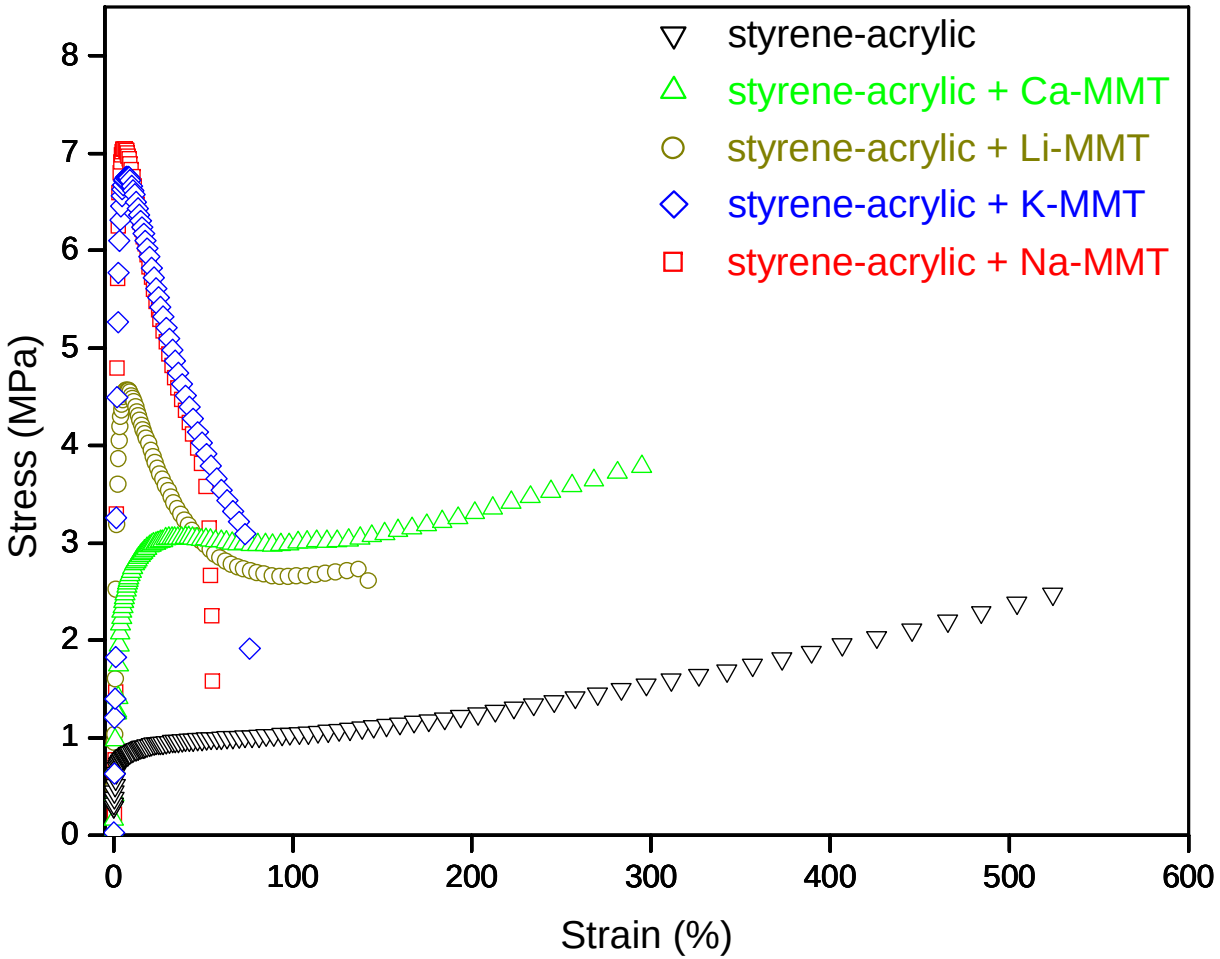
- ICP-OES analysis (inductively coupled plasma optical emission spectrometry)
- Ca^{2+}, Li^{+}, K^{+}, and Na^{+} ions are each prevalent in one of the four ion-exchanged clays

Latex-clay compatibility:ESI-TEM and EELS



- Excellent compatibility between the organic and inorganic phases
- Counter-ions are superimposed to both clay lamellae and polymer

