

# Nanopartículas e nanocompósitos: inventando produtos

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# *Definições*

- *Nanoscience* is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale.
- *Nanotechnology* is the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometer scale.

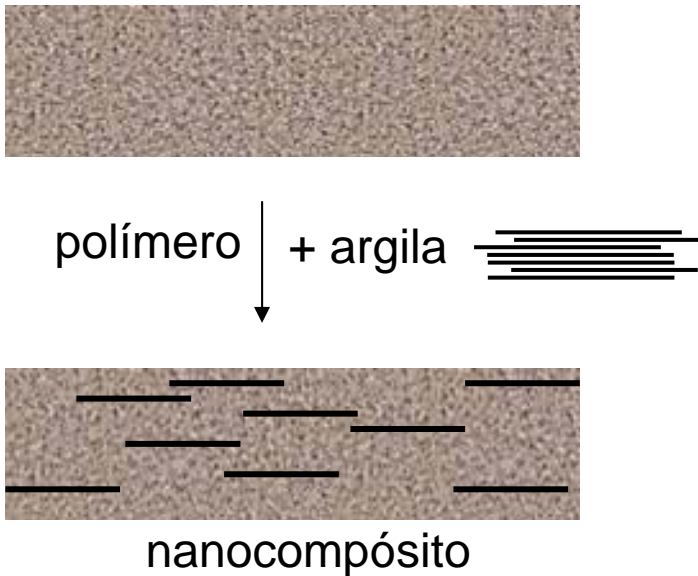
**Source:** <http://www.royalsoc.ac.uk>

# Nanocompósitos poliméricos

- Minerais com morfologia lamelar, fibrosa...
  - Argilas
  - Areias
  - Nanopartículas de sílica
  - Partículas ocas
- Úteis na formação de híbridos
  - Sinergia de propriedades
  - Processos “verdes” de fabricação

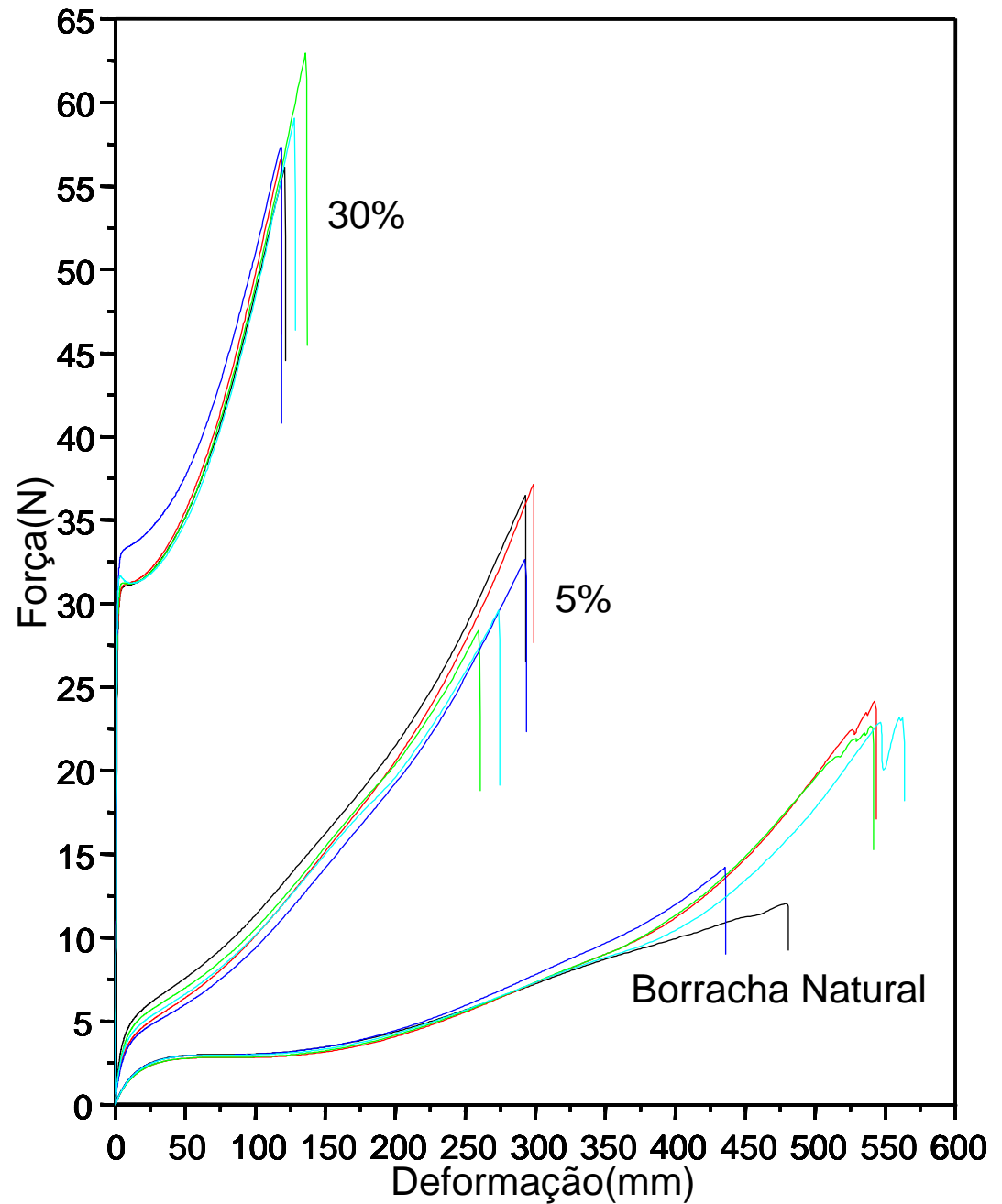
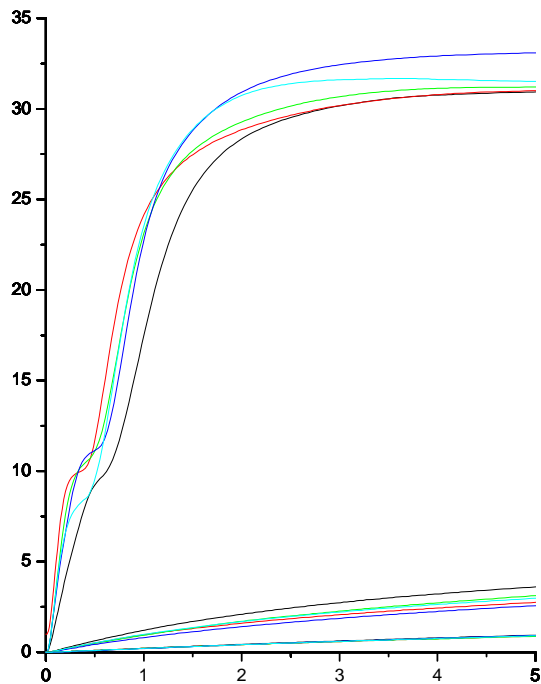
# Design de um produto nanotecnológico: nanocompósito

- Gerar novos materiais poliméricos

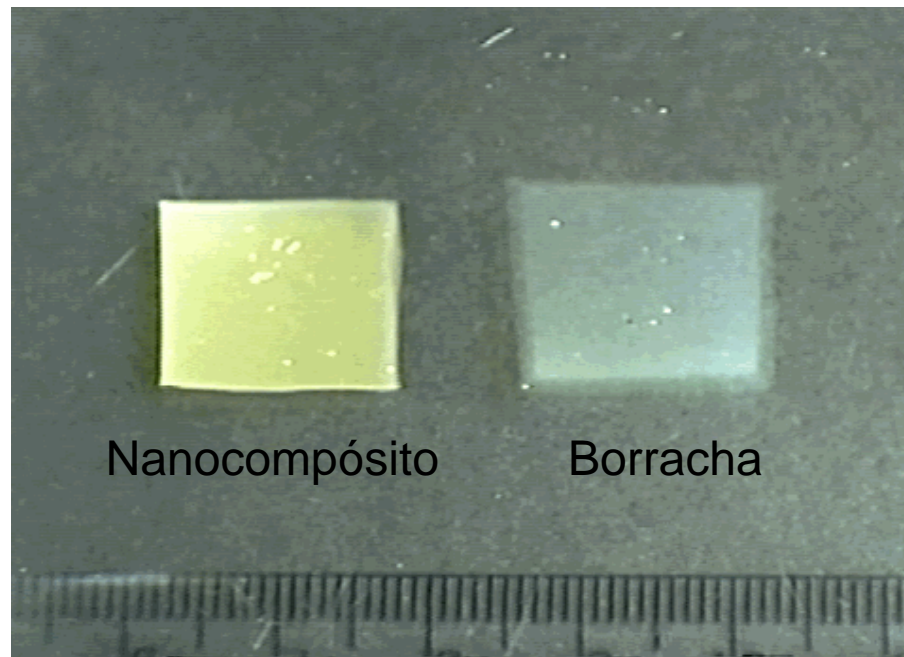


- Separar lâminas de silicato, dispersar e orientar as lâminas em matriz de polímero.
- A permeabilidade do polímero a gases pode ser reduzida a 10% ou menos.
- A resistência do polímero à flexão diminui: aumento da temperatura de trabalho.
- Coeficiente de armazenamento elástico aumenta.

## Propriedades mecânicas inéditas



# Nanocompósitos feitos a partir de látexes: ensaio de intumescimento



Ensaio de intumescimento: Nanocompósito (30 % argila/borracha) e borracha natural imersos em xileno.

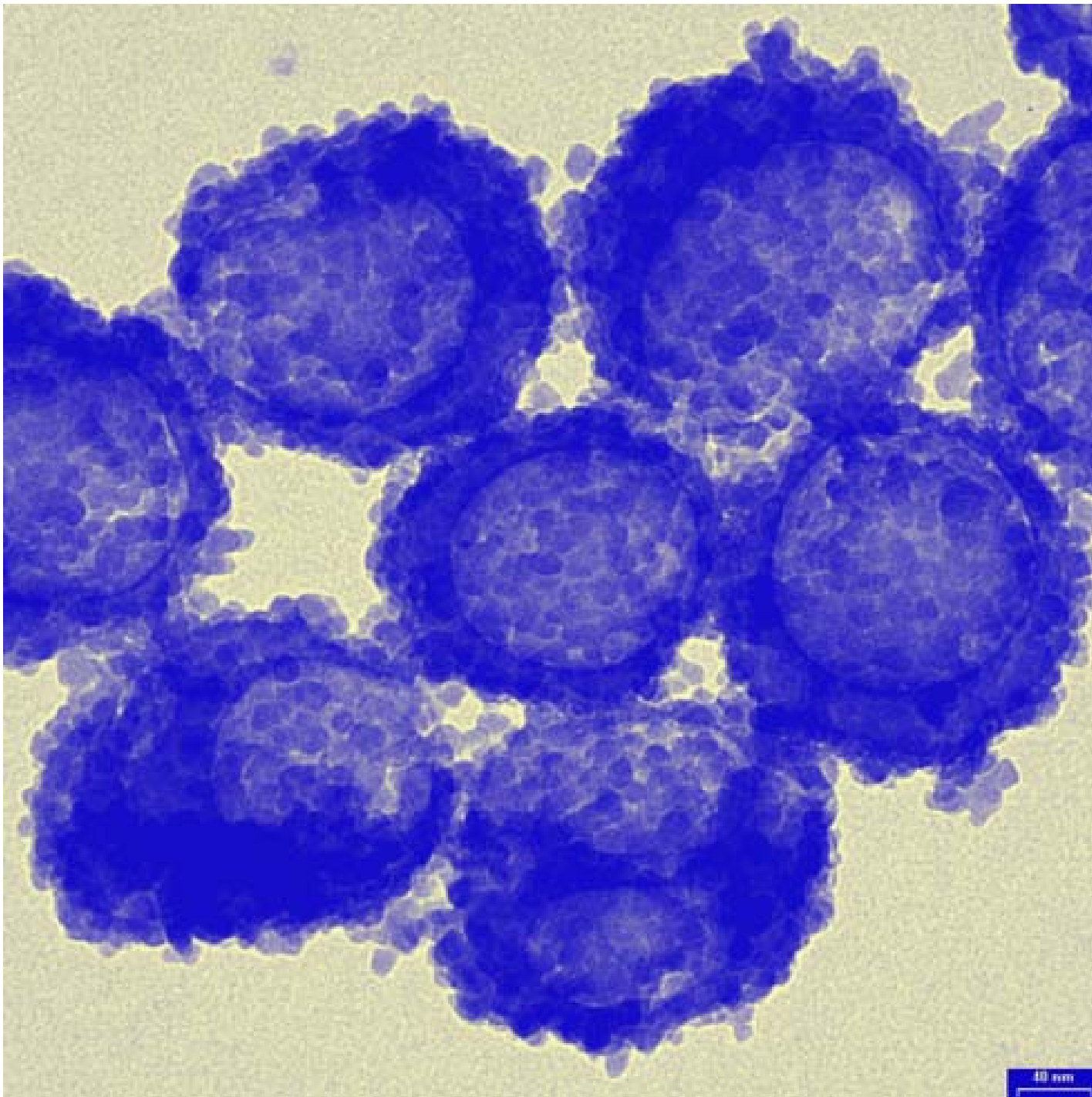
# Um atrativo

- É possível mudar drasticamente as propriedades mecânicas de um polímero, SEM alterá-lo quimicamente.



