The Tony Davies High
Voltage Laboratory

UNIVERSITY OF
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Known Knowns and Known Unknowns

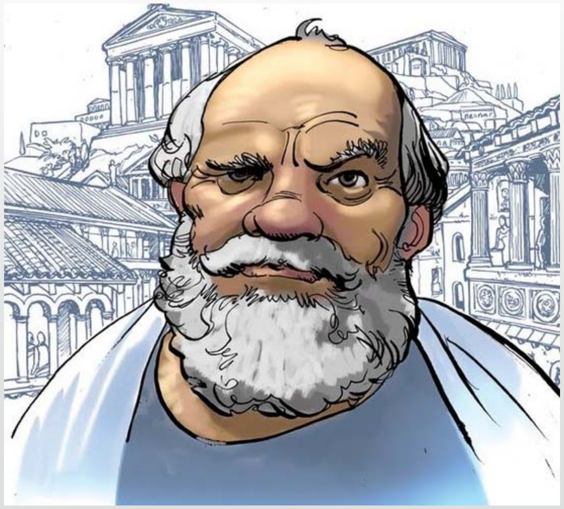
Nanodielectrics

Thomas Andritsch
19 October 2014

Introduction

“Reports that say that something hasn't happened are always interesting to me, because as we know, **there are known knowns**; there are things we know that we know. There are **known unknowns**; that is to say, there are things that we now know we don't know. But there are also **unknown unknowns** – there are things we do not know we don't know.” –Donald Rumsfeld, 2002

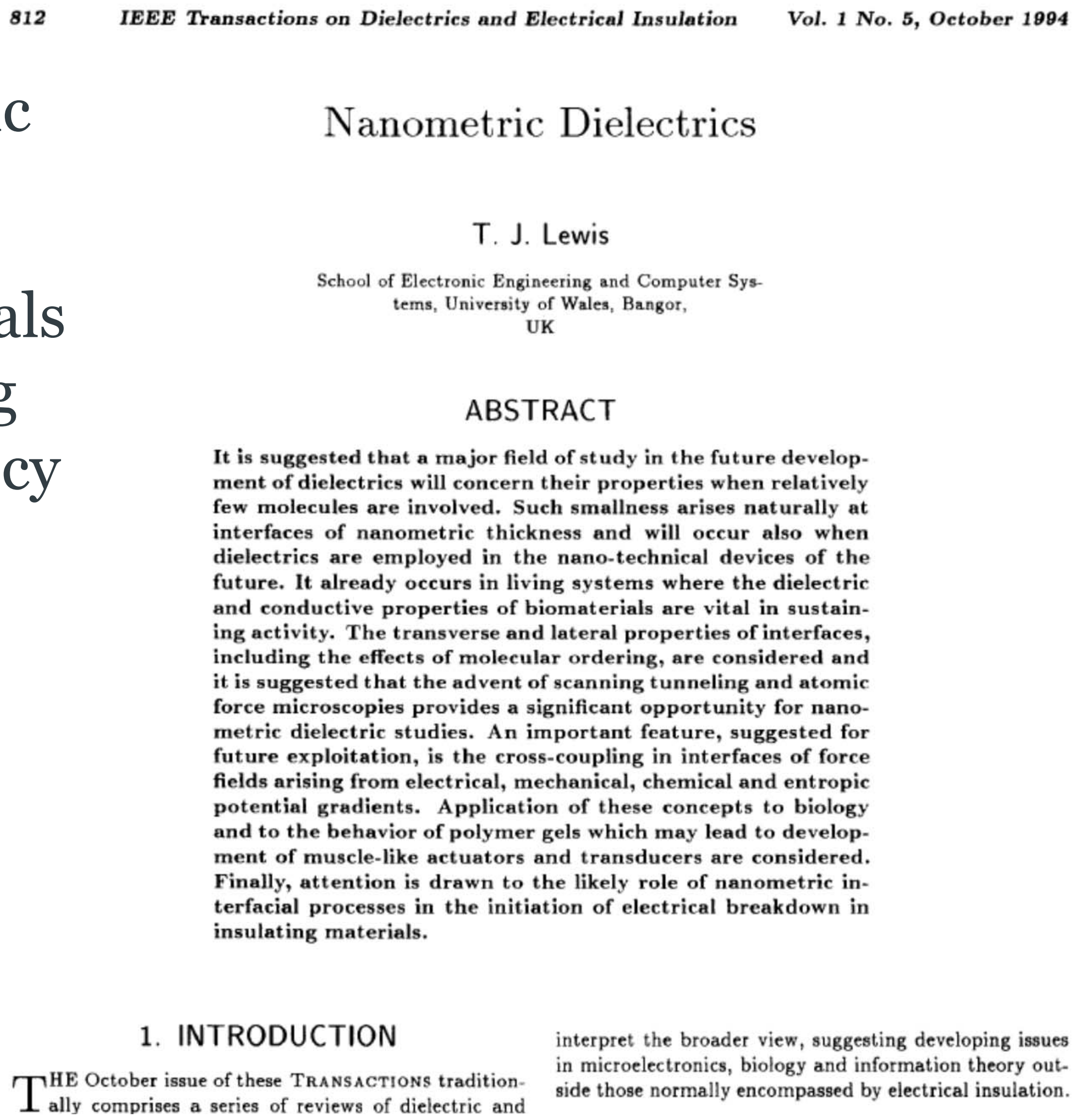
“οὗτος μὲν οἴεταί τι εἰδέναι οὐκ εἰδώς, ἐγὼ δέ, ὥσπερ οὖν οὐκ οἶδα, οὐδὲ οἴομαι”
–Socratic paradox [This man, on one hand, believes that he knows something, while not knowing. On the other hand, I - equally ignorant - do not believe.]



The Unknown Knowns

1994

- The start of “nanometric dielectrics”
- Nanostructured materials in electrical engineering treated as in their infancy



812 *IEEE Transactions on Dielectrics and Electrical Insulation* *Vol. 1 No. 5, October 1994*

Nanometric Dielectrics

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ABSTRACT

It is suggested that a major field of study in the future development of dielectrics will concern their properties when relatively few molecules are involved. Such smallness arises naturally at interfaces of nanometric thickness and will occur also when dielectrics are employed in the nano-technical devices of the future. It already occurs in living systems where the dielectric and conductive properties of biomaterials are vital in sustaining activity. The transverse and lateral properties of interfaces, including the effects of molecular ordering, are considered and it is suggested that the advent of scanning tunneling and atomic force microscopies provides a significant opportunity for nanometric dielectric studies. An important feature, suggested for future exploitation, is the cross-coupling in interfaces of force fields arising from electrical, mechanical, chemical and entropic potential gradients. Application of these concepts to biology and to the behavior of polymer gels which may lead to development of muscle-like actuators and transducers are considered. Finally, attention is drawn to the likely role of nanometric interfacial processes in the initiation of electrical breakdown in insulating materials.

1. INTRODUCTION

THE October issue of these TRANSACTIONS traditionally comprises a series of reviews of dielectric and

interpret the broader view, suggesting developing issues in microelectronics, biology and information theory outside those normally encompassed by electrical insulation.

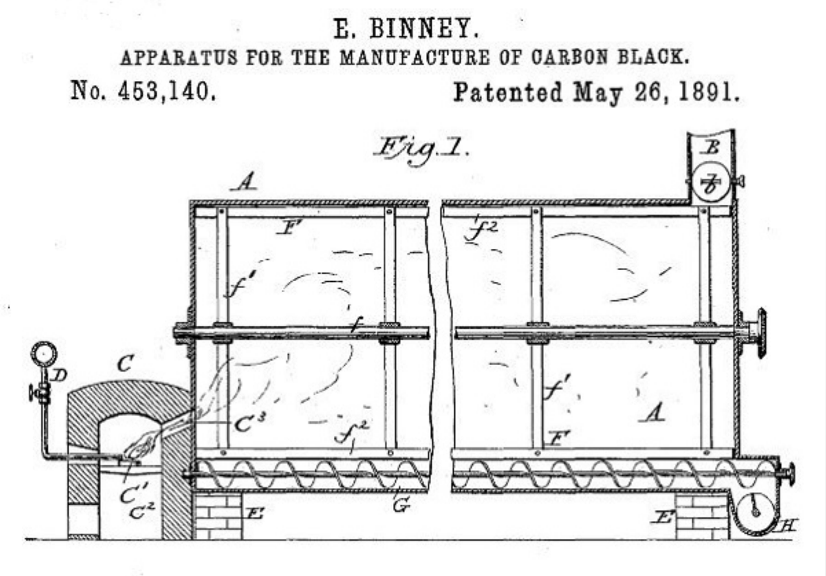
Nanomaterials are Old News

- Damascus steel, developed in India 300 BC (CNT from plant fibres dispersed in steel), Celtic smiths used similar steel

- Lycurgus Cup, 4th Century Roman Empire (Gold & Silver NP dispersed in colloidal form in the glass)

Mass Produced Nanomaterials

- In 1910 Silvertown Co. (London) and later B.F. Goodrich (US) introduced carbon black into rubber tyres to improve their performance and durability

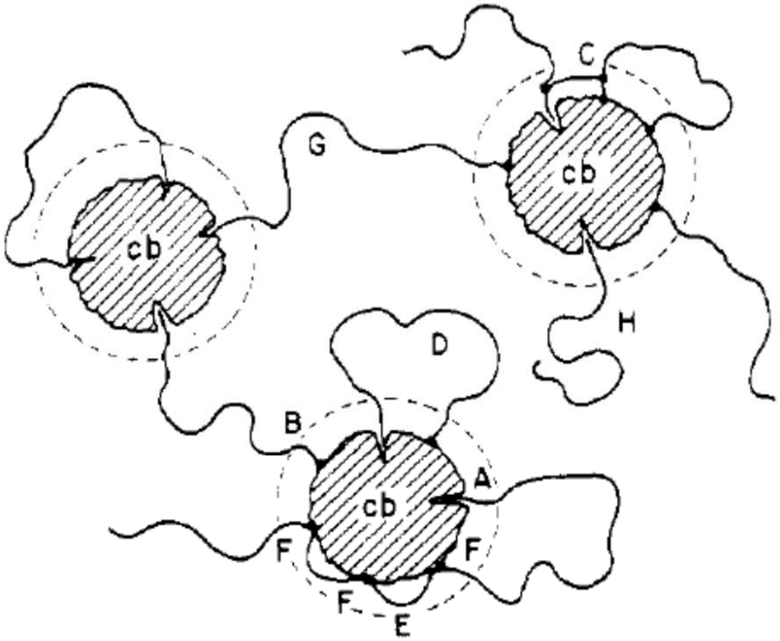


E. BINNEY.

APPARATUS FOR THE MANUFACTURE OF CARBON BLACK.