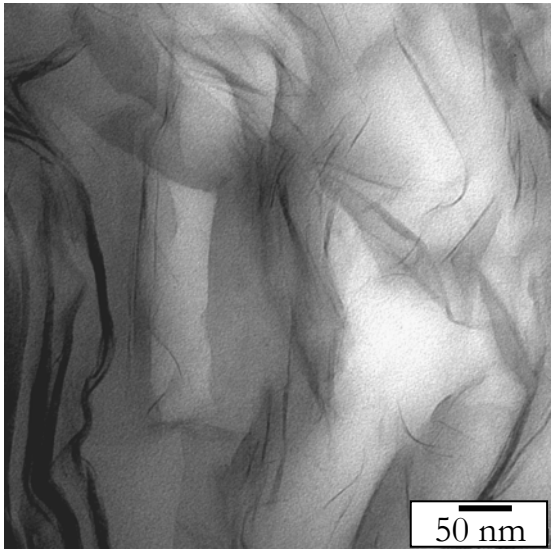
Mechanical properties

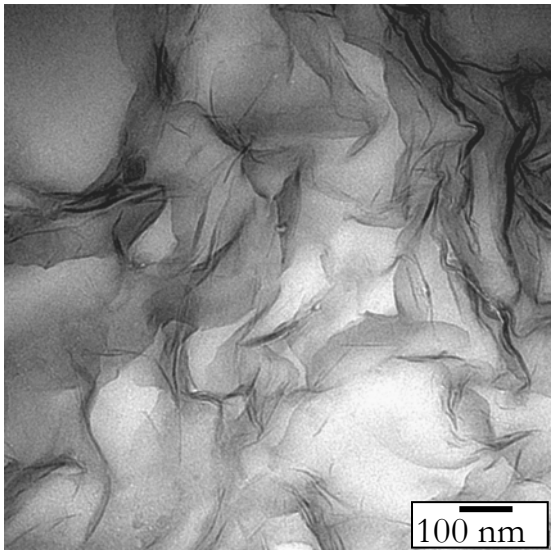


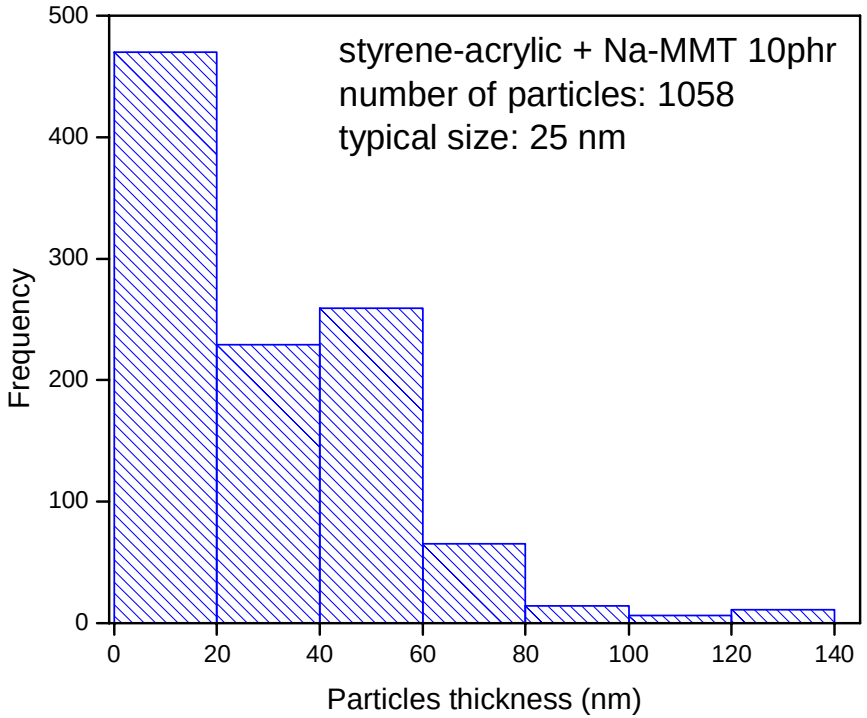
Clay-polymer nanocomposites mechanical behavior under stress varies widely depending on the counterion.

Braganca, F.D.; Valadares, L.F.; Leite, C.A.D.; Galembeck, F. *Chem. Mater.* 2007, 19, 3334.

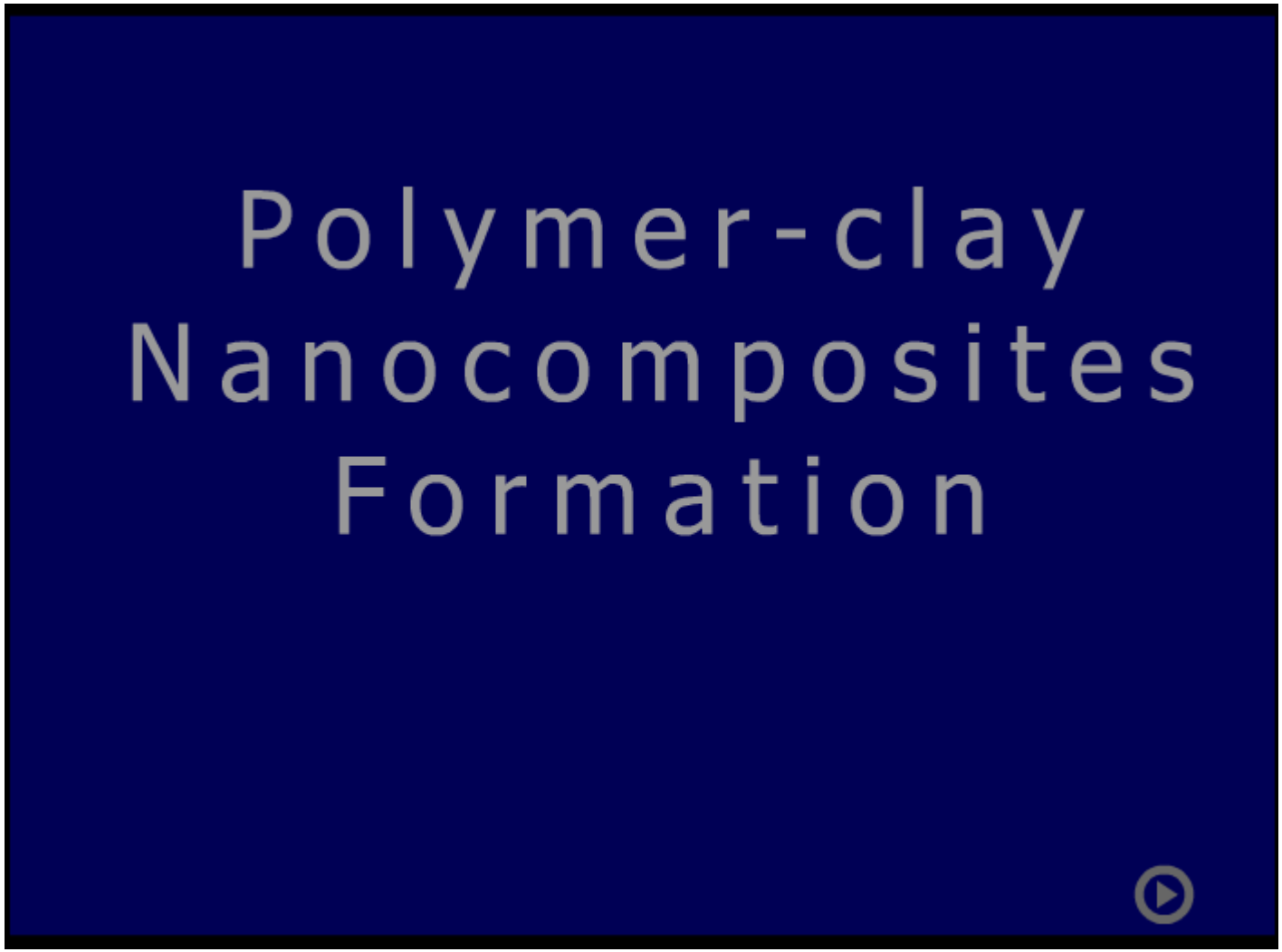
TEM images of the Na-MMT nanocomposite bulk