Sem argila:  
um péssimo  
filme

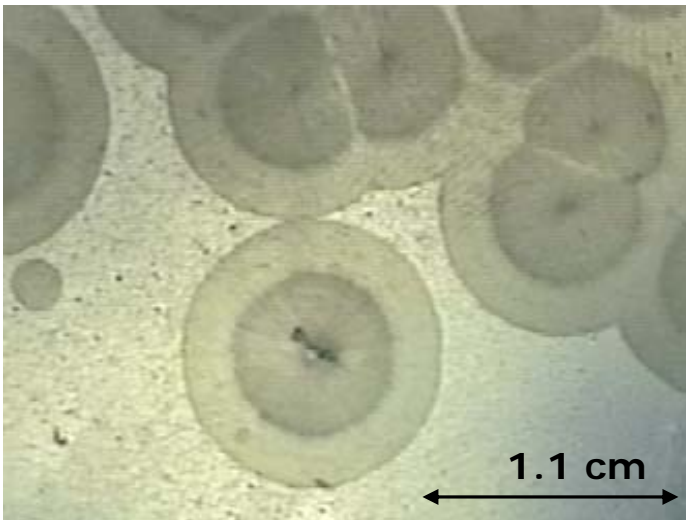
Com argila: um  
filme excelente  
e aderente



**Látex sintético  
com  
nanopartículas  
de sílica**

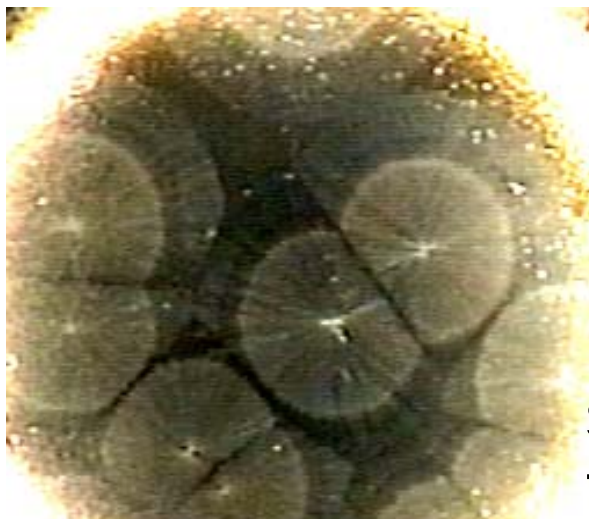
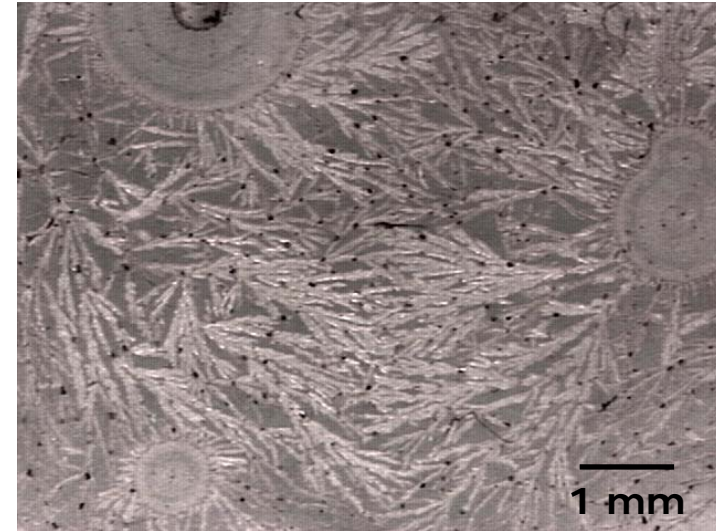
**Tintas  
resistentes a  
riscos e  
abrasão**

# Nanocompósito de borracha natural/tripolifosfato: de sódio: mudanças lentas de morfologia



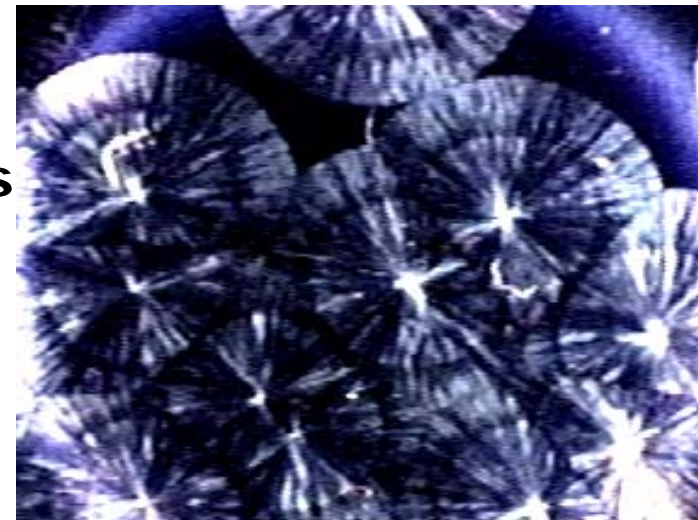
**Visto sob luz  
refletida**

**Diferença na  
cristalização  
depende da  
temperatura  
ambiente**



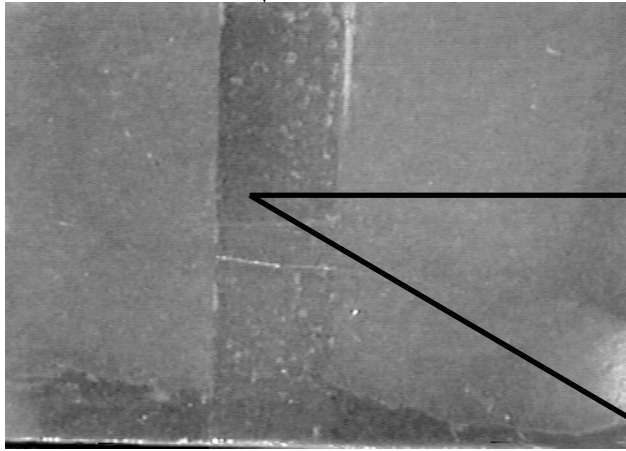
**Entre  
polarizadores  
cruzados**

**Sob luz  
transmitida**



# Modificação do látex de borracha natural pela adição de polifosfato de sódio\*

Fita adesiva-área coberta

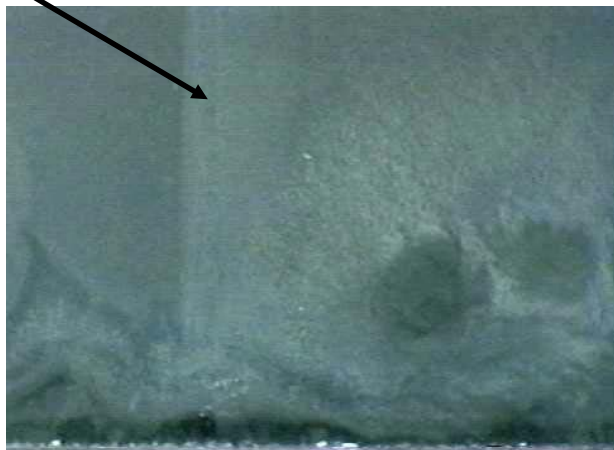


Filme com fita adesiva

## Teste de despelamento com fita

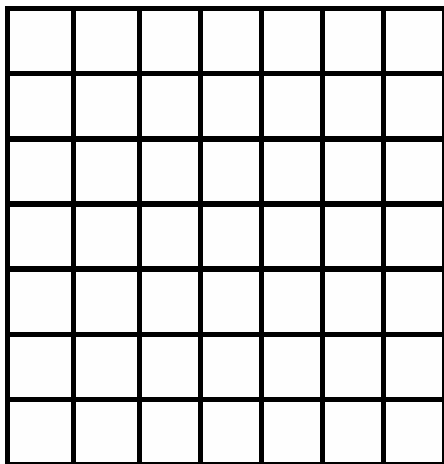


Filme de látex após primeiro despelamento: a borracha é totalmente despelada.



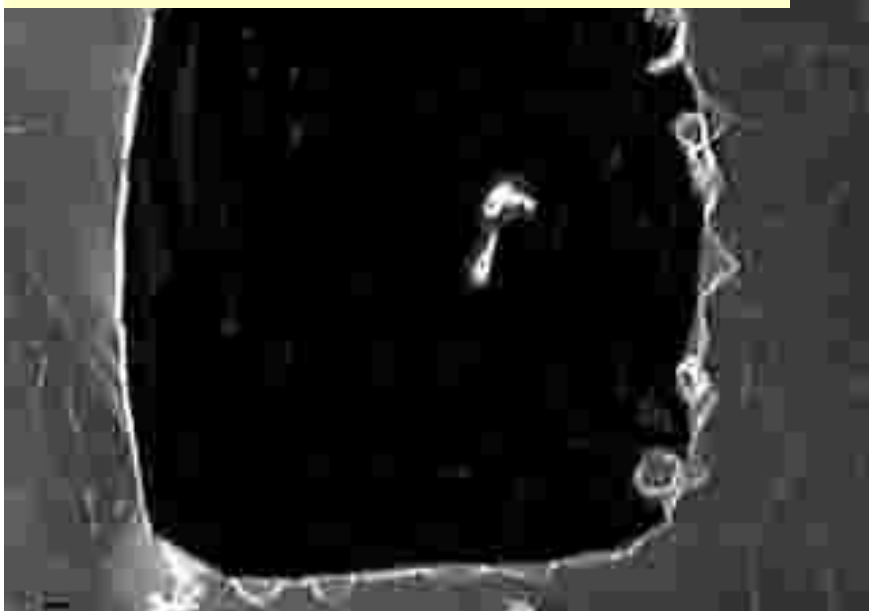
Filme de látex modificado com polifosfato após terceiro despelamento: a borracha não é danificada

# Teste de adesão úmida

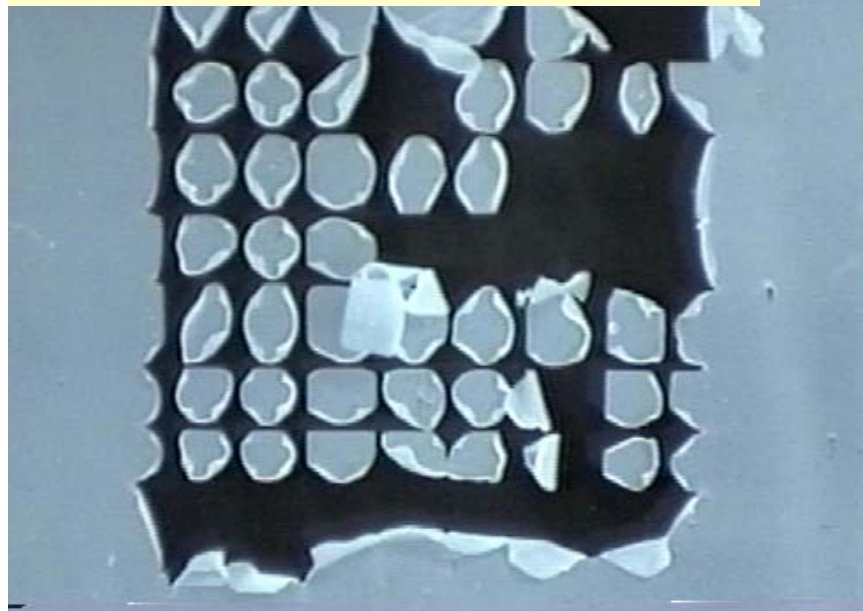


- Uma grátícula é cortada no filme de borracha. O vidro coberto com o filme é imerso em água por 24 h.
- O vidro coberto com o filme é generosamente agitado e retirado da água.