No. 453,140. Patented May 26, 1891.

The Interface (I)



A. PHYSICAL ATTACHMENT
B. CHEMICAL ATTACHMENT
C. CROSS LINKED RUBBER MOLECULE
D. LOOSE FOLD
E. TIGHT FOLD
F. MULTIPLE ADSORPTIVE ATTACHMENTS
G. INTER-PARTICLE LINKAGE MOLECULES
H. CILIA MOLECULES.

Figure 13. Diagram which illustrates the model for the filled rubber system discussed in the text; the dashed circles denote the boundaries of the tightly bound region.

Source: McBrierty et al.: Interaction between Carbon Black and cis-Polybutadiene, **Macromolecules Vol. 9 No. 4** July-August 1976

- Decrease in layer thickness with increasing surface area
- Multiple T_G

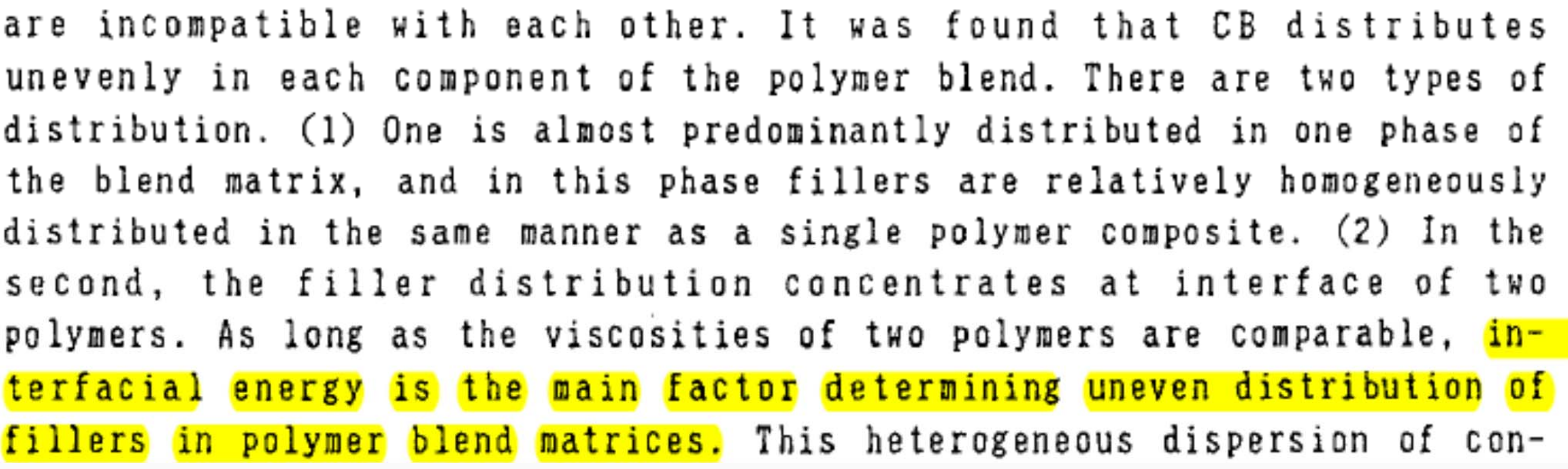
Pliskin & Tokita:

$$BR = \Delta R_0 f \left\{ \frac{\emptyset \rho A}{1 - \emptyset} \right\} + G$$

(J. Appl. Pol. Sci. 16, 473 (1972)

Dispersion

Source: Sumita et al. Polymer Bulletin 25, 265-271 (1991)



are incompatible with each other. It was found that CB distributes unevenly in each component of the polymer blend. There are two types of distribution. (1) One is almost predominantly distributed in one phase of the blend matrix, and in this phase fillers are relatively homogeneously distributed in the same manner as a single polymer composite. (2) In the second, the filler distribution concentrates at interface of two polymers. As long as the viscosities of two polymers are comparable, interfacial energy is the main factor determining uneven distribution of fillers in polymer blend matrices. This heterogeneous dispersion of con-

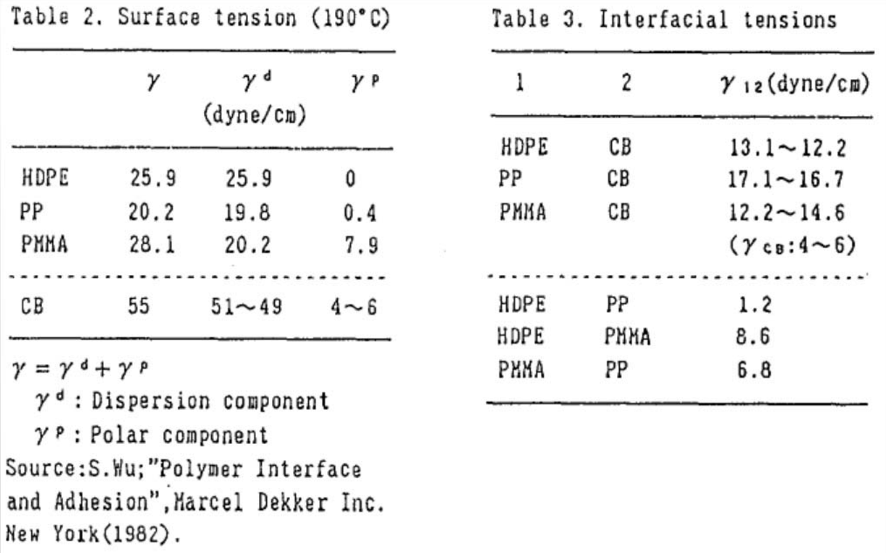


Table 2. Surface tension (190°C)

	γ	γ^d (dyne/cm)	γ^p
HDPE	25.9	25.9	0
PP	20.2	19.8	0.4
PMMA	28.1	20.2	7.9
CB	55	51∼49	4∼6

$\gamma = \gamma^d + \gamma^p$

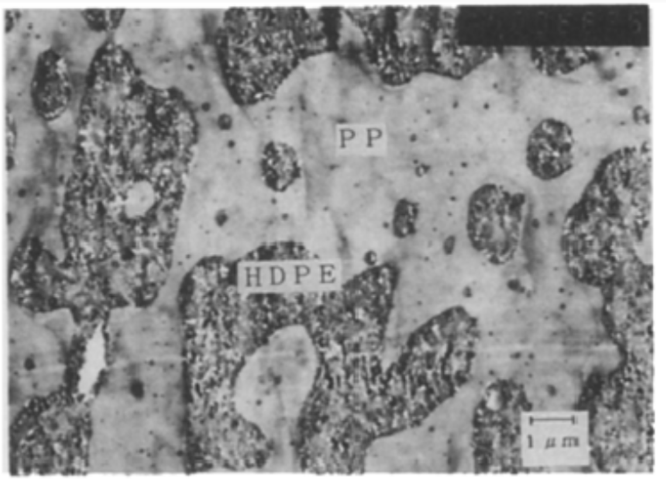
γ^d : Dispersion component

γ^p : Polar component

Source:S.Wu;"Polymer Interface and Adhesion",Marcel Dekker Inc. New York(1982).

Table 3. Interfacial tensions

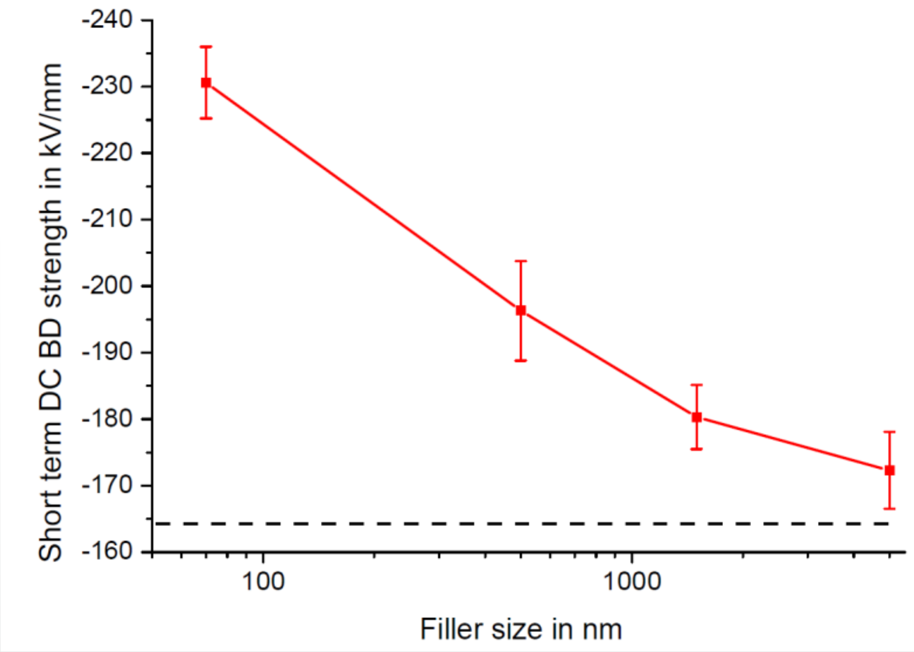
1	2	γ_{12}(dyne/cm)
HDPE	CB	13.1∼12.2
PP	CB	17.1∼16.7
PMMA	CB	12.2∼14.6 (γ_{CB}:4∼6)
HDPE	PP	1.2
HDPE	PMMA	8.6
PMMA	PP	6.8