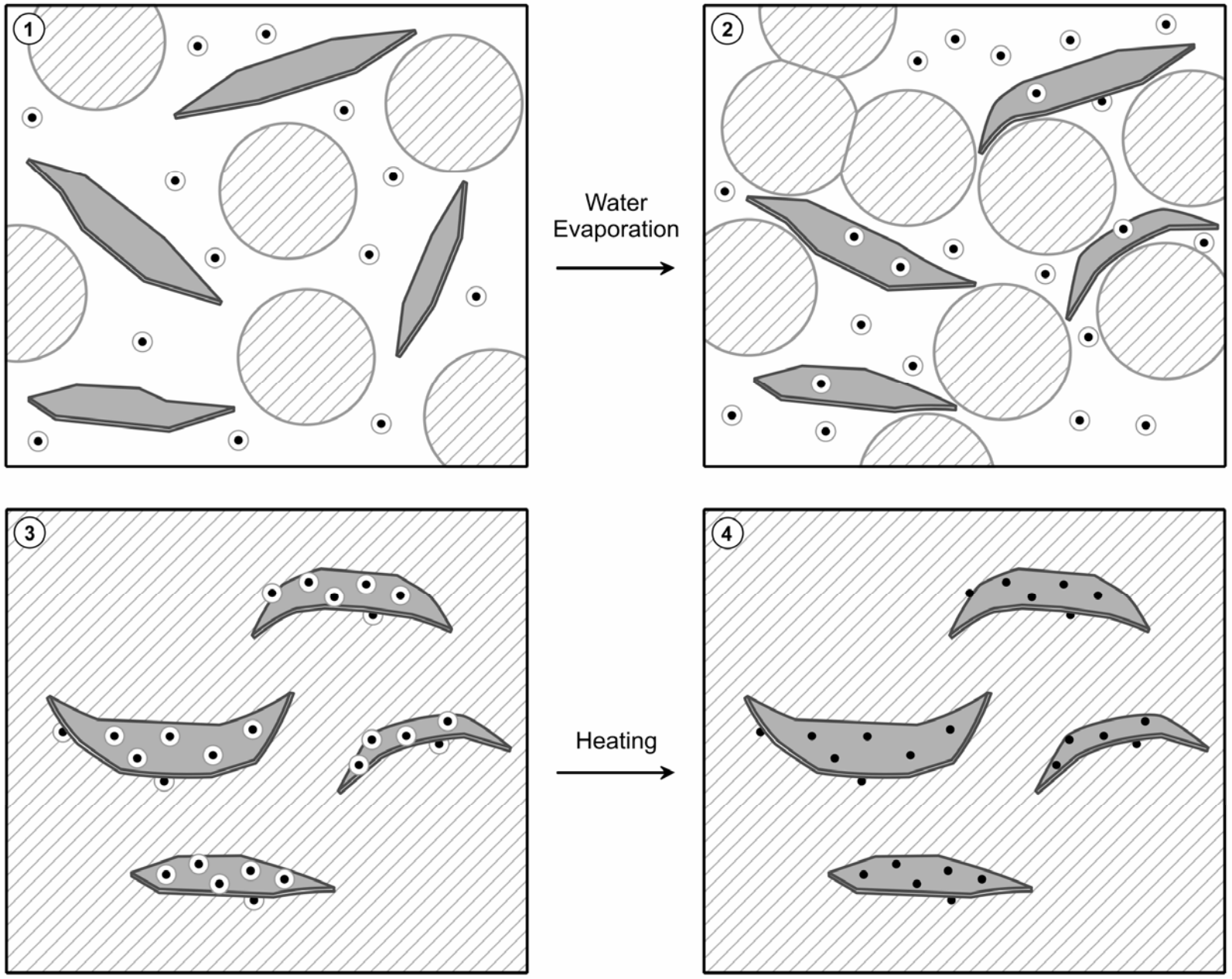




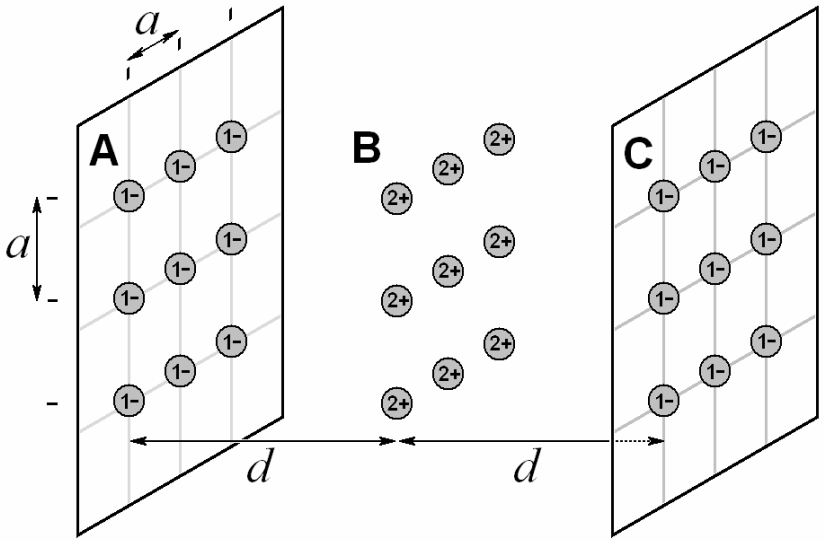
- Individual clay lamellae
- Small clusters