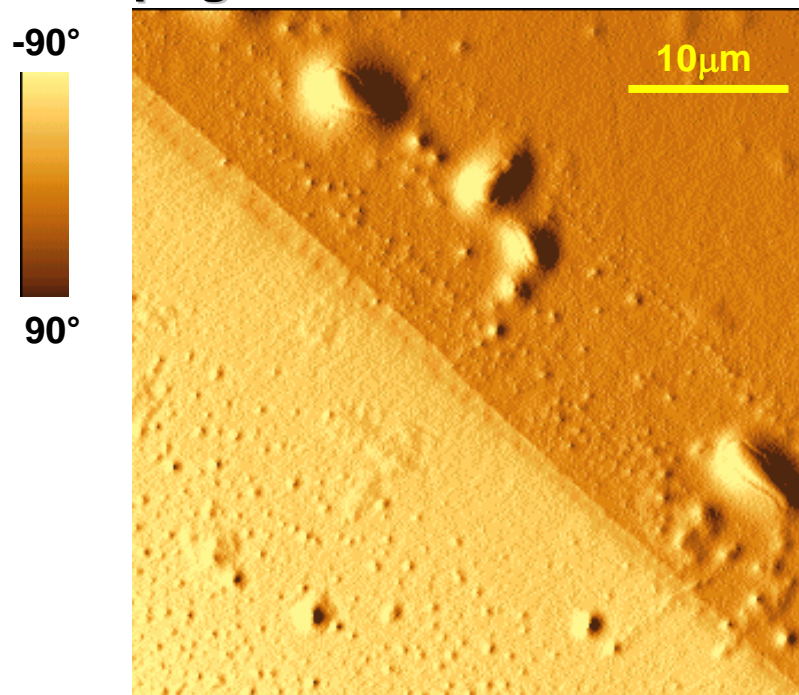
Filme de borracha natural



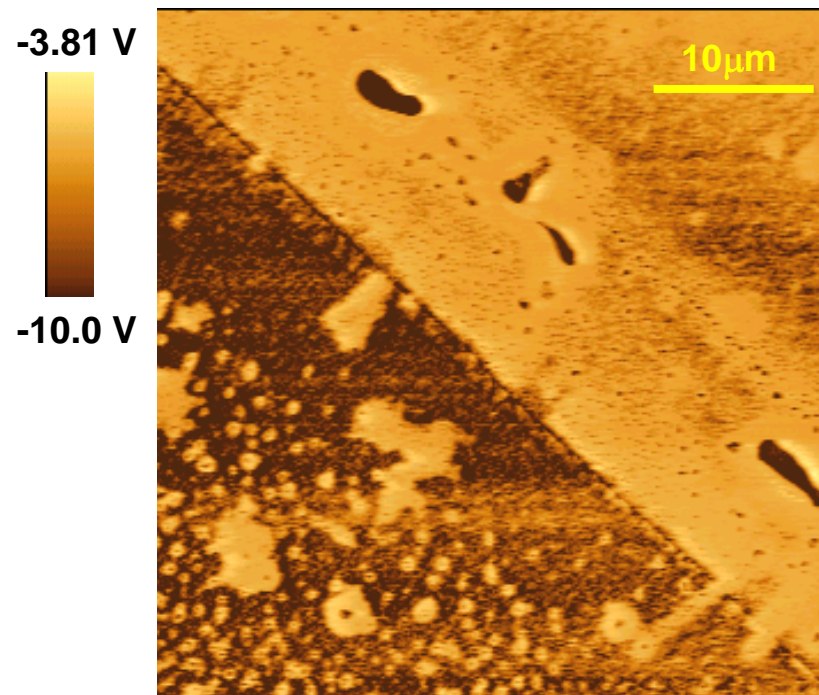
Filme de borracha + polifosfato



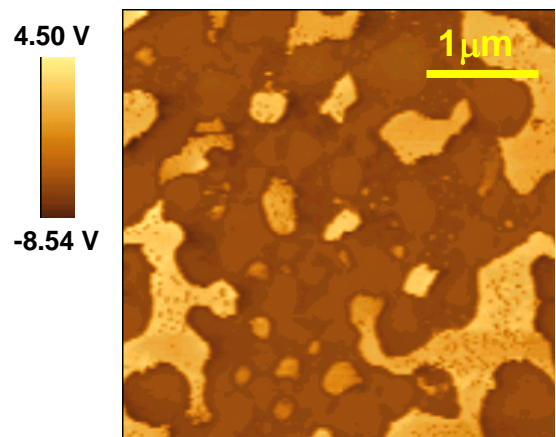
**Topografia iluminada - Fratura**



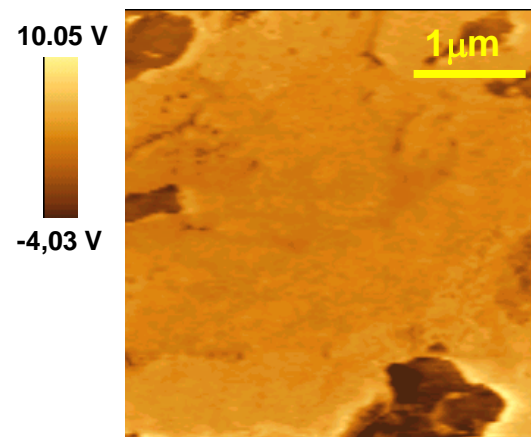
**SEPM - Fratura**

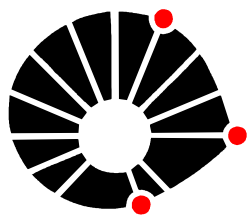


**SEPM - superfície em contato com ar**



**SEPM - superfície em contato com vidro**





UNICAMP



# NANOTECHNOLOGY FOR WATER-BASED PAINT IMPROVEMENT

Fernando Galembeck, Maria do Carmo V.M. da Silva,  
Renato Rosseto, Gilmar O. Pinheiro and João de Brito



**BiPHOR™**  
*The New White Pigment*

# Nanotechnology tools

- Chemical synthesis
  - Well established for over a century
- Self-assembly
  - Widely used by Mother Nature
  - Increasingly used since the 80's
- Nanomanipulation
  - At some point in the future
  - Problem: Avogadro's number is very large

# Aluminum phosphates are versatile materials

- Crystalline or amorphous
- A broad range of synthetic methods
- A **broad range of product properties**
  - Depending on the synthetic method
- Particles, fibers, crystals, films
- Particles are used as
  - Catalyst support
  - Adjuvants in fabrication of vaccines
  - Anti-acid medicines
  - Anti-corrosive paint additives

# Can we make a white pigment out of aluminum phosphate?

- YES, WHITE PIGMENT BASED ON HOLLOW PARTICLE FORMATION
  - ORTOPHOSPHATE
  - POLYPHOSPHATES
- PARTICLE VOIDS ARE
  - PREFORMED
  - FORMED DURING PAINT DRYING
  - AN EMERGING PROPERTY
  - THE OUTCOME OF A RARE NANOSTRUCTURE FORMATION PROCESS

# Characteristics of BiPHOR™ aluminum phosphate

- Non-crystalline solid
- Controllable stoichiometry and hydration
- Nano-structured particles with core-and-shell structure
- Nanosized particles are easily dispersed
  - stable towards settling
- Nanoparticles are strongly compatible with latex particles and other particulate solids
- Non-corrosive

# **Free** of environmental and toxicological problems

- Green chemistry process
- Wet-chemistry under mild conditions
- Zero-effluents
- Residues can be safely discarded
  - composting

# Biological Tests

**The tests were conducted in compliance with U.S. Environmental Protection Agency's by ABC Laboratories, USA.**

**Title: Aluminum Polyphosphate: Acute Toxicity to the Fathead Minnow, *Pimephales promelas*, Determined Under Static Test Condition.**

Nominal concentrations of BiPHOR™ in water: 0 (control), 0.01, 0.10, 1.0, 10, 100, and 1,000 mg/L.

**Results: Mortality and sub-lethal responses were not observed in any of the control or test substance treatments after 96 hours of exposure.**

**Source: ABC Laboratories, Inc. 7200 E. ABC Lane, Columbia, Missouri.**

# A deep scientific basis

- Beppu MM, Lima ECDO, Galembeck F.; Aluminum phosphate particles containing closed pores. Preparation, characterization, and use as a White pigment; JOURNAL OF COLLOID AND INTERFACE SCIENCE, 1996, 178 (1): 93-103.
- Lima ECD, Beppu MM, Galembeck F, Valente JF, Soares DM.; Non-crystalline aluminum polyphosphates: Preparation and properties; JOURNAL OF BRAZILIAN CHEMICAL SOCIETY, 1996, 7 (3): 209-215.
- Lima ECD, Beppu MM, Galembeck F.; Nanosized particles of aluminum polyphosphate; LANGMUIR, 1996, 12 (7): 1701-1703.
- Beppu MM, Lima ECD, Sassaki RM, Galembeck F.; Self-opacifying aluminum phosphate particles for paint film pigmentation; JOURNAL OF COATINGS TECHNOLOGY, 1997, 69 (867): 81-88.
- De Souza EF, Bezerra CC, Galembeck F.; Bicontinuous networks made of polyphosphates and of thermoplastic polymers; POLYMER, 1997, 38 (26): 6285-6293.

- Monteiro VAD, de Souza EF, de Azevedo MMM, Galembeck F.; Aluminum polyphosphate nanoparticles: Preparation, particle size determination and microchemistry; JOURNAL OF COLLOID AND INTERFACE SCIENCE, 1999, 217 (2): 237-248.
- De Souza EF, da Silva MDCVM, Galembeck F.; Improved latex film-glass adhesion under wet environments by using an aluminum polyphosphate filler; JOURNAL OF ADHESION SCIENCE AND TECHNOLOGY, 1999, 13 (3): 357-378.
- Azevedo MMM, Bueno MIMS, Davanzo CU, Galembeck F.; Coexistence of Liquid Phases in the Sodium Polyphosphate-Chromium Nitrate-Water System; JOURNAL OF COLLOID AND INTERFACE SCIENCE, 2002, 248 (1): 185-193.

# Theses and Dissertations

- 1990: Obtenção de Novos Materiais pelo Processo Sol-Gel; Óxidos e Fosfatos de Ferro. PhD Thesis, P.P. Abreu-Filho
- 1991: Obtenção e Caracterização de Metafosfatos de Alumínio: um Novo Pigmento Branco. MSc Dissertation, Emília C.de Oliveira Lima.
- 1995: Gelificação termorreversível em soluções aquosas de polifosfato de alumínio. PhD Thesis, Emília C. de Oliveira Lima.
- 1996: Géis, vidros e compósitos de polifosfatos de cálcio, de ferro (III) e mistos. MSc Dissertation, Nancy C. Masson.
- 1996: Obtenção e caracterização de fosfatos de alumínio amorfos. MSc Dissertation, Marisa M. Beppu.
- 1998: Vítor Augusto do Rego Monteiro. Nanopartículas de polifosfato de alumínio. MSc Dissertation, V.A. do Rego Monteiro.

# Patents

- 1991: Processo de Obtenção de Pigmentos Brancos, PI 9104581-9. *E.C.O. Lima and F. Galembeck*
- 1994: Processo de Síntese de Partículas Ocas de Fosfato de Alumínio. PI 9400746-2. *M.M. Beppu and F. Galembeck*
- 1995: Processo de Obtenção de Partículas Ocas de um Metafosfato Duplo de Alumínio e Cálcio em Látex Poliméricos. PI 9500522-6. *E.F. de Souza and F. Galembeck*
- 1997: Processo de síntese de partículas de fosfato e polifosfatos de ferro (III), simples duplos ou múltiplos, não-cristalinos. PI: 9700586-0. *E.F. de Souza and F. Galembeck*

# Current product and process

- 2004 - Produto e Processo de Fabricação de um Pigmento Branco Baseado na Síntese de Partículas Ocas de Ortofosfato ou Polifosfato de Alumínio. PI0403713-8
- 2005 - PCT Patent Applications: Aluminum Phosphate or Polyphosphate Particles for Use as Pigments in Paints and Method of Making Same