(b)HDPE/PP

The Known Knowns

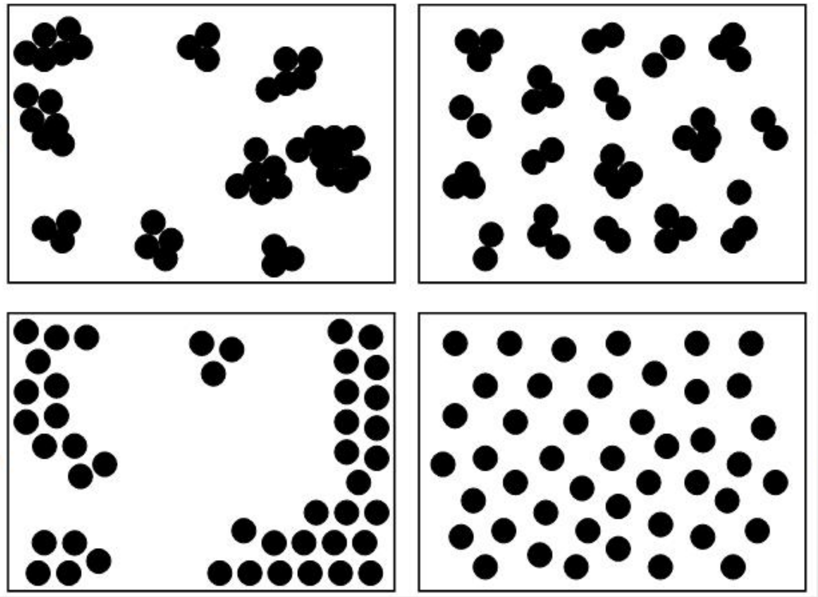
The Promise of Nanomaterials



- Short-term DC BD results for epoxy NC with 10 wt.% BN filler
- Filler size between 70nm and 5µm
- Unfilled epoxy: dashed line

➢ Increase of BD strength with decreasing filler size

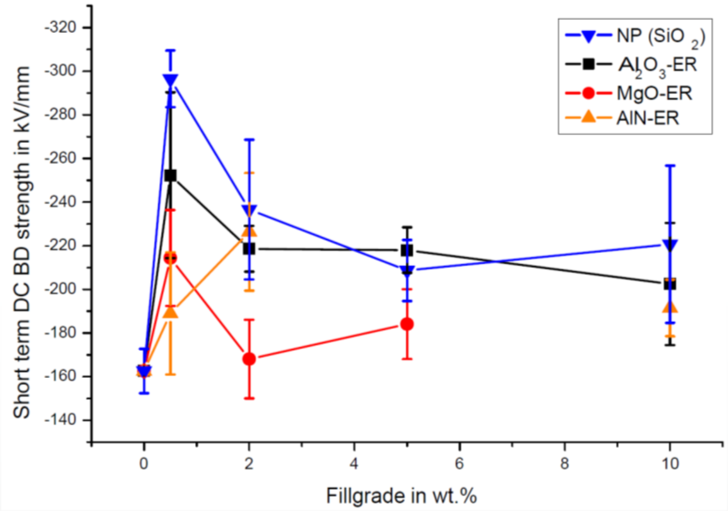
The Problem with Nanofillers…

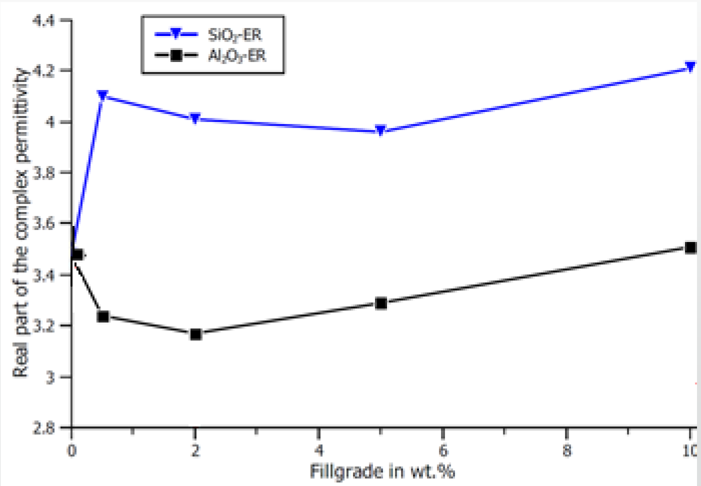


- Difficult to achieve good dispersion of nanoparticles in a polymer
- Verification of said dispersion difficult and time consuming
- Toxicity of nanoparticles often very different to conventional sized particles
- Procedures used to create samples in laboratories difficult to scale up for industry

Dielectric Properties

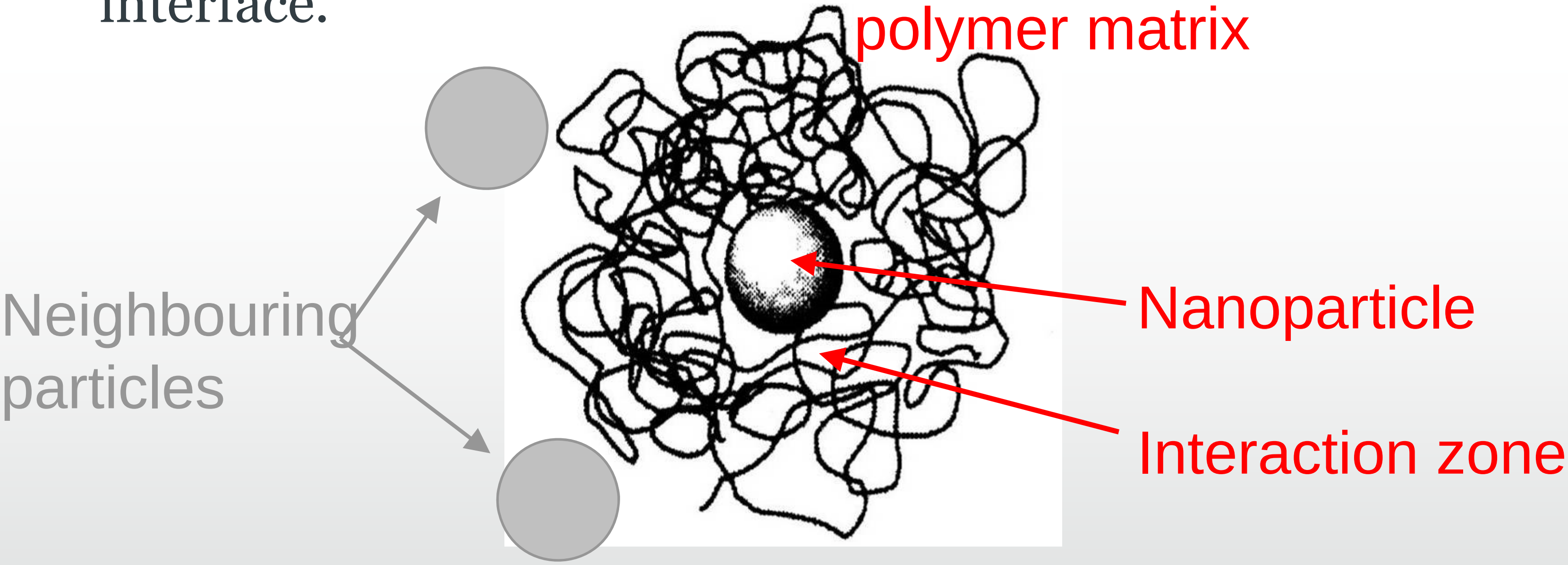
- Even small amounts of nanoparticles can lead to a significant change in the material structure
- Decrease of BD strength with increasing fillgrade
- Decrease or increase of permittivity with introduction of nanoscale filler
- Behaviour disagrees with common rules of mixture





The Interface (II) – Key Feature of Nanodielectrics

- The volume surrounding a nanoparticle, and including the contact or bonding to the polymer matrix, is referred to as the “interface.”



Illustrated morphology of a polymer around a metal oxide

Source: C.W. Reed “Nanodielectrics 101” CEIDP 2011

Multi-Core Model

- Widely used to describe nanodielectrics' behaviour
- Interfaces of certain thickness with altered dielectric properties
- Why can't we see them?

(1) a bonded layer (the first layer)
(2) a bound layer (the second layer)
(3) a loose layer (the third layer)
(4) an electric double layer overlapping the above three layers