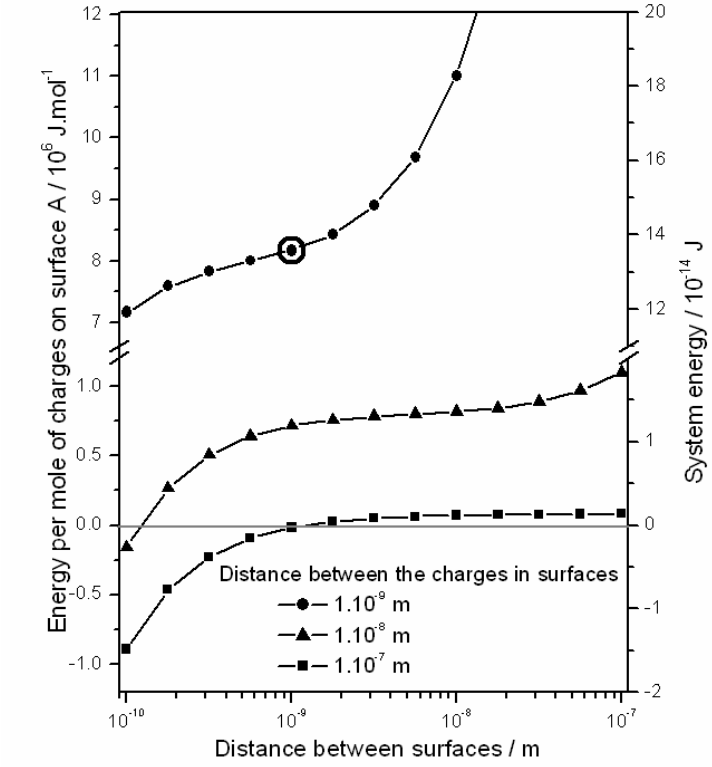

Polymer-clay
Nanocomposites
Formation

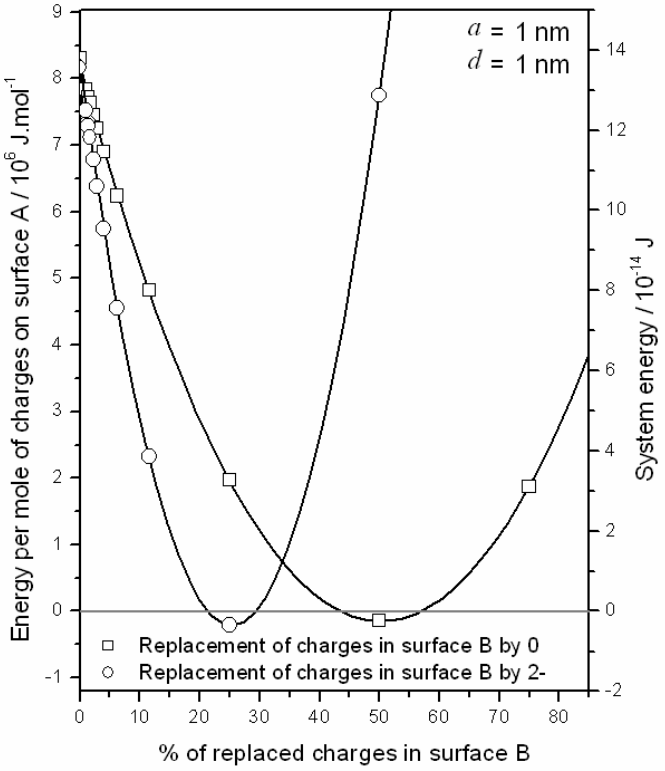
Model:



Calculation: electrostatic adhesion energy







Model vs. measurement

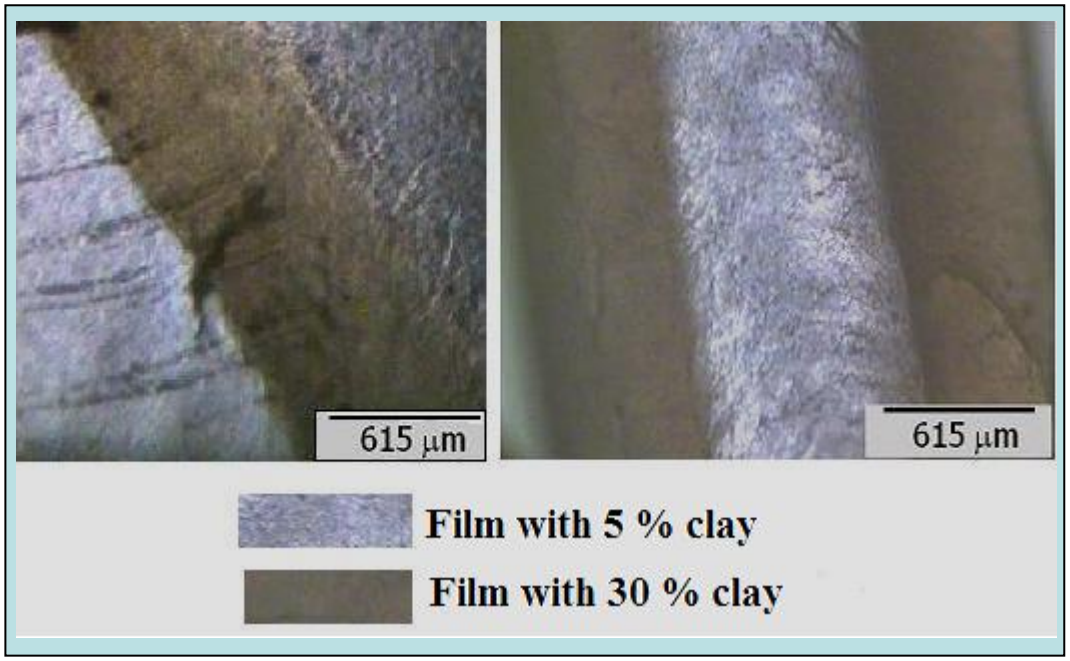
	Work for 1% deformation (J)	Difference between nanocomposite and rubber (J)	Mols of ions in the test sample	Elastic energy per mol of ions (J/mol)
Rubber	$0.386 .10^{-3}$			
Rubber - $Li^{+}MMT$	$2.17.10^{-3}$	$1.79.10^{-3}$	$2.43.10^{-5}$	73.6
Rubber - $Na^{+}MMT$	0,00497	0,00459	4,914E-05	93.3
Rubber - $K^{+}MMT$	0,00466	0,00428	2,999E-05	143

From the model:
151 J/mol, for monovalent cations and 50.5% replacement of positive charges by voids