*Inventors: F. Galembeck and J. de Brito*

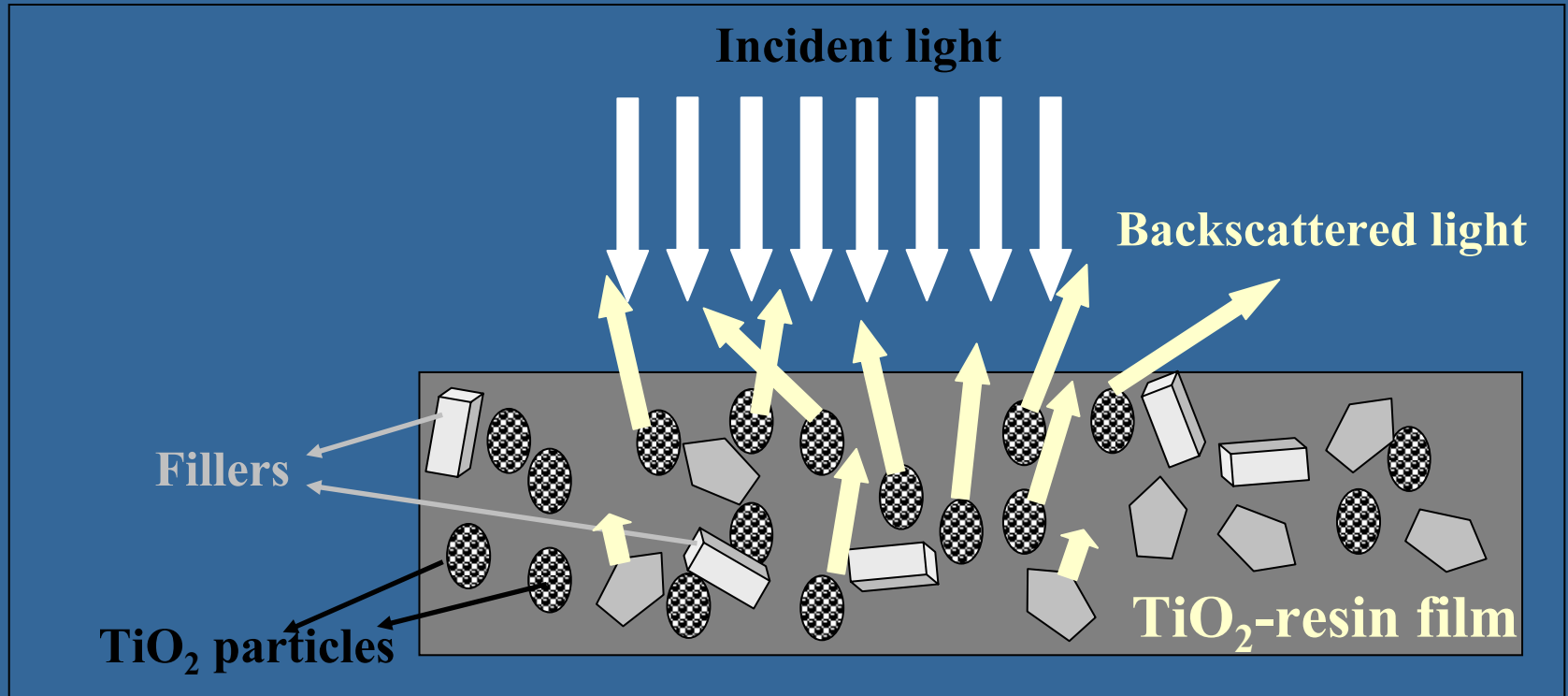
*Assignees: Unicamp and Bunge*

# *HOW ALUMINUM PHOSPHATES WORK?*



**BiPHOR™**  
*The New White Pigment*

# *Light Backscattering by $\text{TiO}_2$ -Pigmented Resin Film*

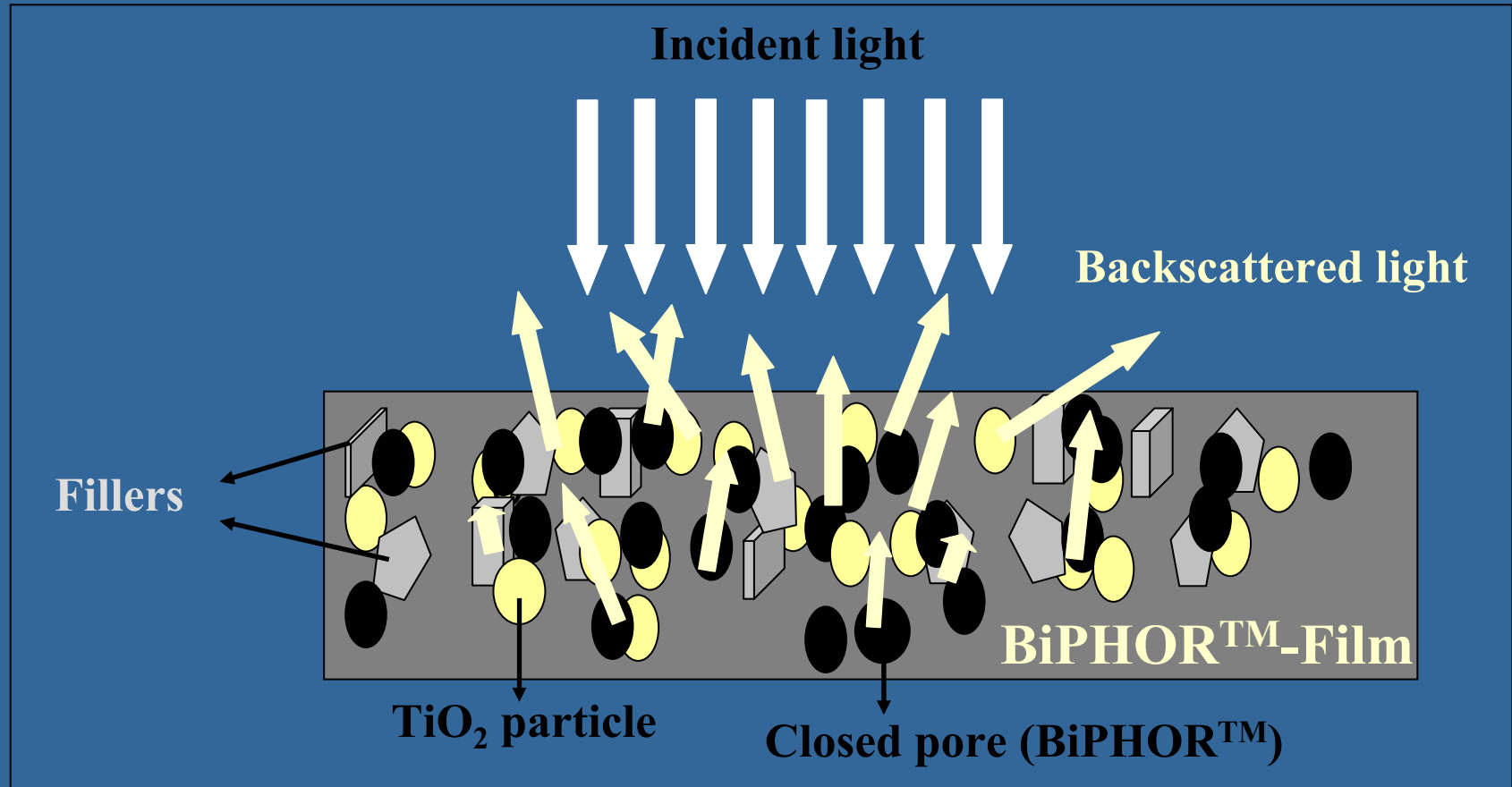


Pigment and filler particles are dispersed throughout the film  
and they backscatter incident light

Large refractive index difference between the resin and the  
particles

Near-UV light absorption

# *Light Backscattering by BiPHOR™-Resin Film*



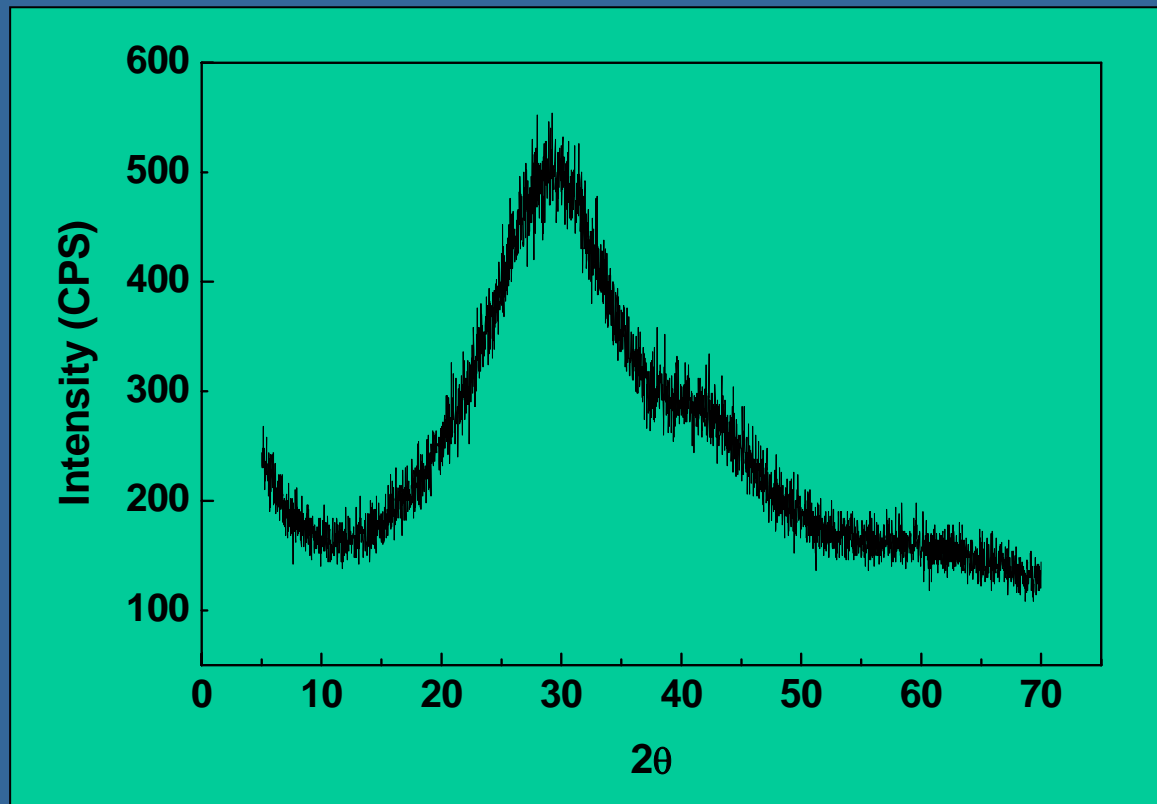
**Pigment particles as well as closed pores are scattered and they backscatter incident light**

**Large refractive index difference between the resin and the particles or closed pores**

# *CHARACTERIZATION*

- X-Ray Diffraction
- X-Ray Fluorescence
- Thermogravimetry
- Infrared
- Transmission Electron Microscopy
- others

# *X-Ray Diffraction (dry powder)*

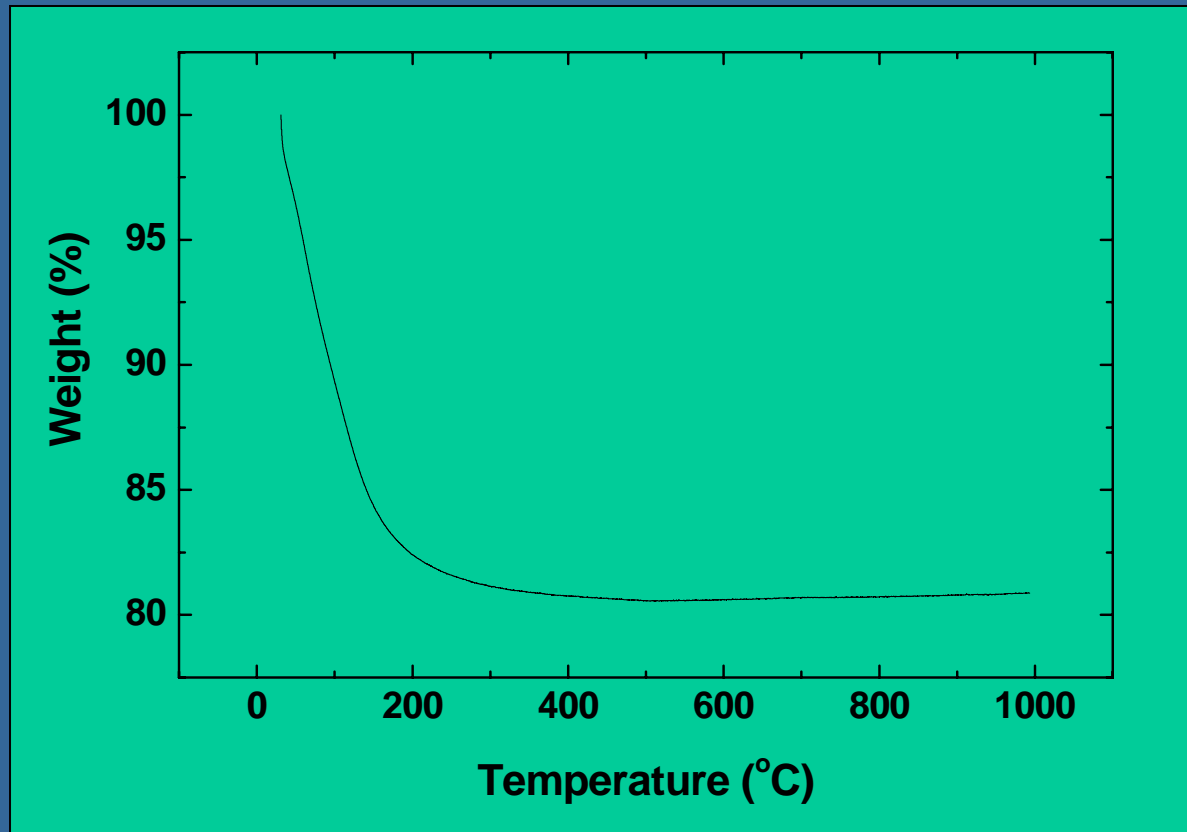


*Amorphous halo (Broad bands)*  
*Non-crystalline powder*  
*Average P-O and Al-O distances*

*X-Ray Fluorescence  
Elemental Composition of BiPHOR™ grades  
Variation in P/Al Ratio*