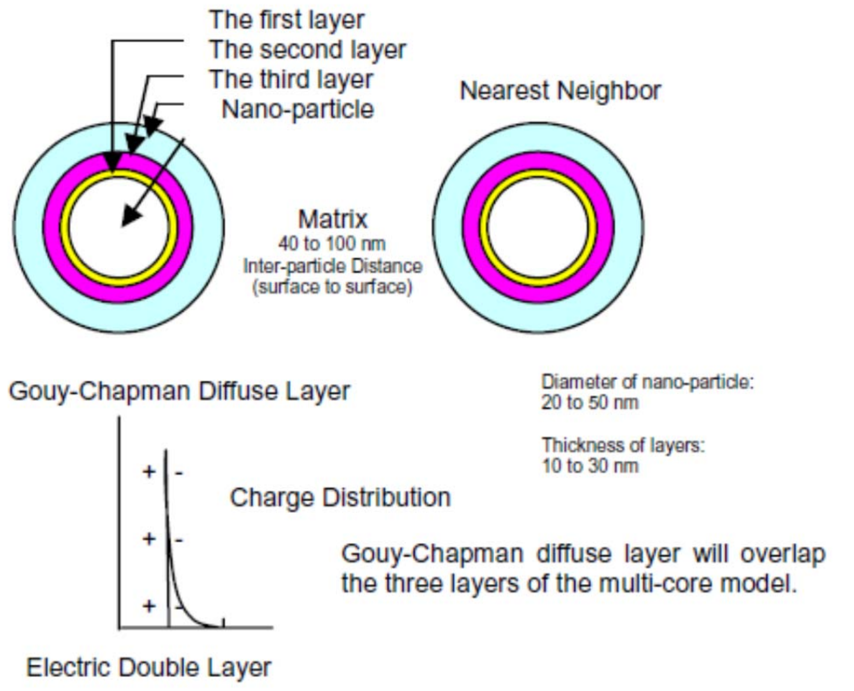
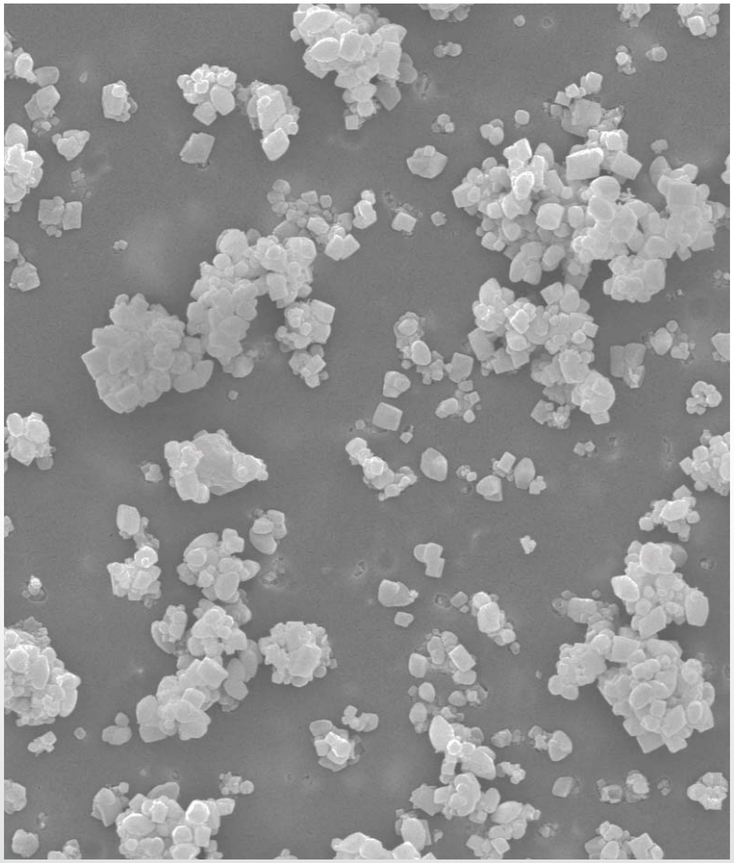
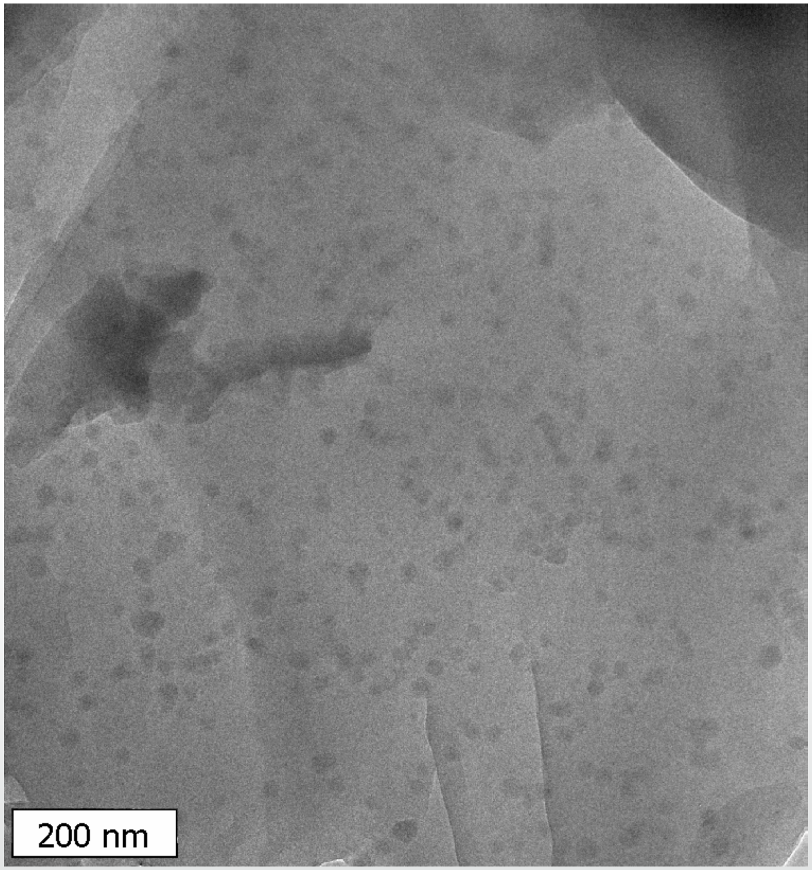


Figure 1. Outline of the multi-core model for polymer nanocomposites.

Amorphous Polymers...

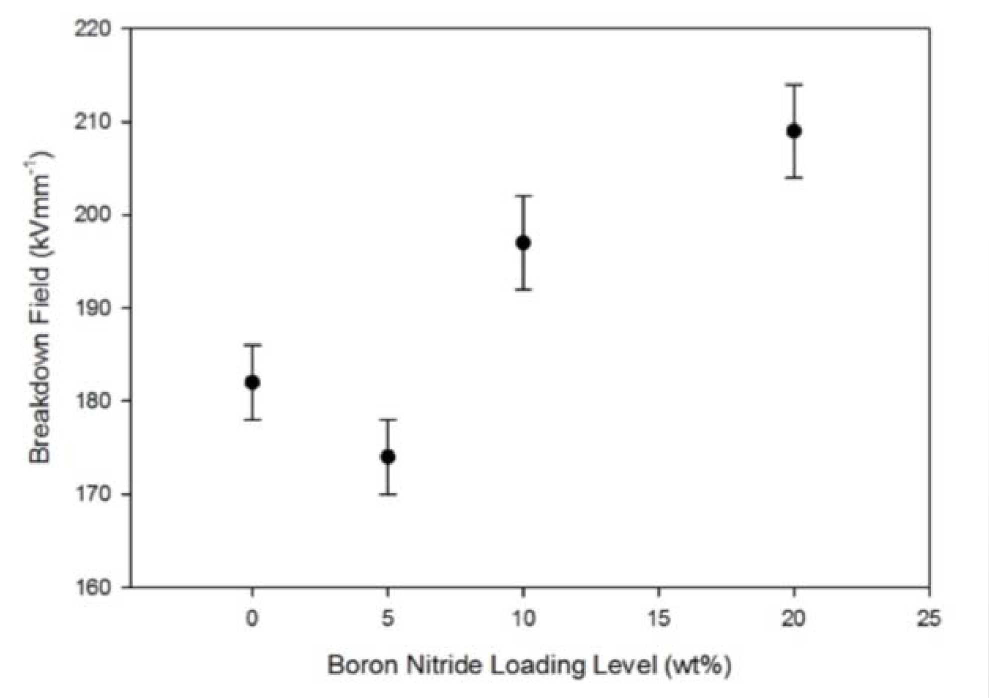


Polystyrene



Epoxy Resin

Breakdown Strength in PS



- hBN in PS
- Lowest for 5% by weight
- Afterwards monotonic increase
- No surface modification
- hBN adsorbs little moisture

Results from Raed Ayoob, visit his poster at Session 8A

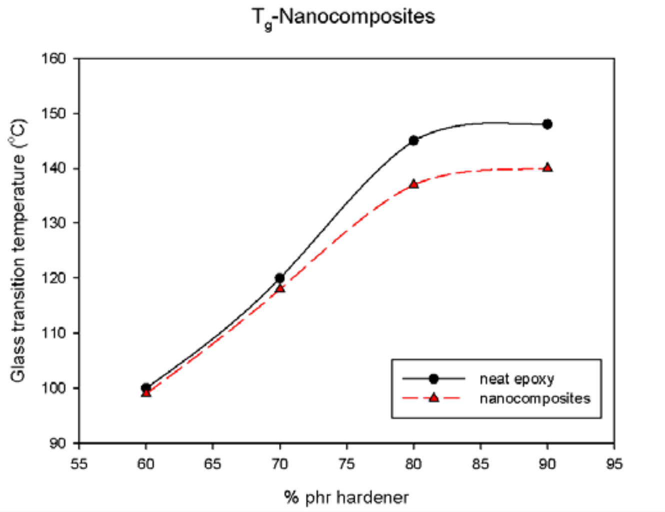
Epoxy…

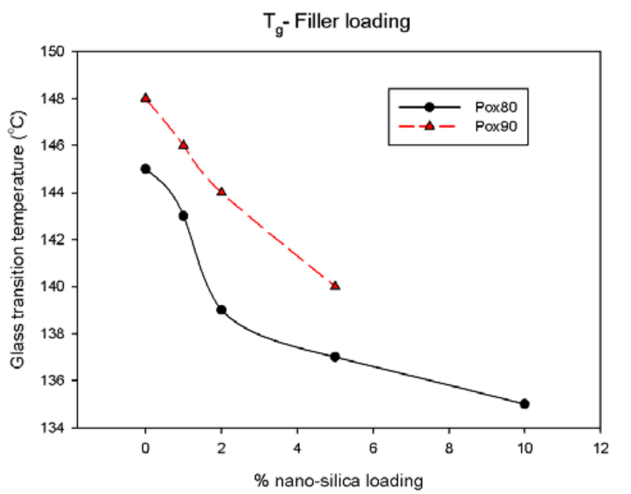
Epoxy very sensitive to changes of:

- Stochiometry
- Curing temperature
- Curing time
- Oxygen/pressure levels

- More than 50 substances that fit the definition
- Several hundred suitable hardeners
- Solvent might deteriorate the matrix and produce ions

T_G in Epoxy/Silica System





- Comparison of T_g for unfilled and silica filled (5%) systems
- Tg is suppressed in nanocomposites of optimum stoichiometry
- The value of Dc_p varies systematically with stoichiometry/filling
- All glass transitions in epoxy based composites are singular
- Width of T_g is constant within experimental error

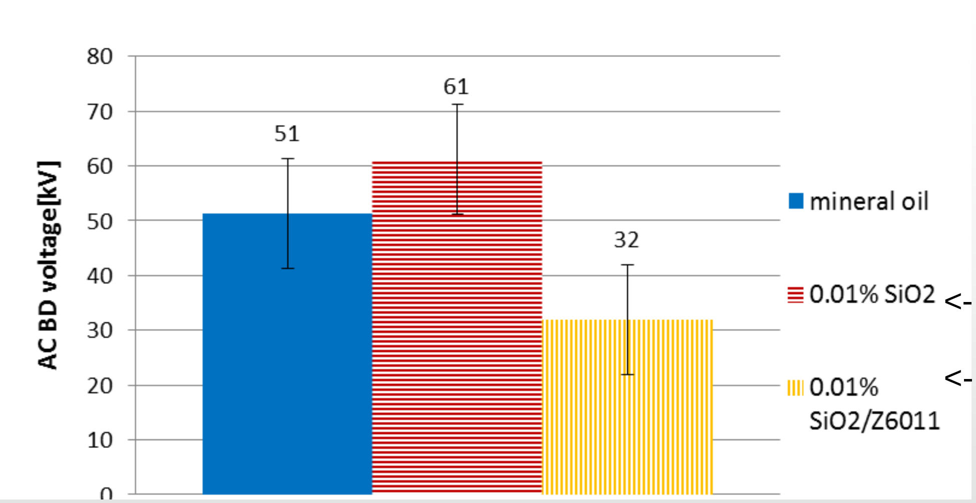
The complete system is being affected

Polyethylene

- In PE a change of the morphology can be seen due to introduction of nanoparticles
- Difficult to determine the precise distribution in PE based composites
- No distinct interfaces but widespread change
- Not a good polymer to analyse as long as some fundamental questions are not answered