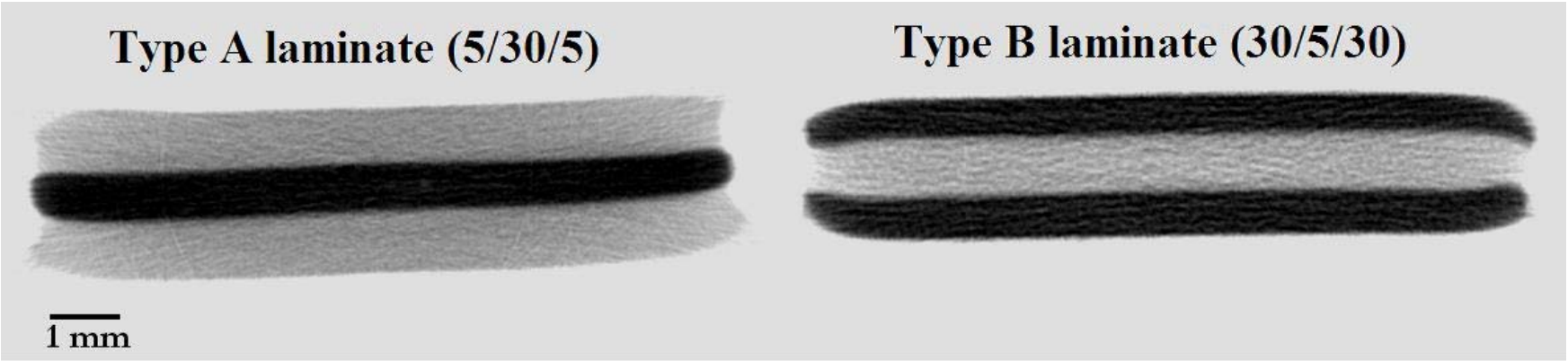
Positive counterions play an important role on the properties of polymer-clay nanocomposites.

Polymer-clay interfacial adhesion is mediated by ionic bridges between the two immiscible negative phases.

Laminate nanocomposites: compatibility between hard and soft materials



- Strong adhesion at interface region
- No lacks



NEW MECHANISMS FOR POLYMER ELECTROSTATIC CHARGING

Fernando Galembeck, Sérgio Bertazzo and Thiago A. Burgos

Institute of Chemistry
Universidade Estadual de Campinas – Brazil
Millenium Institute for Complex Materials

Electrostatic charging: an old but still unsolved problem

"Surprisingly, although electrostatic charging is well known, it remains among the most poorly understood areas of solid-state physics."

"Most researchers believe that insulator charging is a surface phenomenon."

Schein LB, Recent progress and continuing puzzles in electrostatics. *Science*, 316, 1572-1573 (2007).

ALSO: Bailey AG, The charging of insulator surfaces. *J. Electrostat.*, 51-52, 82-90 (2001), Castle GSP, Contact charging between insulators. *J. Electrostat..*, 40-1, 13-20 (1997)

...still unsolved problem

"Through the years many "models" or correlations have been suggested for insulator charging.

...correlations with dielectric constant,

...the basic and acidic nature of the materials,

...polymer "work function,"

...surface chemistry determined by measuring the residence time of probe molecules using inverse gas chromatography.

However, no reasonable explanation of the effective electric field has yet emerged."

Schein LB, Recent progress and continuing puzzles in electrostatics. *Science*, 316, 1572-1573 (2007).

Consequences

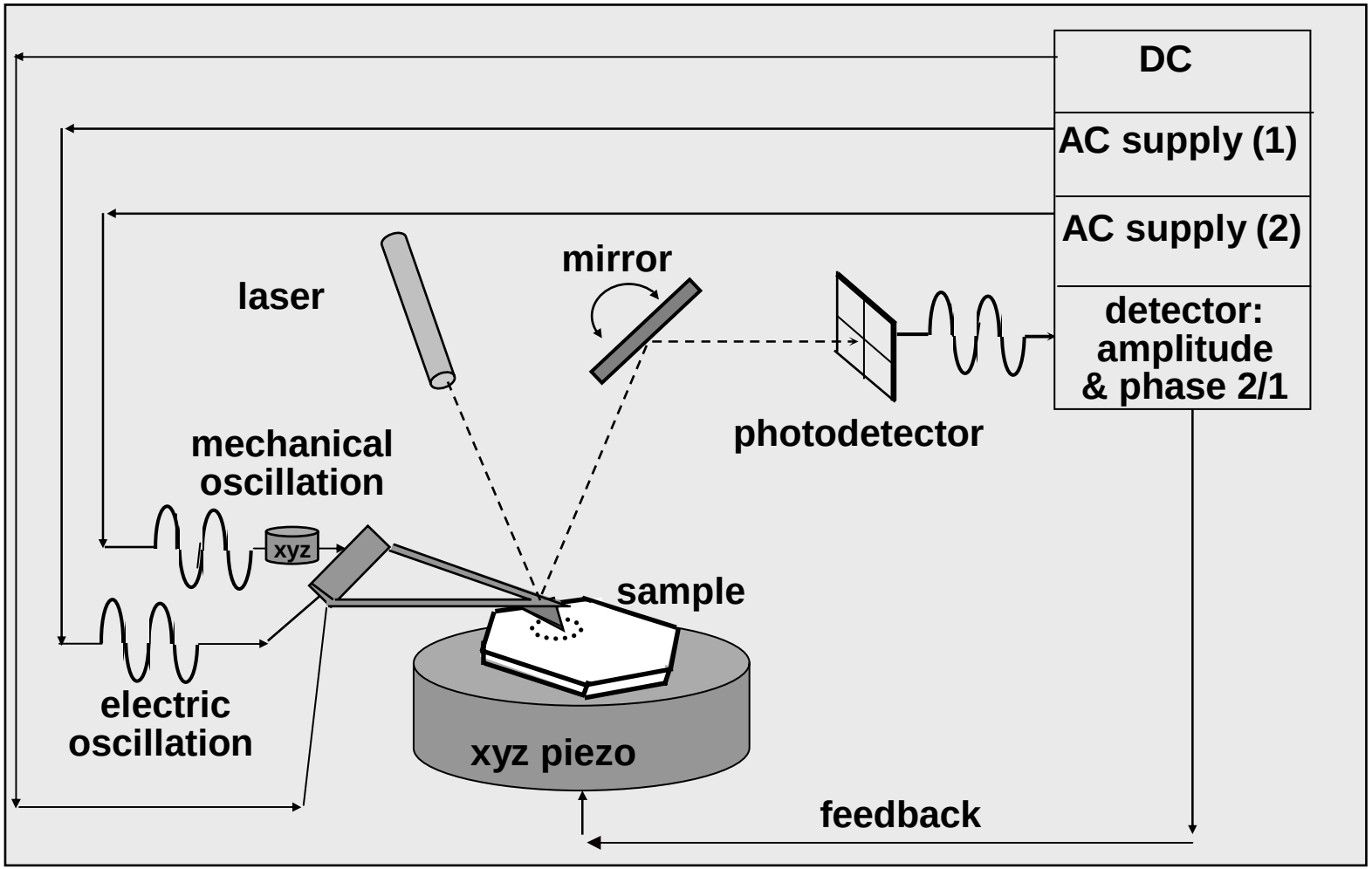
- **Safety problems**
  - **Dust explosions**
  - **Fires**
  - **Pharmaceuticals**
- **Important technologies**
  - **Polymer recycling**
  - **Electrospinning**
  - **Solid paint**
  - **Electrocopying**