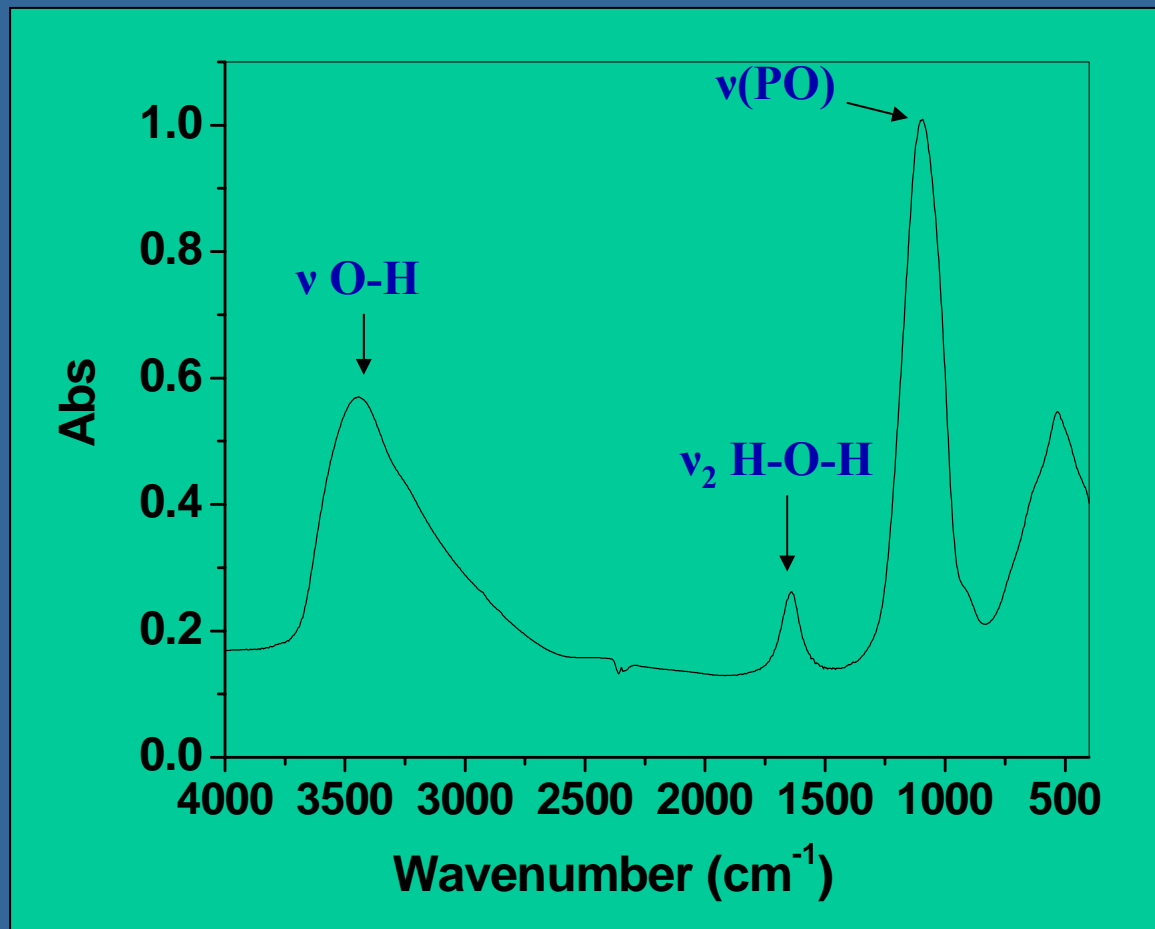
Grade	P	Al	S	Si	Fe	Ca
1	1	0.800	nil	0.067	0.0006	0.0005
2	1	0.820	nil	0.049	0.0005	0.0014
3	1	0.769	0.026	0.058	0.0007	0.0012
4	1	1.26	0.54	0.04	0.019	nil

# *Thermogravimetry*



*Water strongly bound to the ionic network*

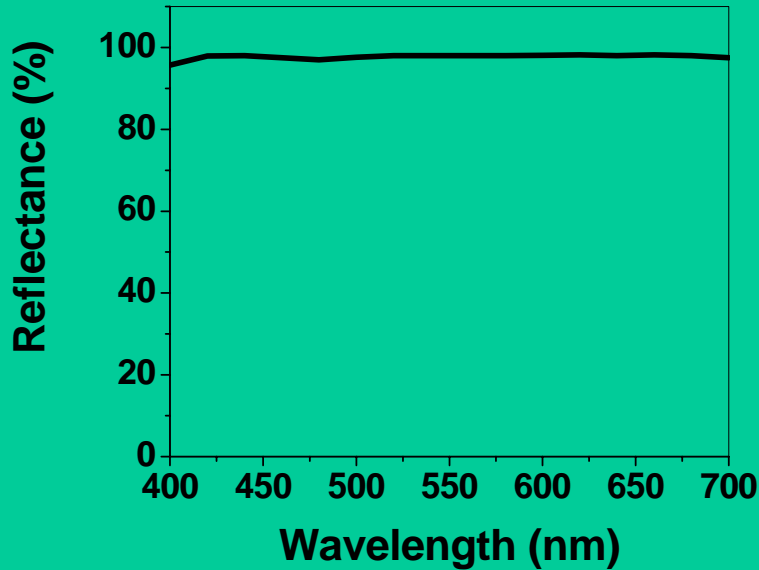
# *Infrared spectrum of dry powder in KBr*



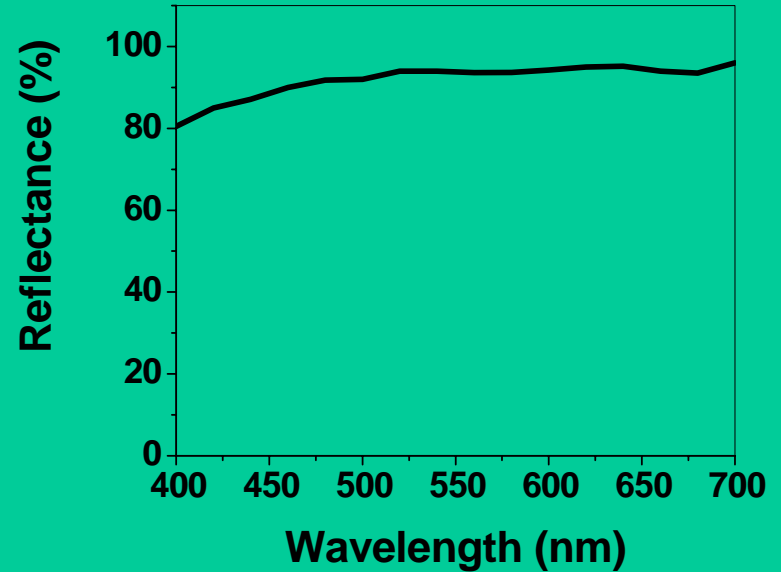
*The large band at 3700-2700  $\text{cm}^{-1}$  is due to the extensive hydration of the particles*

# Absence of absorption in the visible range

## Dried Powder

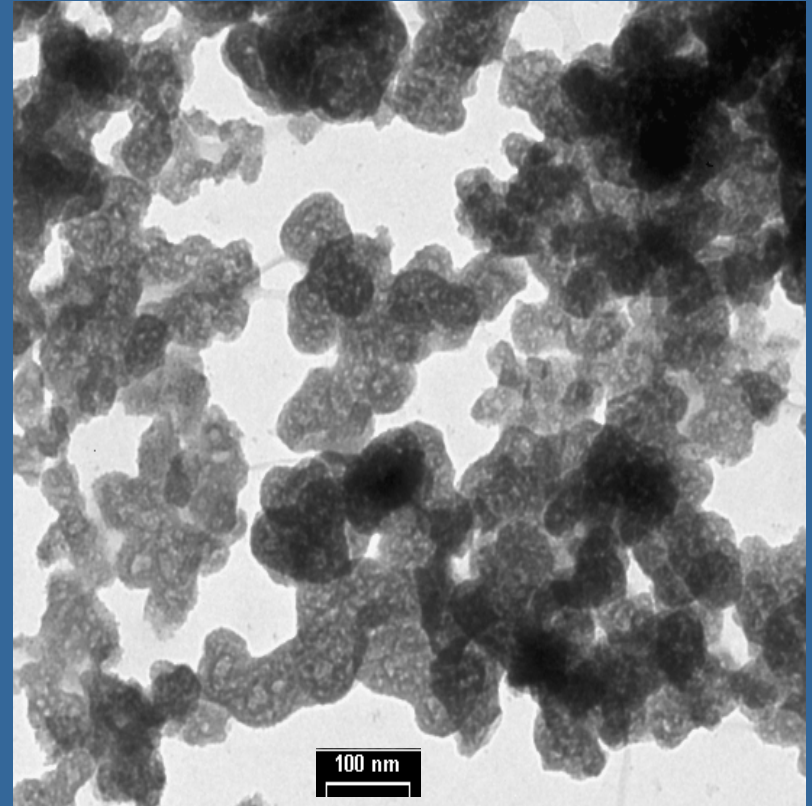
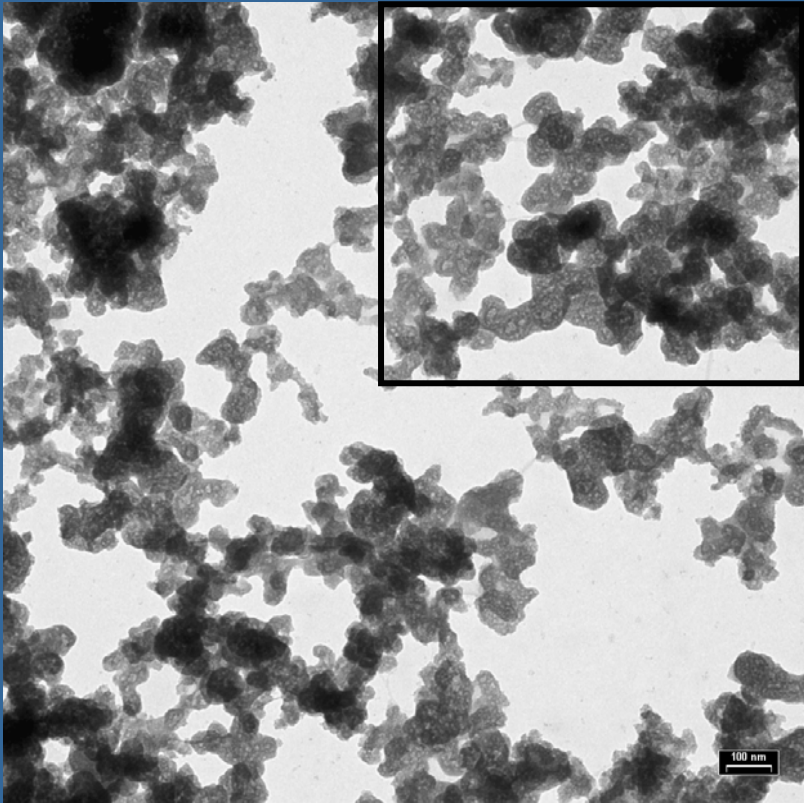


**BiPHOR™**



**TiO<sub>2</sub>**

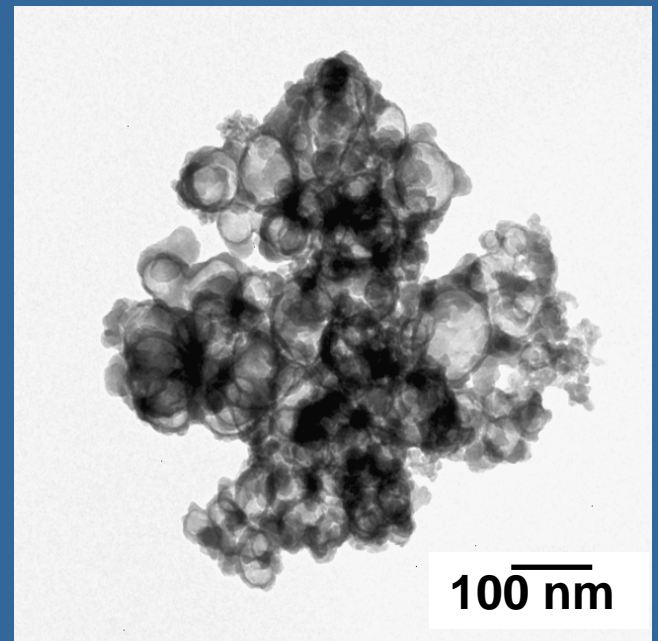
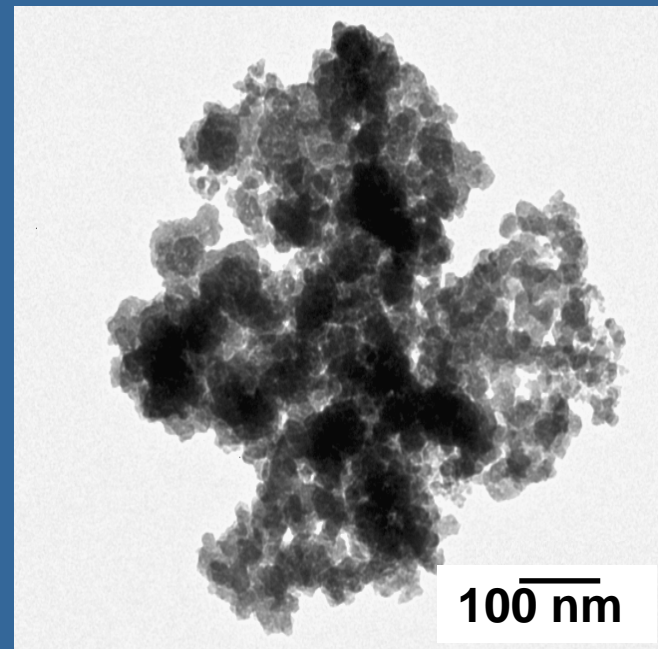
# *Transmission Electron Microscopy*