The Interface – Moisture

- Water adsorption by nanoparticles (silica)
- Changes in BD strength: nano-effects or just moisture?
- In Nanofluids probably the latter:



<- hydrophilic

<- hydrophobic

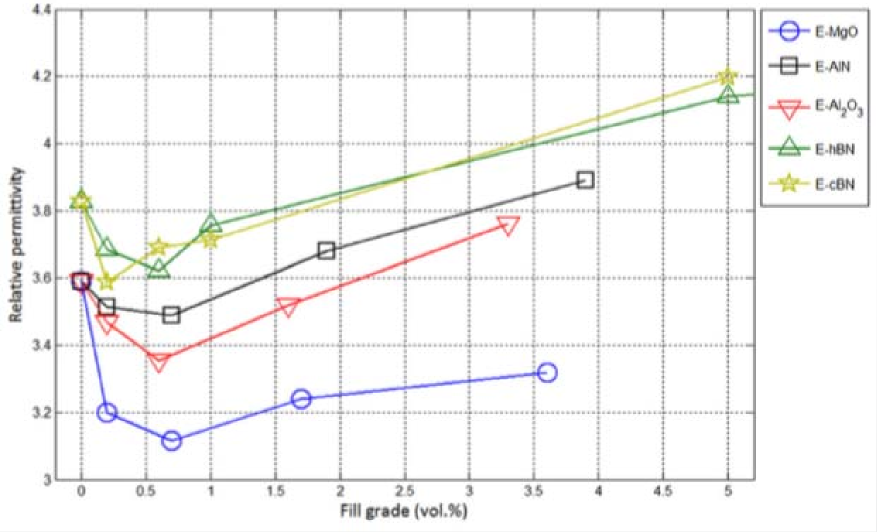
AC BD of mineral oil, pure silica nanofluid and silica/Z6011 nanofluid.

Source: Jin et al. TDEI Vol. 21, No. 3, pp. 1105-1114 (2014)

The Interface – Humid Environment

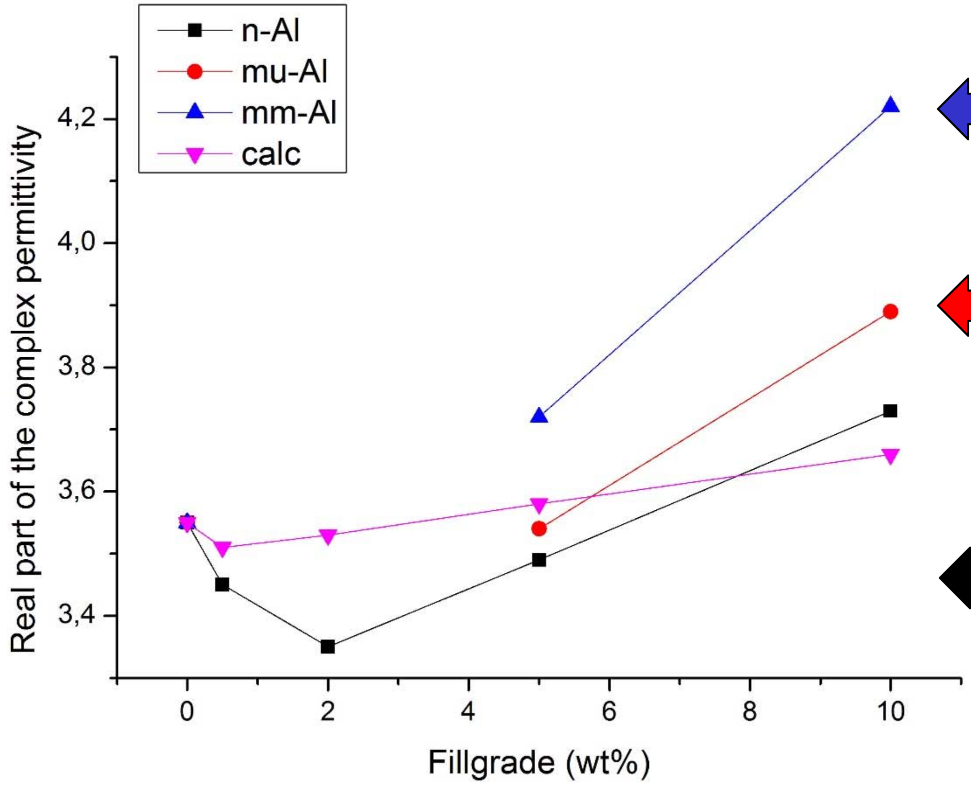
- Permittivity reduction due to chain restriction

+ Increase due to moisture (ions) at the polymer-particle interface



Source: Tsekmes et al. J. Phys. D: Appl. Phys. **47** (2014)

Permittivity – Inconsistent Effects?



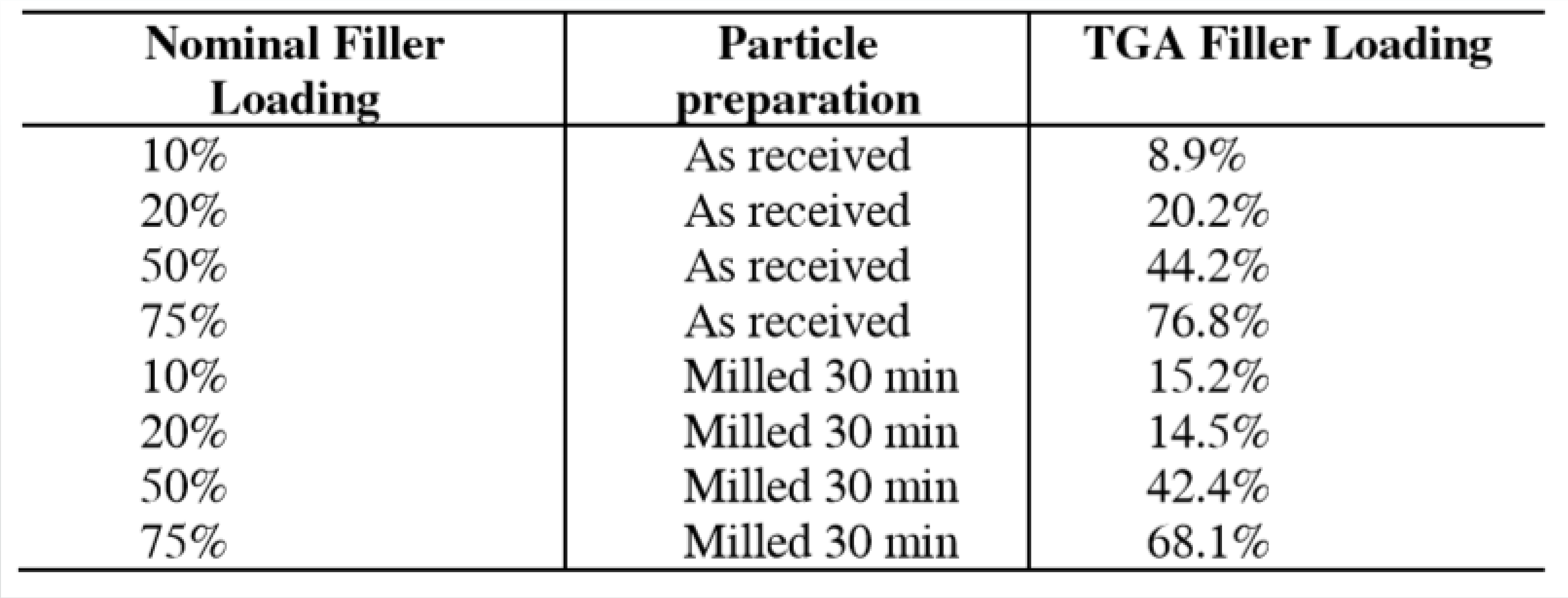
Surface treatment results in increase

Not treated

Surface treatment results in decrease

Fillgrade – Facts versus Fiction

- Experimental results for dielectric spectroscopy inconsistent
- TGA of composites showed that actual filler loading was differing from assumed filler loading



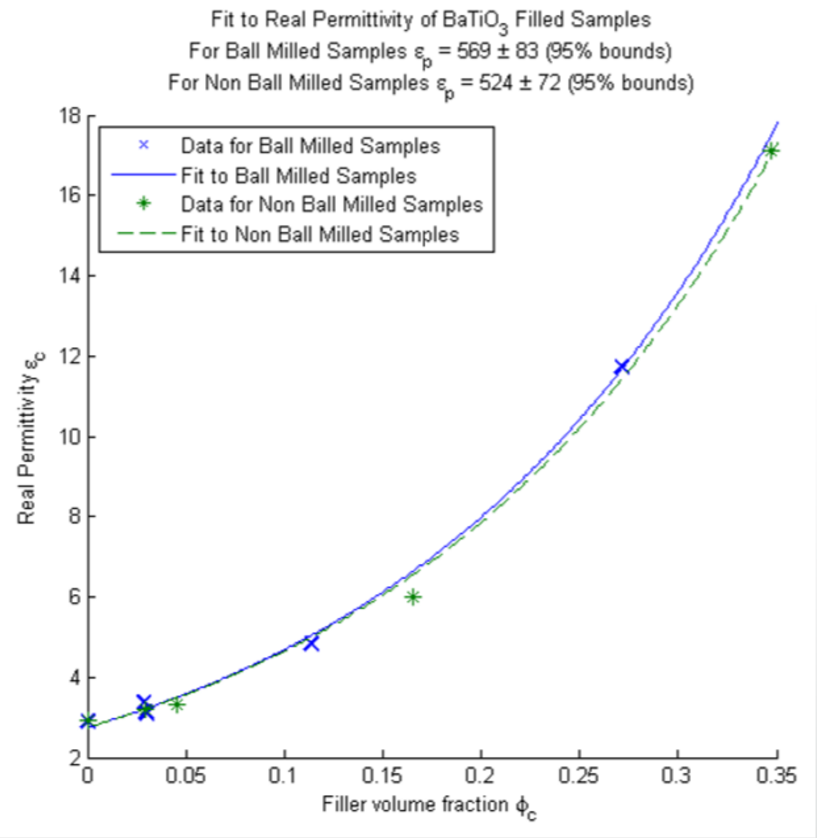
Nominal Filler Loading	Particle preparation	TGA Filler Loading
10%	As received	8.9%
20%	As received	20.2%
50%	As received	44.2%
75%	As received	76.8%
10%	Milled 30 min	15.2%
20%	Milled 30 min	14.5%
50%	Milled 30 min	42.4%
75%	Milled 30 min	68.1%