- **For nanotechnology:**

  Electrostatic force is even larger than the inertial force, for micromachine parts made of insulators.

  - *The electrification of the insulator is not well understood, especially at the micro-scale. Fujisawa and Enomoto, AIST*
- **For space research:**
  - *Space suit generates 20 kV*

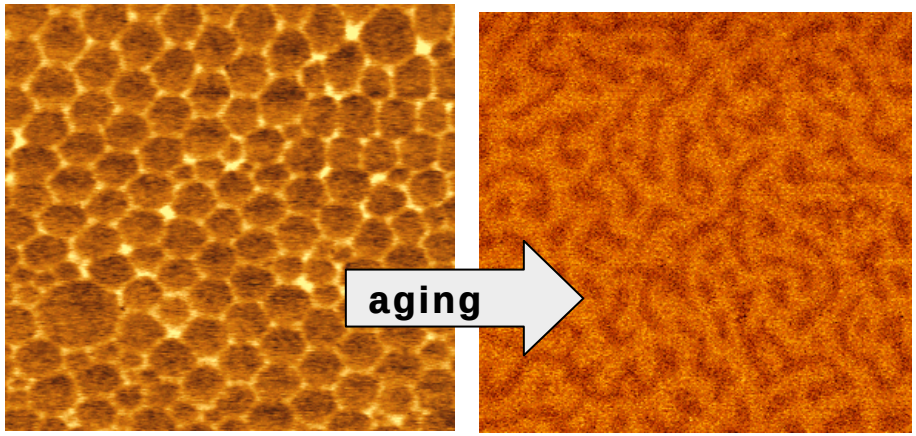
SEPM: scanning electric potential microscope
Kelvin method with force detection



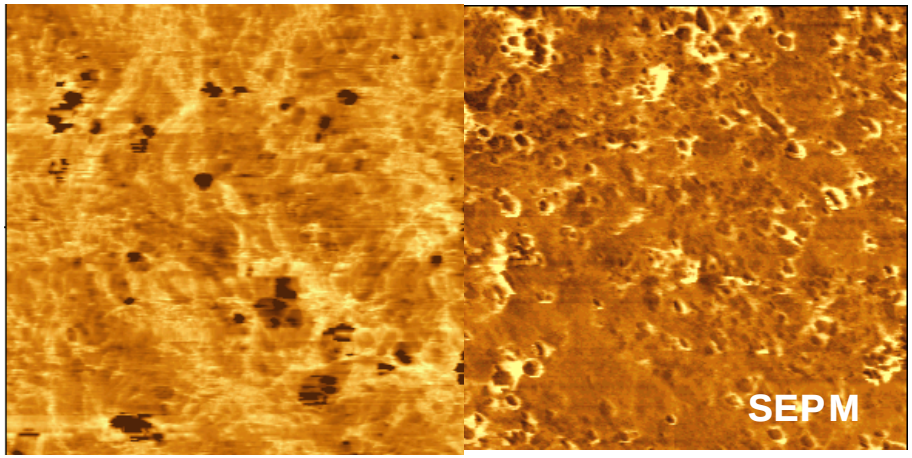
& a home-made Kelvin macroscope

Complex potential distribution patterns and large electric potential gradients in every insulator examined

Poly(styrene-butyl acrylate-acrylic acid)