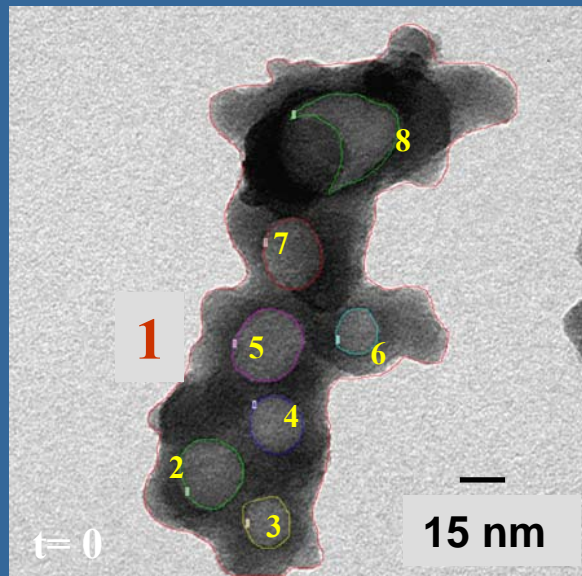
*hollow particles (closed pores)*

# Evidence for Core-Shell Structure

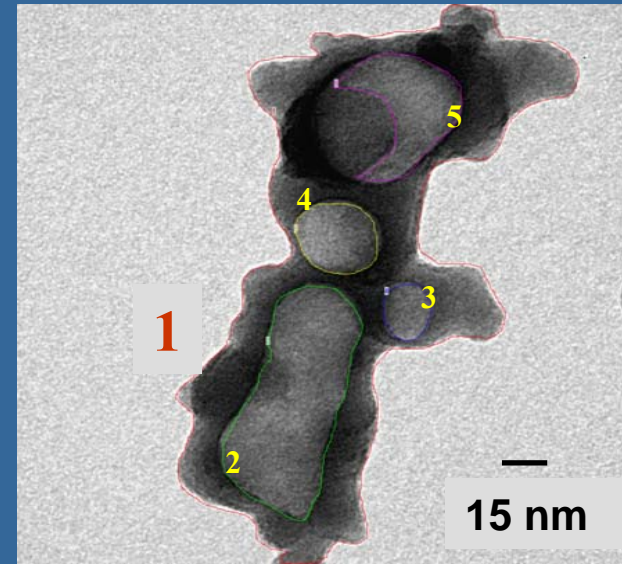
- Particles under the microscope beam loose material from the bulk without major outer volume changes
- Larger voids are formed
- Plastic interiors, stiffer walls



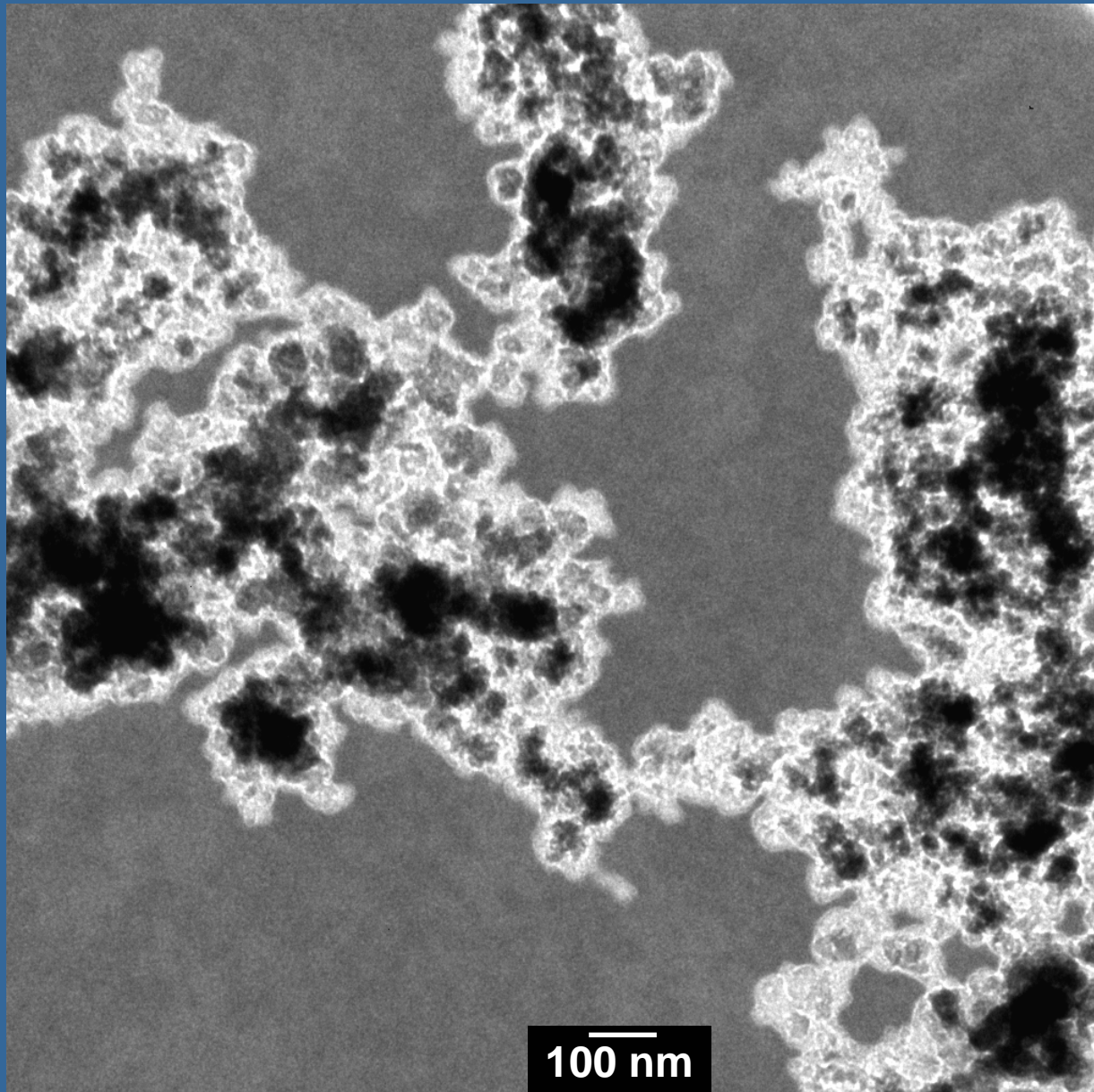
The perimeter of shells remains unaltered while the interior voids become larger with electron beam effect



electron beam

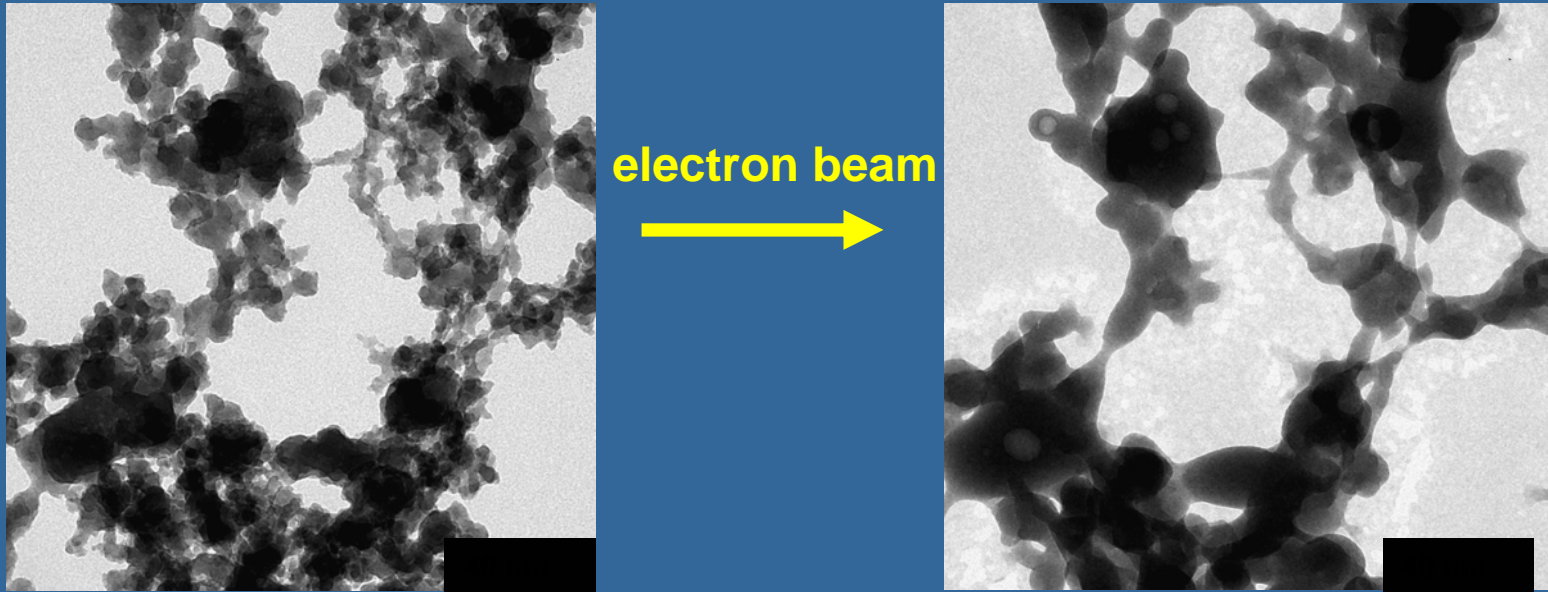


<i>Perimeter (nm) / Area (nm<sup>2</sup>)</i>	
<i>Before exposure to electron beam</i>	<i>After exposure to beam</i>
1) 733.8 / 11.718	1) 733.5 / 11.975
2) 85 / 407 3) 62 / 229 4) 71 / 283 5) 91 / 457 <div style="display: inline-block; vertical-align: middle; font-size: 3em; margin: 0 10px;">}</div> 309 / 1.376	2) 229 / 2.283
6) 57 / 179	3) 65 / 240
7) 82 / 384	4) 99 / 557
8) 137 / 602	5) 180 / 899



Another evidence, from plasmon imaging: **particle contours are brighter** than the particle interiors

*Amorphous aluminum phosphate (P/Al =2.5) following Hem's procedure. (Vaccine, 2001, 19, 275)*



- Dry particles do not show small voids by TEM
- The particles undergo large morphological changes upon heating
- The extensive formation of “necks”, where the particle surfaces are very deformable

# *BiPHOR™ Slurry Specifications*

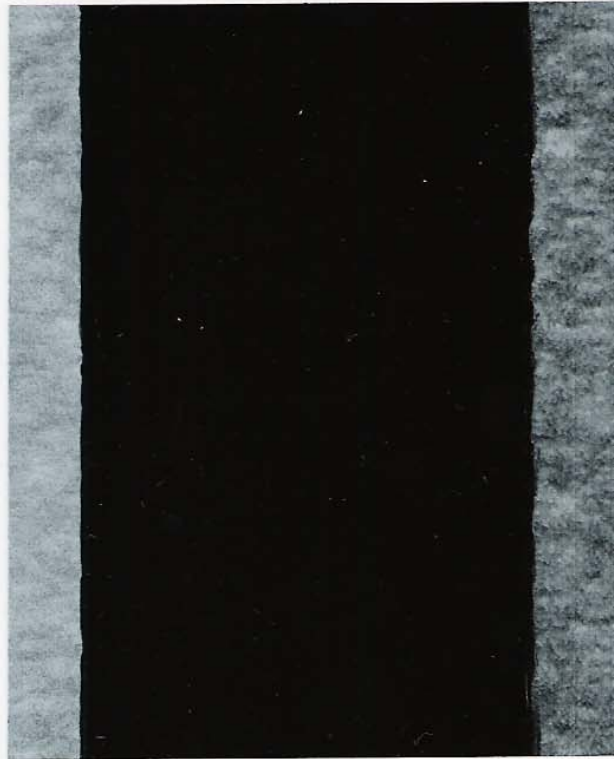
<i>Description</i>	<i>BiPHOR™</i>
<b>Hegman Grind</b>	<b>7H (ASTM D 1210)</b>
<b>Density (at 26% solids)</b>	<b>1.3 ± 0.1 g/mL (ASTM D1475)</b>
<b>Viscosity (at 26% solids)</b>	<b>53 ± 2 KU (ASTM D 562)</b>
<b>Non-volatile %</b>	<b>34 ± 1 (ASTM D 1644)</b>
<b>pH</b>	<b>&gt; 6.5 (ASTM D 4584)</b>
<b>Opacity (%)</b>	<b>94.1 ± 0.2 (ASTM D 2805)</b>
<b>Reflectance (%)</b>	<b>90.7 from 400 to 700 nm (ASTM E 1331)</b> <b><i>l</i> = 96.5; <i>a</i> = -0.2; <i>b</i> = + 0.5</b>
<b>Yellowness (%)</b>	<b>0.4 (ASTM E 313)</b>
<b>Whiteness (%)</b>	<b>95.9 (ASTM E 313)</b>
<b>Particle size diameter</b>	<b>200-2000 nm (light dynamic scattering)</b>

# Formulating with Biphor

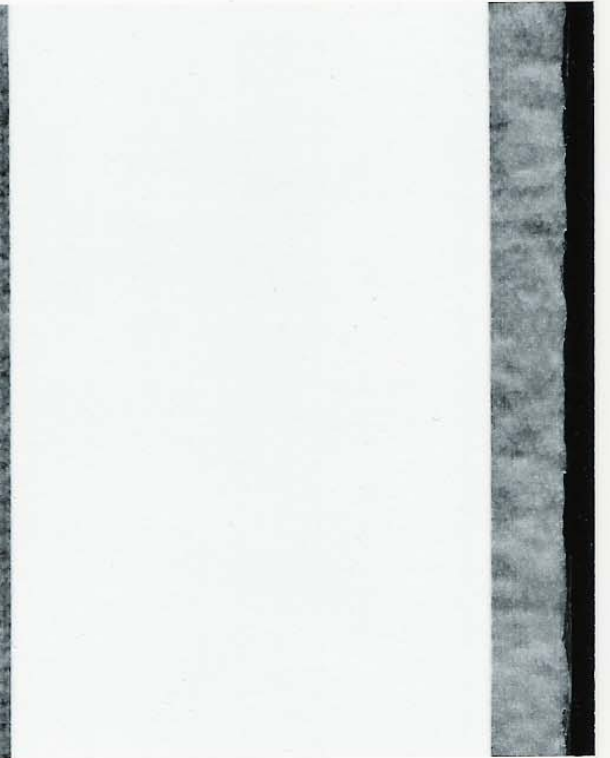
<i>Component</i>	<i>Standard Formula (g)</i>	<i>Formula using BiPHOR™ slurry (g)</i>
Water	839.79	361.86
Propyleneglycol	30.00	30.00
Thickener/rheology modifier	84.00	4.50
Antifoaming/Coalescing agent	0.60/60.00	1.17/43.47
Tetrapyrophosphate/Dispersant	0.87/20.94	9.00/11.00
Anti-oxidant	0.87	0.90
AFE anionic	7.86	7.86
Biocides	9.00	9.00
NH <sub>4</sub> OH 25%	7.11	15.00
Titanium dioxide	534.00	267.00
BiPHOR™ slurry 35%		763.00
Inorganic Fillers	690.96	690.96
Acrylic resin	735.00	591.00
Total	3030.00	2816.72

# Excellent hiding power

**Control: 100% TiO<sub>2</sub>**



**50% BiPHOR™**



# Performance tests

- 50%  $\text{TiO}_2$  replacement on formulas of testing laboratories
  - DL Labs, Inc. 74 Kent Street Brooklyn, New York
  - Stonebridge Technical Services. 6223 Linden Road, Fenton, MI, USA
- 50%  $\text{TiO}_2$  replacement on premium formulations used in Brazil.