More details at poster session 8A, Paper 8A-11

Permittivity: the Bigger Picture

- Lichtenecker-Rother fits data well in PS
- TGA vital to perform analysis
- Independent of dispersion state

➢ Only volume matters



More details at poster session 8A, Paper 8A-11

Looking for Immobility – NMR

Arantes et al. used NMR spectroscopy to study nanocomposites based upon styrene-butadiene rubber (SBR) and titania. Although ^{13}C NMR results revealed significant shifts in peak positions, which have been taken to indicate interactions between nanoparticles and polymer chains, spin lattice relaxation experiments suggest that the ***molecular mobility in both systems is equivalent***.

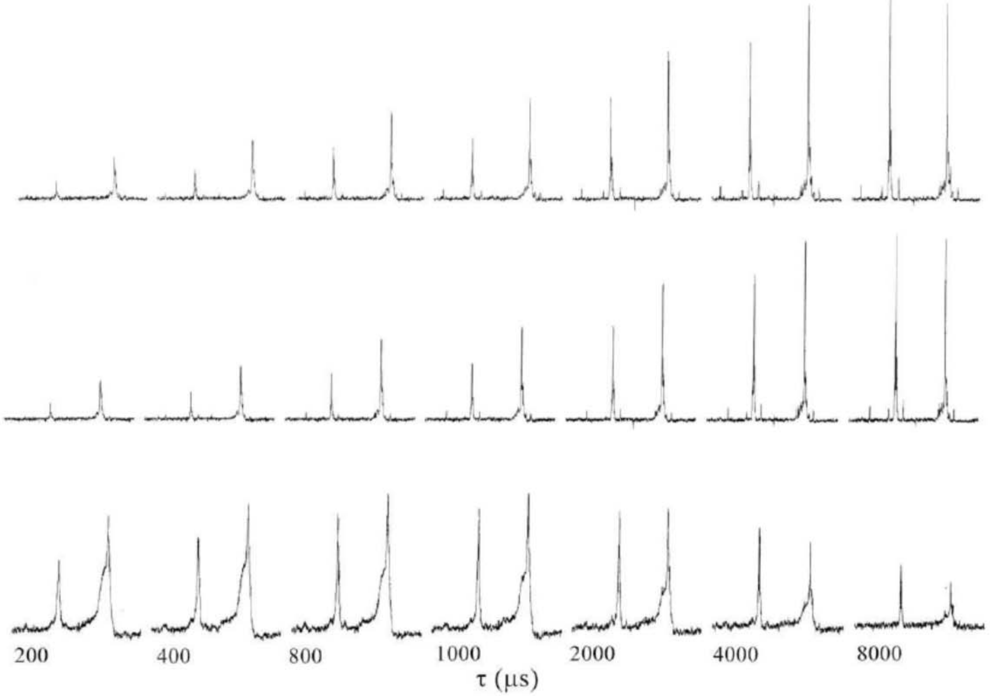


Fig. 3. ^{13}C NMR CP/MAS spectra with variable contact-time experiment (VCT): (a) SBR, (b) SBR/TiO$_2$ nanocomposite and (c) SBR/TiO$_2$ photodegraded nanocomposite.

Source: T.M. Arantes et all "NMR study of styrene-butadiene rubber (SBR) and TiO2 nanocomposites", Polymer Testing 28 (2009) 490–494

Looking for Immobility – ESR

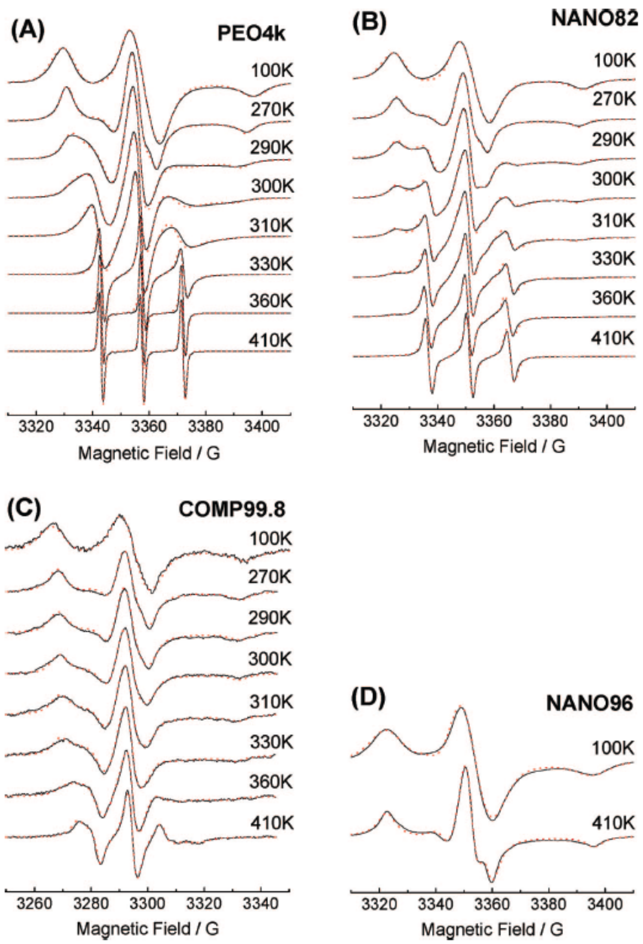
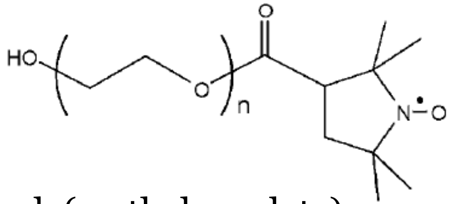


Figure 5. Temperature variation of ESR spectra (experimental spectra: full black lines; simulated spectra: red dotted lines) for PEO4k (A), NANO82 (B), COMP99.8 (C), and NANO96 (D).

Chart 1. Spin-Labeled PEO Chain



Nanocomposites of poly(methyl acrylate) (PMA) and synthetic fluoromica, in which the PMA had been modified to include a so-called spin label. That is, a stable free radical, commonly nitroxide, which is introduced into a material that does not have an intrinsic paramagnetic response.

This work showed that, **in exfoliated systems, the mobility of PMA chains is reduced** due to the interactions with the nanofiller.

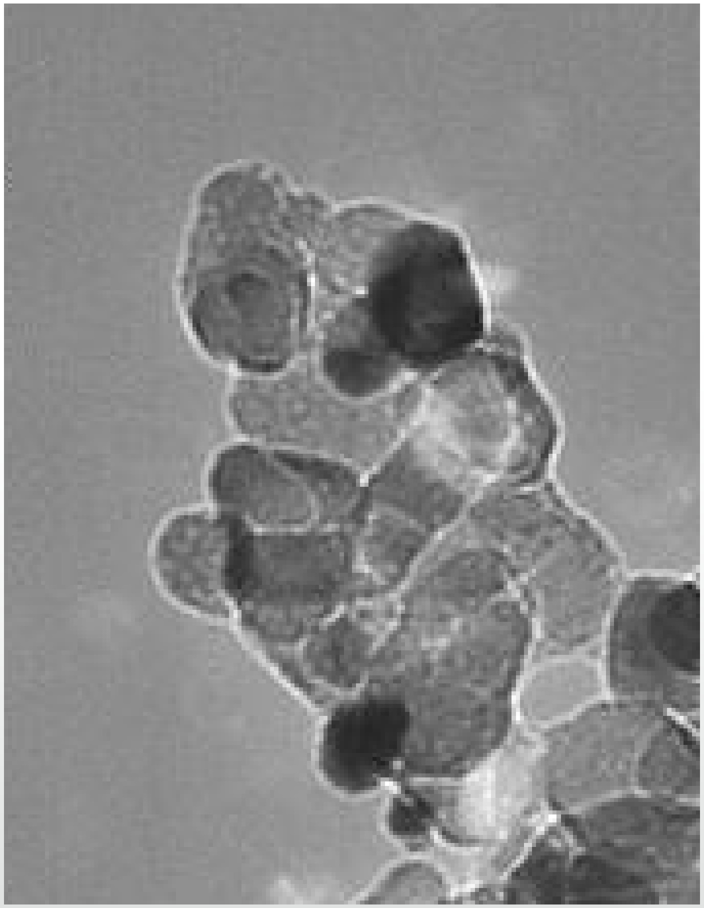
The thickness of the rigid interface region was estimated to be in the range 5-15 nm. In intercalated materials similar results were obtained, in that **a fraction of constrained chain segments were detected at the clay interface together with another with a higher mobility**.