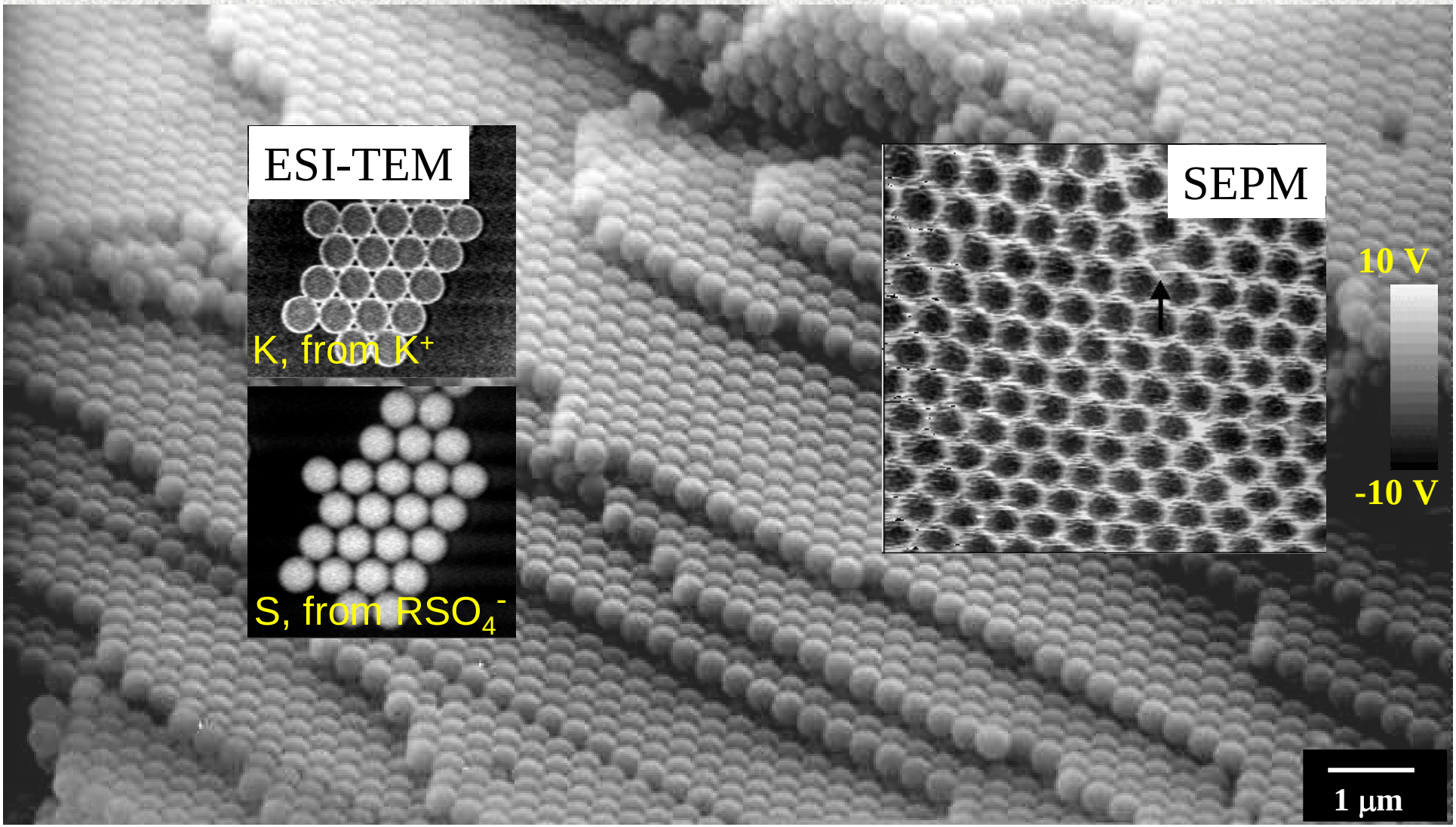


Polyethylene



Polypropylene

Charge patterns of polystyrene and other “neutral” polymers: PS-HEMA macrocrystal is actually a positive mesh with negative particle cores



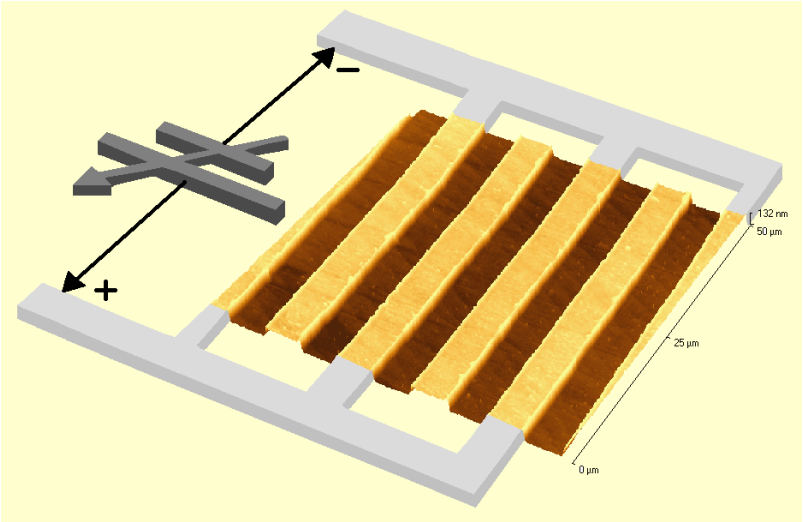
Charge carriers

- In latexes and latex films: ions bound to the polymer chains (from polymerization initiators) and counter-ions.
- Identified by the combination of SEPM and analytical electron microscopy (ESI-TEM).
- In cellulose, polyethylene, polypropylene, polystyrene...?