<i>TEST</i>	<i>Standard Formula</i>	<i>Formula using BiPHOR™ slurry</i>
<b>Description</b>	<b>100% TiO<sub>2</sub></b>	<b>50% BiPHOR™ + 50% TiO<sub>2</sub></b>
<u><b>Hiding</b></u>		
At 9.8 m <sup>2</sup> /L (%)	92.5	92.1
At 6.6 m <sup>2</sup> /L (%)	94.4	94.5
<u><b>At 6.6 m<sup>2</sup>/L (%)</b></u>		
Reflectance (%)	90.1	90.1
Whiteness Index (%)	79	78.8
Yellowness Index (%)	4.0	4.2
Gloss - 60° (units)	2	2
Sheen - 85° (units)	1	2
<u><b>Washability – Reflectance Recovery</b></u>		
Before washing (%)	87.6	87.0
After washing (%)	54.0	53.1
Reflectance Recovery (%)	61.7	61.0

Source: DL Labs, Inc. 74 Kent Street Brooklyn, New York.

<i>TEST</i>	<i>Standard Formula</i>	<i>Formula using BiPHOR™ slurry</i>
Description	100% TiO <sub>2</sub>	50% BiPHOR™ Slurry + 50% TiO <sub>2</sub>
Fineness of Grind (Hegman)	5	4
% Non-volatile	58.3	53.6
Density	12.0	11.4
Stormer Viscosity (KU)	96	99
<u>0.003” Drawdowns</u>		
85 °C	1.0	1.1
Contrast Ratio	0.9207	0.9108
Reflectance (white)	0.9086	0.9082
Yellowing Index (D1925)	3.76	3.76
Yellowing Index (E313)	3.33	3.34
Whiteness Index (E313)	78.79	78.76
<u>0.0015” Drawdowns</u>		
Contrast Ratio	0.7763	0.7632
Reflectance (white)	0.8807	0.8800

Source: Stonebridge Technical Services. 6223 Linden Road, Fenton, MI, USA.

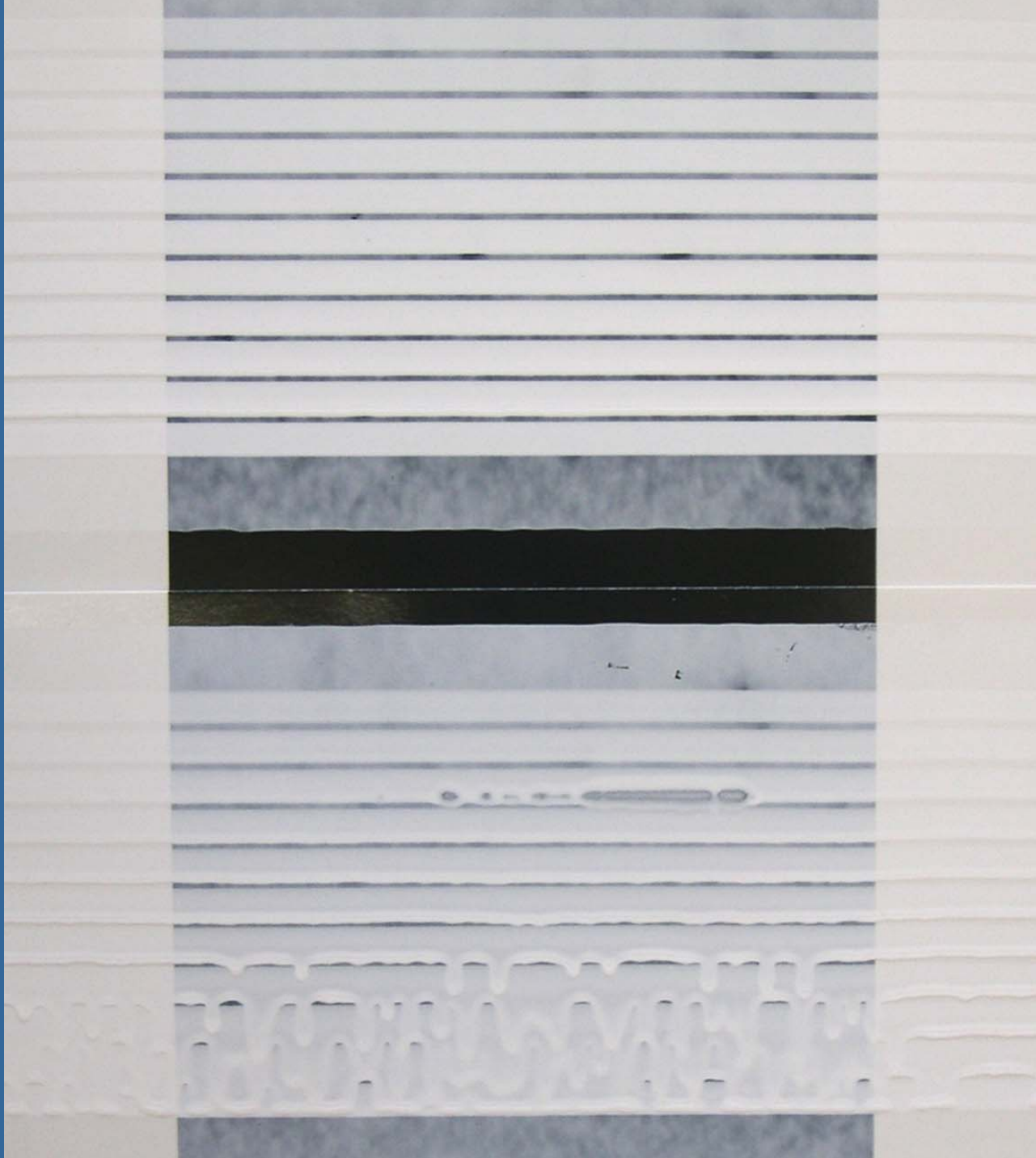
<i>TEST</i>	<i>Standard Formula</i>	<i>Formula using BiPHOR™ slurry</i>
<b>Block resistance</b>	<b>6</b>	<b>8-9</b>
<b><u>Color Acceptance</u></b>		
<b><math>\Delta E_{XYZ}</math> Wet-on-Wet Rub</b>	<b>0.39</b>	<b>0.38</b>
<b><math>\Delta E_{XYZ}</math> Wet-on-Dry Rub</b>	<b>0.46</b>	<b>0.85</b>
<b><math>\Delta E_{XYZ}</math> Wet-on-Dry Brush</b>	<b>0.34</b>	<b>0.44</b>
<b>Y-Reflectance Drawdown Black</b>	<b>0.4870</b>	<b>0.4772</b>
<b>Y-Reflectance Drawdown White</b>	<b>0.4873</b>	<b>0.4781</b>
<b>Y-Reflectance Wet-on-Wet Rub</b>	<b>0.4842</b>	<b>0.4802</b>
<b>Y-Reflectance Wet-on-Dry Rub</b>	<b>0.4906</b>	<b>0.4701</b>
<b>Y-Reflectance Wet-on-Dry Brush</b>	<b>0.4909</b>	<b>0.4728</b>
<b><u>Washability</u></b>		
<b>Y-Reflectance (before/after)</b>	<b>0.8839/0.4335</b>	<b>0.8790/0.3402</b>
<b>Gloss (before/after)</b>	<b>1.8/2.6</b>	<b>2.2/4.2</b>
<b>Leveling (NYPC Drawdown)</b>	<b>7</b>	<b>7</b>
<b>Sag Resistance</b>	<b>5.6</b>	<b>8.4</b>

**Source: Stonebridge Technical Services. 6223 Linden Road, Fenton, MI, USA.**

*50% BiPHOR™  
paint*

Considerably  
less sag

*Control formula*





*Field application test: a house painted with a  
BiPHOR<sup>TM</sup>-based paint*

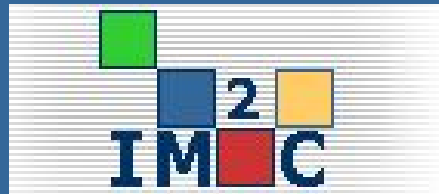
# To sum up

- Outstanding performance at high levels of TiO<sub>2</sub> replacement
- Absence of UV absorption and catalytic resin photo-oxidation
- Ample supply of raw materials
- Environmentally friendly process and product
- For further details: [www.biphorpigments.com](http://www.biphorpigments.com)

# *ACKNOWLEDGMENTS*

*PADCT/CNPq*

*Instituto do Milênio de Materiais Complexos*



Brazilian funding agencies: Capes, CNPq, Fapesp,  
Finep for supporting the Unicamp laboratory

## **Former Unicamp students that contributed to our knowledge on amorphous phosphates and their sponsors**

- Emília C. de Oliveira Lima (CNPq)
- Nancy C. Masson (CNPq)
- Marisa M. Beppu (Fapesp and CNPq)
- Renato M. Sassaki (CNPq)
- Elizabeth F. Souza (Fapesp)
- Vítor A. do Rego Monteiro (CAPES)

# Projeto Tensopol

- Problema: como as propriedades de um látex são afetadas pelos tensoativos usados na polimerização em emulsão?
  - Látex escolhido: estireno-acrilato de butila-ácido acrílico

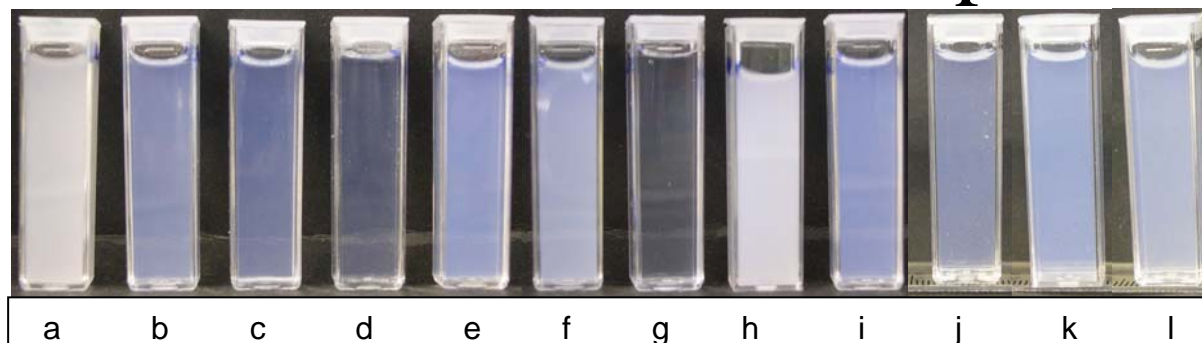
# TENSOATIVOS USADOS

Nome	Cadeia apolar derivada de	Número de EO	Látex obtido
Renex 40, 120, 230, 400 e 1000	Nonilfenol	4, 12, 23, 40 e 100	RE040A ~ RE1000A
Ultrader 500	Nonilfenol	50	UTD50A
Unitol L90 e L230	Álcool laurílico	9 e 23	UNL09A ~ UNL23B
Unitol O200	Álcool oleico	20	UNO20A
Ultroil R400	Óleo de mamona	40	UOR40A
Surfom OP230	Octilfenol	23	SOP23A
Alkifos 40, 60, 95 NPK	Nonilfenol fosfatado	4, 6 e 9,5	AK040A ~ AK095A
Hostapal BVQ09	Nonilfenol sulfatado	9	HBV09A