Source: Yohei Miwa et al. "Detection of the Direct Effect of Clay on Polymer Dynamics: The Case of Spin-Labeled Poly(methyl acrylate)/Clay Nanocomposites Studied by ESR, XRD, and DSC", Macromolecules 2006, 39, 3304-3311

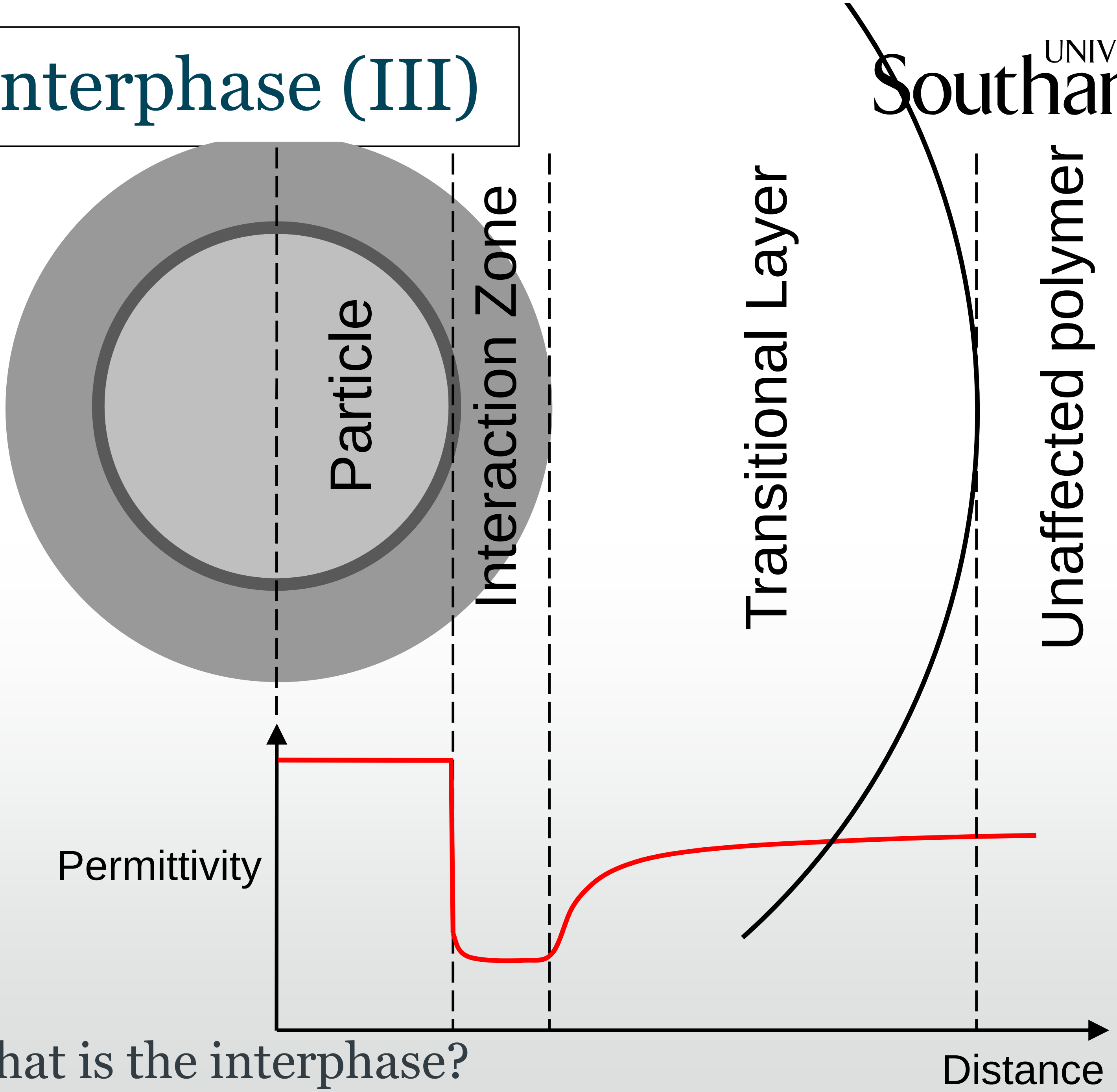
The Known Unknowns

Material Properties?

- What is the permittivity or dielectric BD strength of a nanoparticle?
- How does the surface *actually* look like?
- What is more important?
  - Surface
  - Bulk
  - Shape



The Interphase (III)



- What is the interphase?

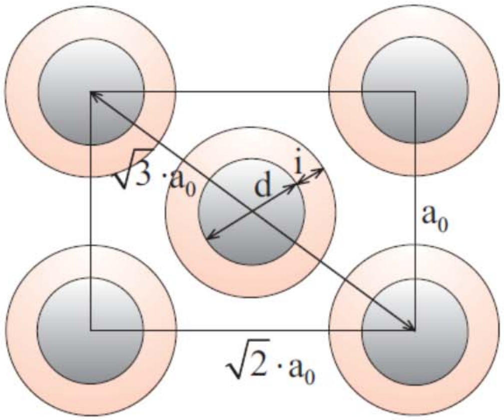


Fig. 3. Interphases do not overlap

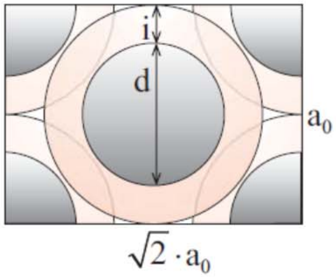


Fig. 4. View on the diagonal of the basic element; the interphases do overlap

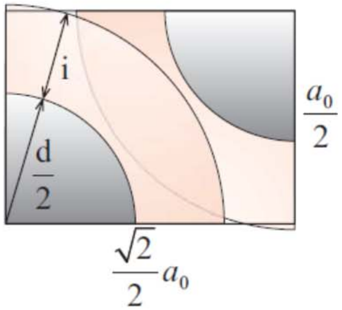
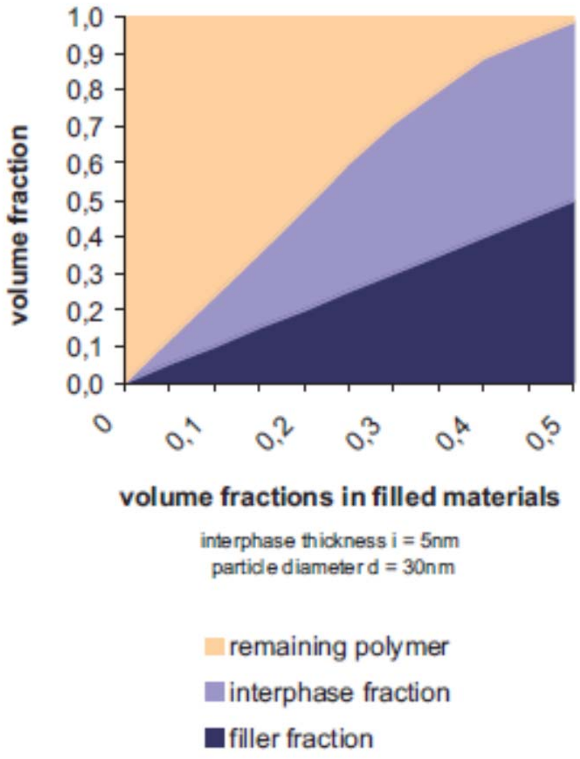


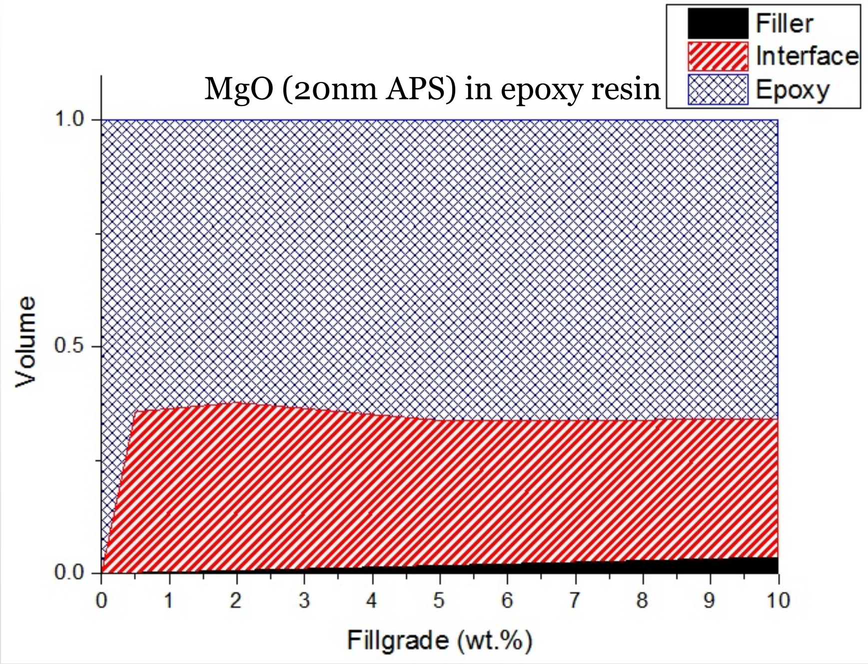
Fig. 5. The whole polymer consists of interphase only

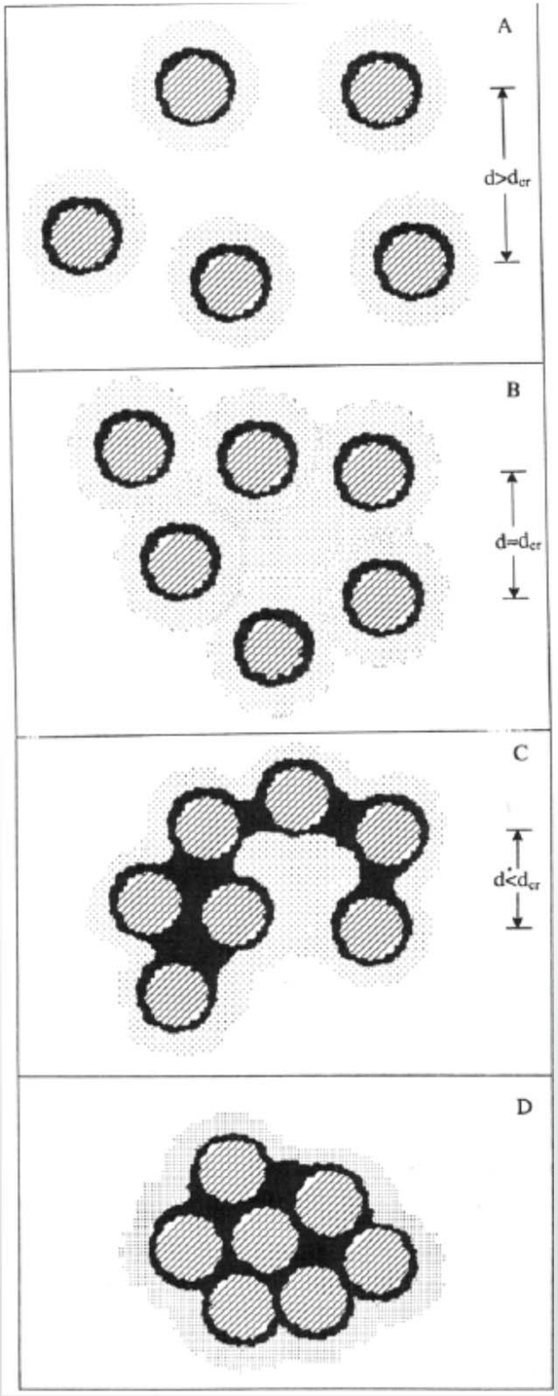


- What does an overlapping interphase mean?