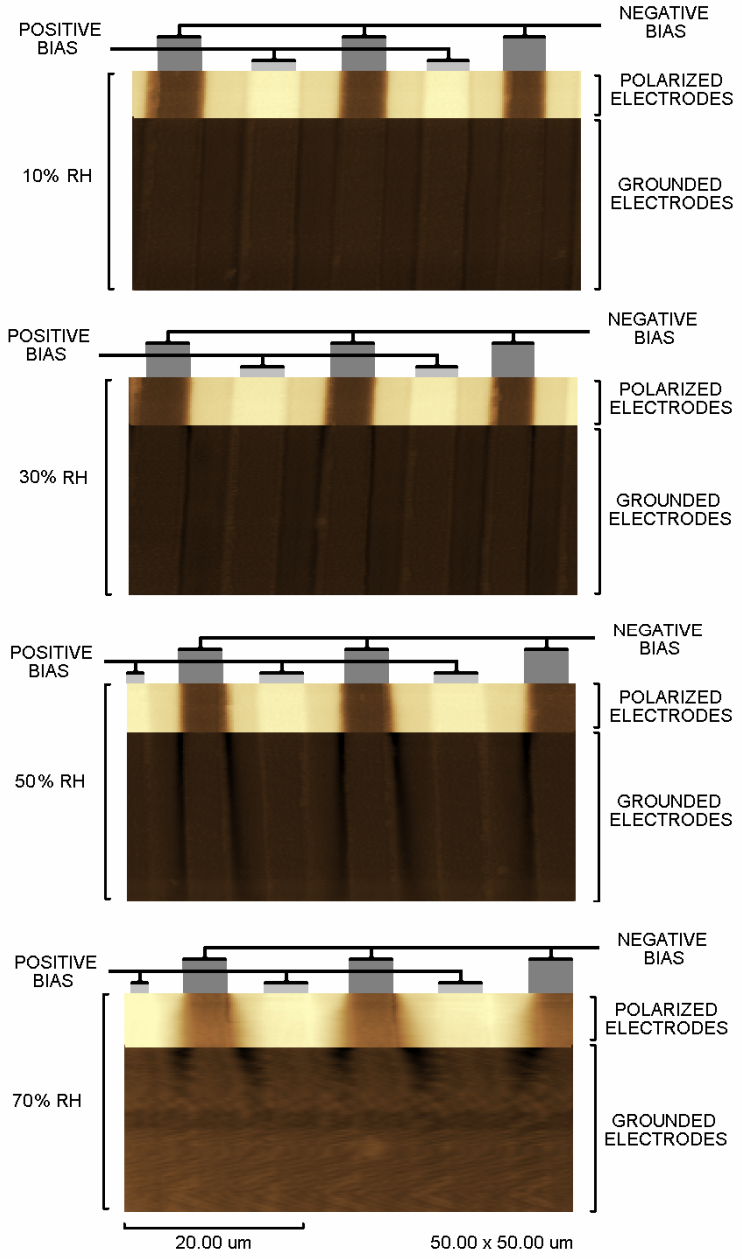
Problem: SEPM calibration

Calibration sample: electrodes evaporated on Ti, over silica film on silicon wafer

- Electrodes are polarized using an external power supply



R. F. Gouveia, C. A. R. Costa, and F. Galembeck Electrostatic Patterning of a Silica Surface: A New Model for Charge Build-Up on a Dielectric Solid, J. Phys. Chem. B 2005, 109, 4631-4637



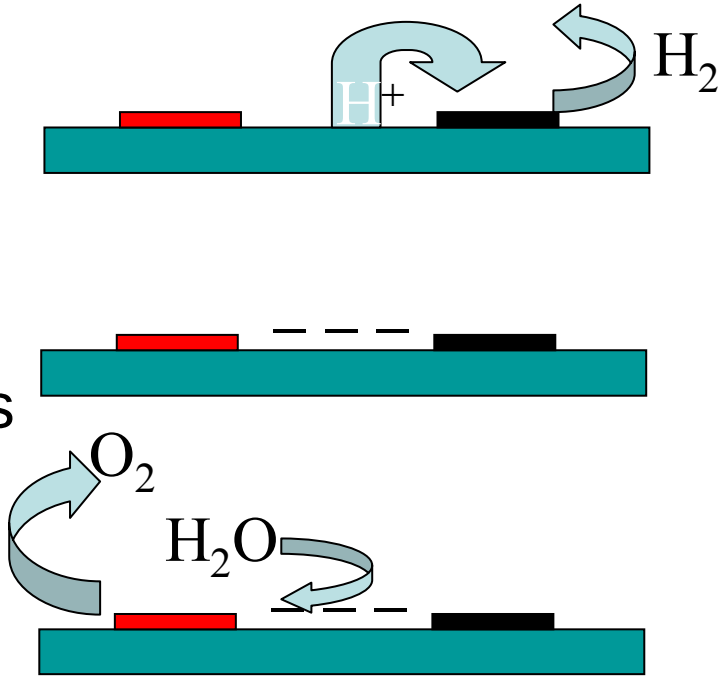
Effect of humidity

10-30% RH: steady potentials on silica

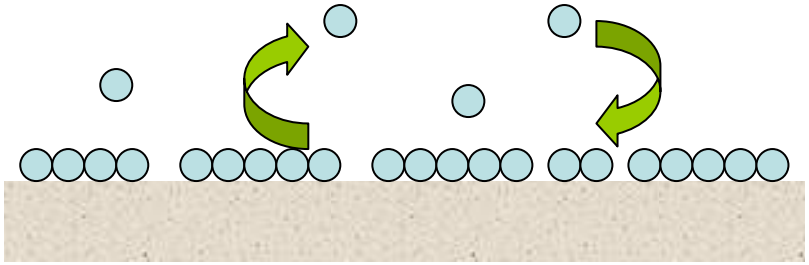
50-70%: potentials vary slowly. Silica acquires charges that dissipate slowly.

Model for charge build-up on silica

- Surface silanol groups: Si-O-H
- H^+ discharge on polarized electrodes
- Immobile $Si\text{-}O^-$ groups persist, producing domains with excess negative charges
- Grounded electrodes: vapor adsorption followed by discharge of OH^-
- Verification: charge and discharge rates depend strongly on relative humidity



General model for dielectric charging



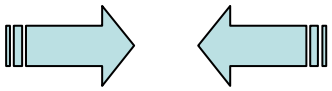
- Adsorbed water acquires excess positive or negative charge under V
  - $\mu_i = \mu_i^\circ + RT\,(\ln x) + zFV$
  - excess $[H^+]$ under negative V (or $[OH^-]$ under V>0)
- To reach equilibrium under V, charges are transferred to and from the sample
- Charge transfer is done by water vapor adsorption-desorption events
- Potential stability depends on the rate of adsorption-desorption events

What for?

- Solving safety problems
  - From persons, houses, plants…
- New devices
- Can we tap the electrical energy in the atmosphere?
- …remember Tesla.

New Science & New Products

Non-crystalline ionic solids	Biphor (Bunge) New type of cationic latex (IQT)
Electrostatic adhesion	Latex nanocomposites (Orbys, Oxiteno)
Natural rubber	Thermoplastic elastomers
Dielectric charging	Perhaps: electrets, electrostatic motors, energy
Self-arraying and wetting	Perhaps: nanolitography, self-cleaning
Polymer heterogeneity	*High-voltage insulators (Pirelli)*



Conclusion

- Many new challenges, demands and threats.
- These have to be faced under both global and local perspectives.
- The interests of the scientist and of the investor converge: maximum benefits come from very new ideas and very new products.
- Keywords: collaboration, AND not OR, listen and talk.

More requirements to fulfill

- In the past
  - Technical and economic viability
- Today, any candidate new product is evaluated using many criteria:
  - Technical and economical
  - Environmental
  - Ethical
  - Sustainability
  - Social impacts

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- CNPq and Finep/MCT: fellowships, Pronex, Millenium Institutes Program
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- Bunge Fertilizers
  - Aluminum phosphate white pigments
- IQT
- Oxiteno
  - Colloidal polymers
- M&G (former Rhodia-Ster)
- Orbys
  - Polymer nanocomposites
- Pirelli
  - Insulators