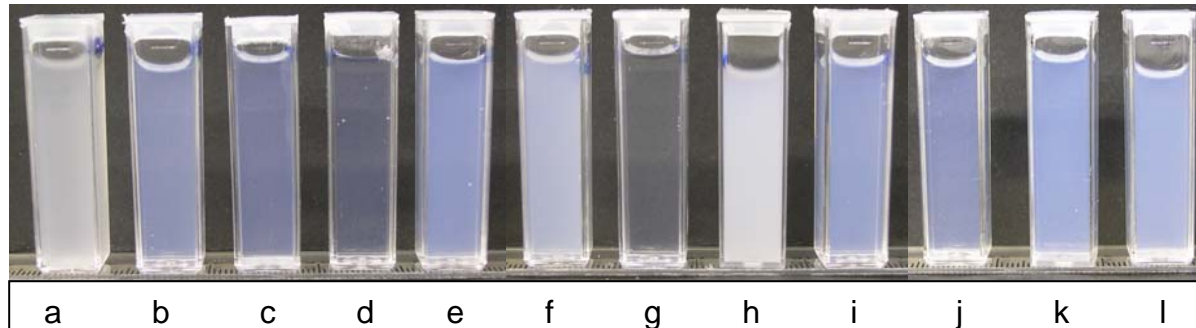
# Resultados de resistência coloidal dos látices a eletrólitos em diferentes tempos

- a) RE040A
- b) RE230A
- c) RE400A
- d) RE400B
- e) SOP23A
- f) UOR40A
- g) ULS23A
- h) UNO20A
- i) UNL23A
- j) R1000A
- k) RE440A
- l) RE230B

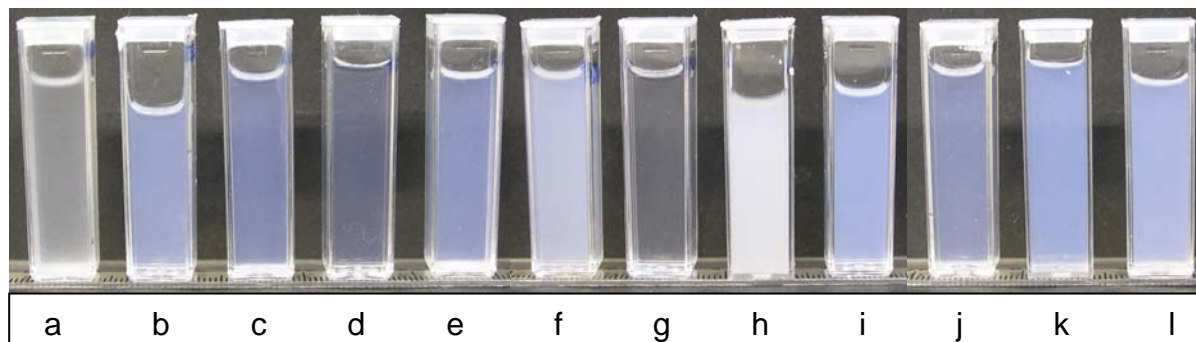
Tempo:  
0 h



24 h



96 h



# Adesão de látex a filme de LDPE



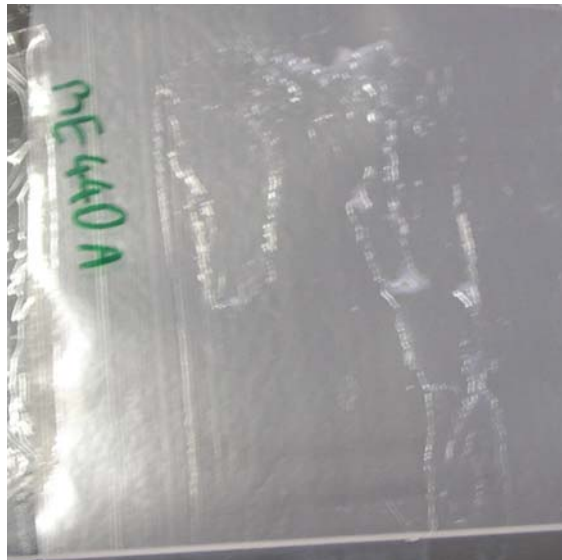
RE040A



RE440C (90/10)



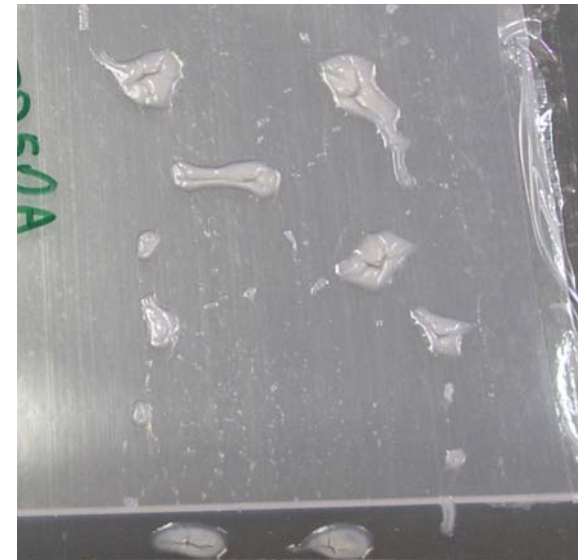
RE440B (75/25)



RE440A (50/50)



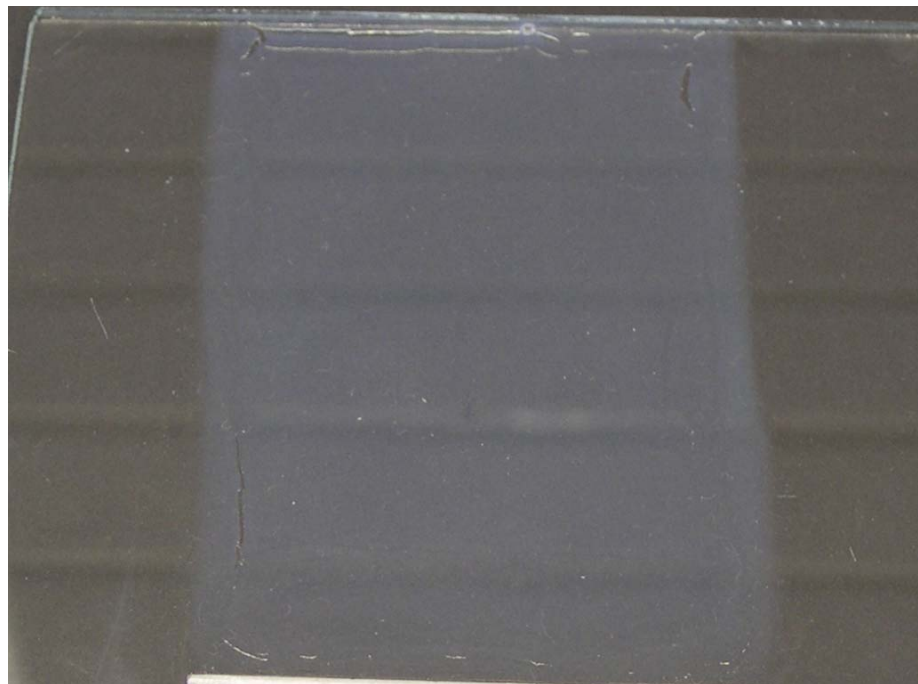
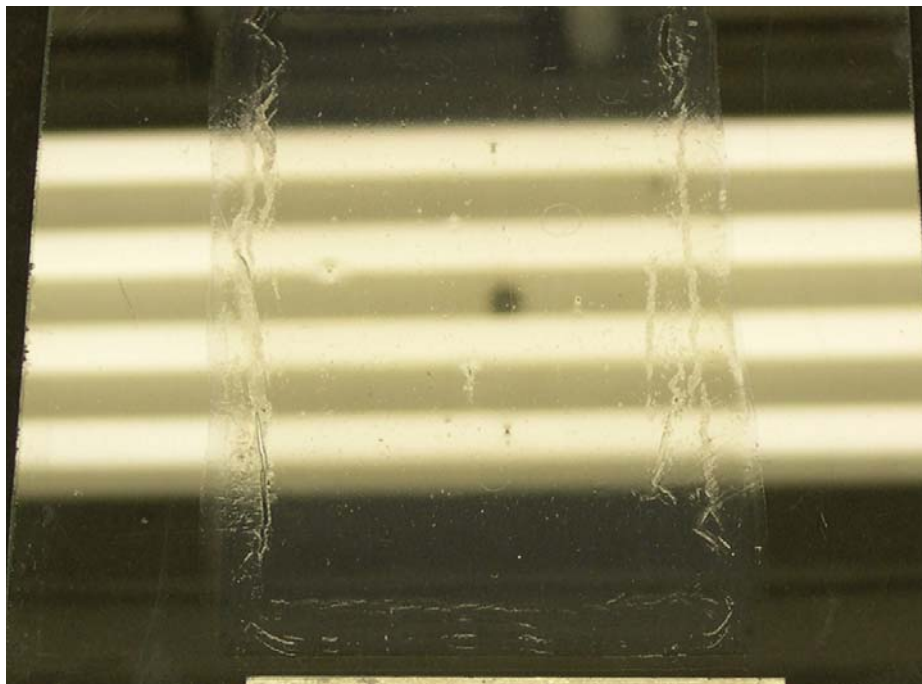
RE230B



UTD50A

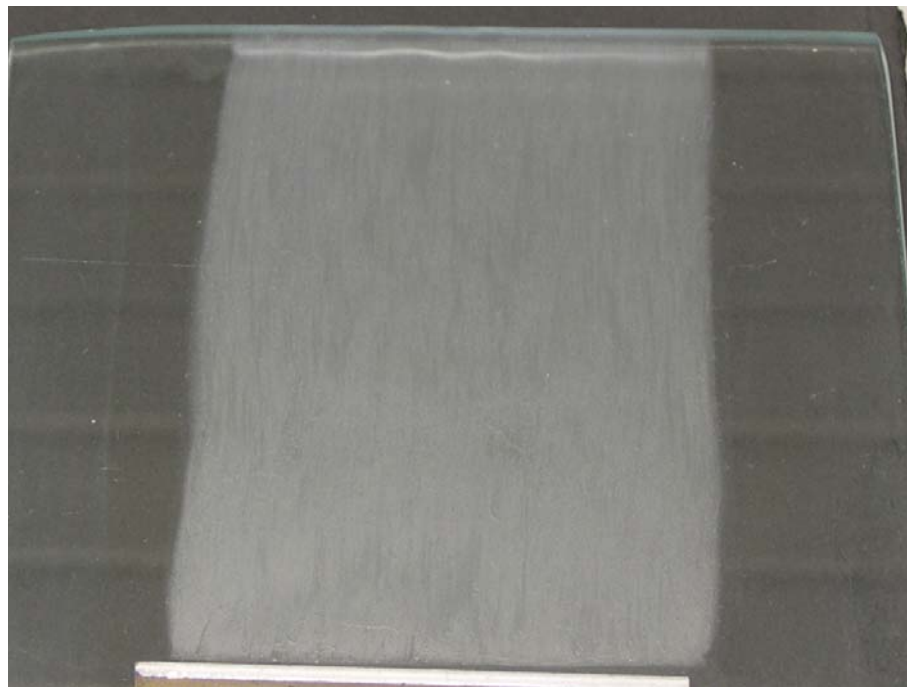
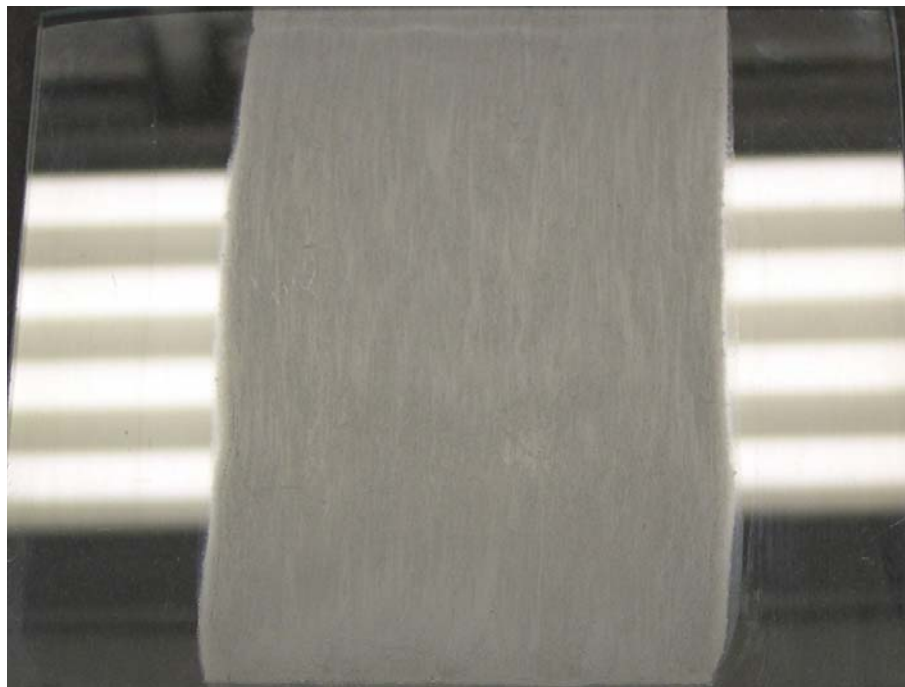
# RE440B

(nonilfenol 4 + 40 EO 75/25)



# R1040A

(nonilfenol 40 + 100 EO 75/25)



Luz refletida, fundo negro

AK095A

HBV09A

R1000B

R1040A

R1040B

RE120C

RE440B

RE440C

RE440D

UTD50A



# Apoio e parcerias

- Capes
- CNPq
- Fapesp
- Finep
- PADCT
- Bunge Fertilizantes
- Carol Química
- Indústria Química Taubaté S/A
- CTMESP/Radicci Fibras
- Orbys
- Oxitenó
- Rhodia-Ster (Mossi & Ghisolfi)