Source: Rätzke et al. IEEK Trans. Vol. 126 No. 1 (2006)

- Experimental results for permittivity easier to model when variable interphase is taken into account





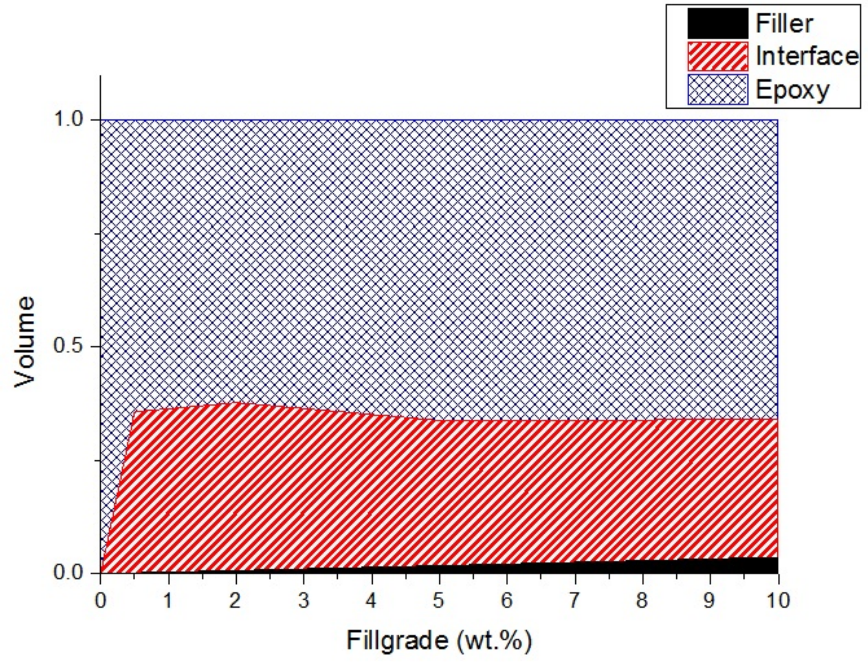
McBrierty et al. 1976

“Crowded Bus” Theory?

- Extent of interphase changing depending on fillgrade?

Different approach:

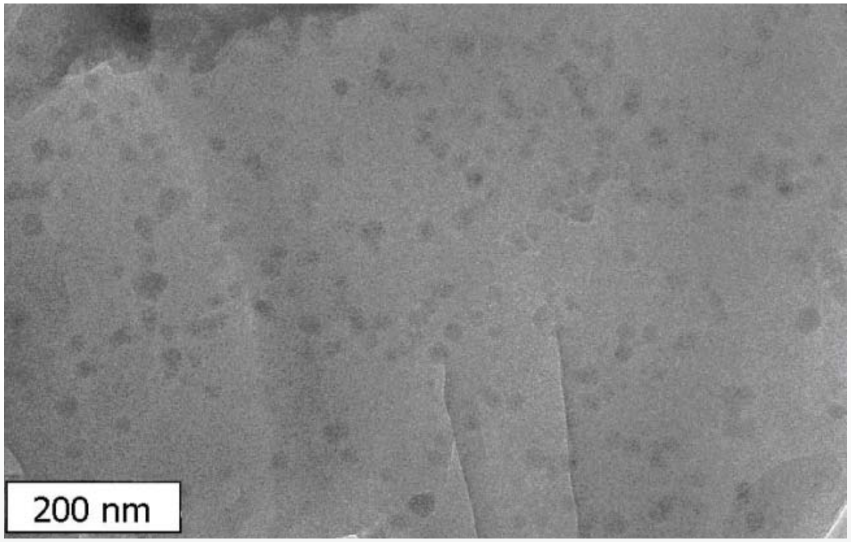
- Fillgrade does not seem to matter for the amount of polymer affected
- NP fillgrade just another processing variable like time and temperature?

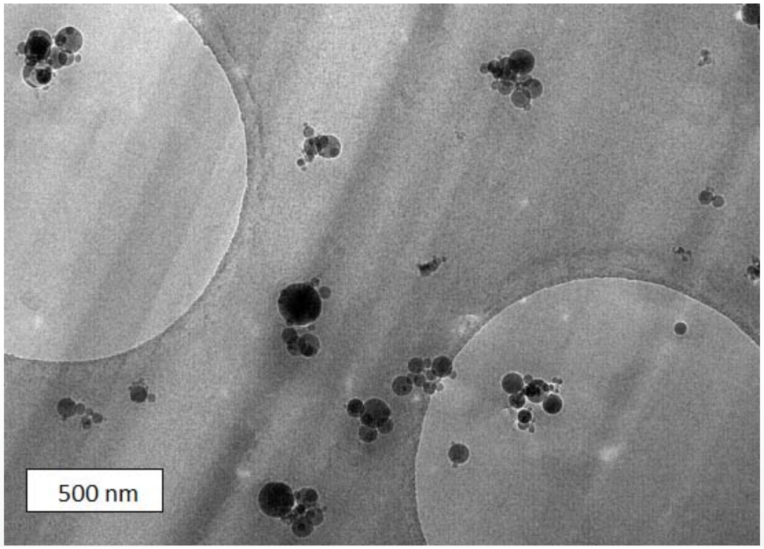


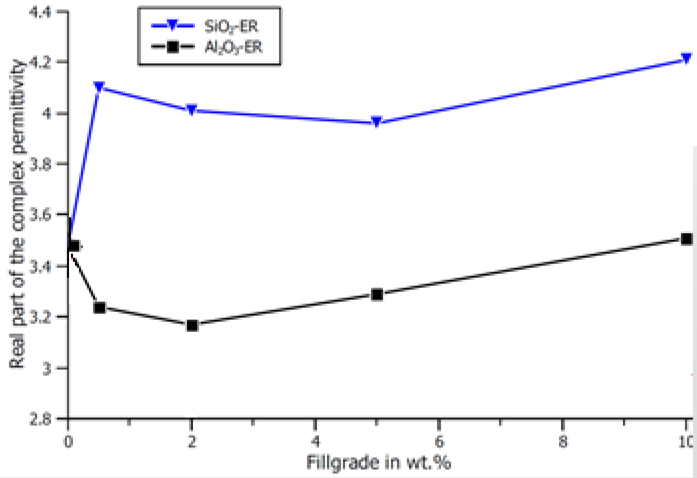
Impact of Ingredients or Processing?

- What has more impact on dielectric properties?
- What is the optimal way to disperse nanoparticles?
- Is the optimal way also practical?

Sol-gel process vs. Mechanical Mixing

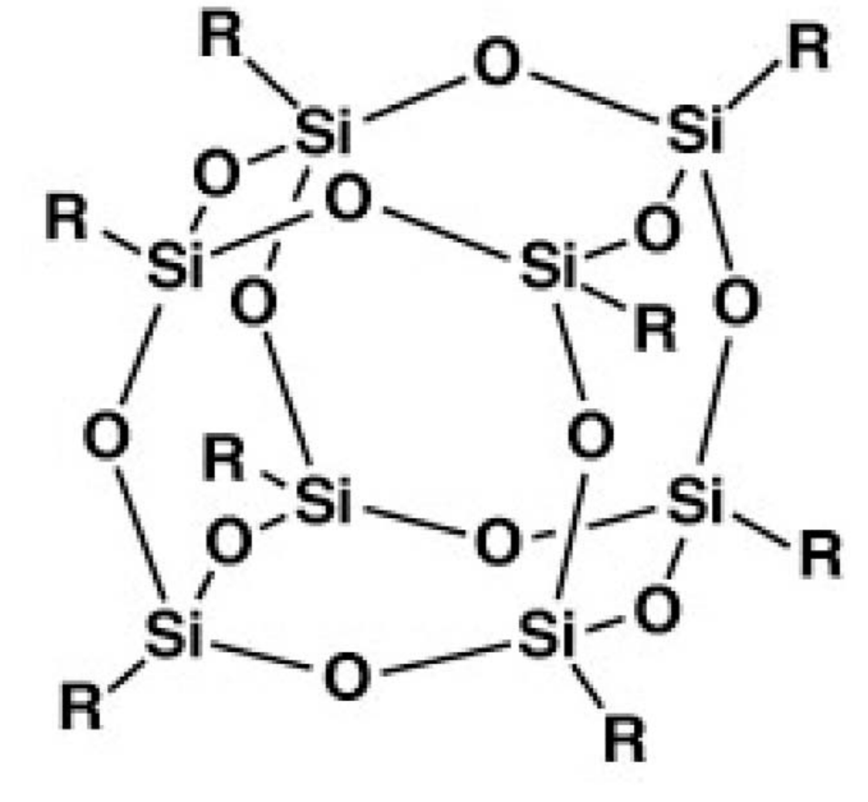






POSS

- Octamethyl polyhedral silsesquioxane (POSS or om-POSS)
- The smallest possible silica nanoparticle available (~1.5 nm)
- Improve BD strength and time to BD (Horwath et. al. CEIDP 2005, Takala et. al. 2008)



The Unknown Unknowns

(don't know...)

What Now?

Interphase Layers are not the (only) Answer

- Interphase theory not applicable for every polymer
- Very convenient tool
- A number of polymers show little signs of interphases or chain restriction to a significant extent
- Claims about restriction of chain mobility need solid evidence for the polymer investigated
- Staring at SEM is not enough

What Now?

- Nanodielectrics are not in their ‘infancy’ anymore
- We know quite a lot (morphology etc.) but less than we should (esp. about interfaces themselves)
- Still a lot of seemingly contradictory results and more systematic research is needed
- Surface chemistry is important but we also need better understanding how to characterize these surfaces
- Change to morphology may not be limited to interfaces

The End