

**NANO-CLAY FILLERS FOR
POLYMER COMPOSITES.**

**AN OVERVIEW OF TYPES AND
APPLICATIONS**

by

PROFESSOR ROGER ROTHON

WHAT IS A NANO- FILLER ?

A VERY SMALL PARTICLE FILLER

LOOSE NOMENCLATURE

GENERALLY < 20 nm

NANO-FILLERS NOT NEW

e.g.

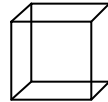
CARBON BLACKS

FUMED AND PRECIPITATED SILICAS

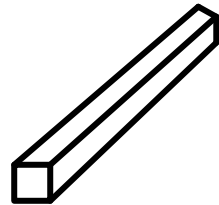
**PRECIPITATED CALCIUM
CARBONATES**

NOVELTY IS IN FIBRES AND PLATES

FIGURE 39. VARIOUS NANO-FILLER SHAPES



**LAYER
MINERALS**



**CARBON
NANOTUBES**

CLAYS PROVIDE ROUTE TO NANO-PLATES

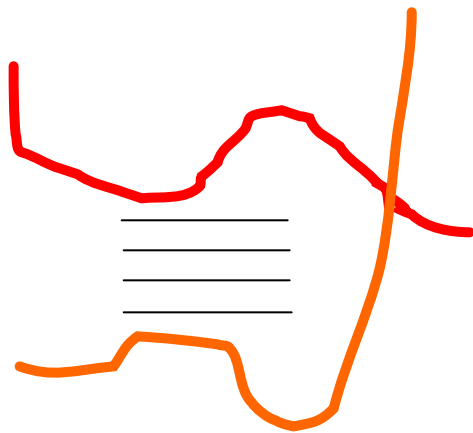


CLAY LAYER STRUCTURE

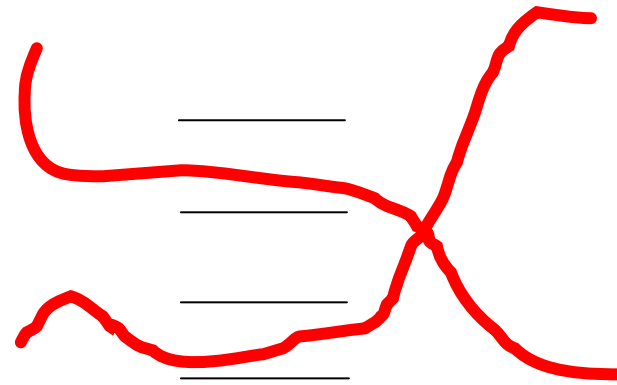
CAN GIVE THIN PLATES (ca 1 nm)



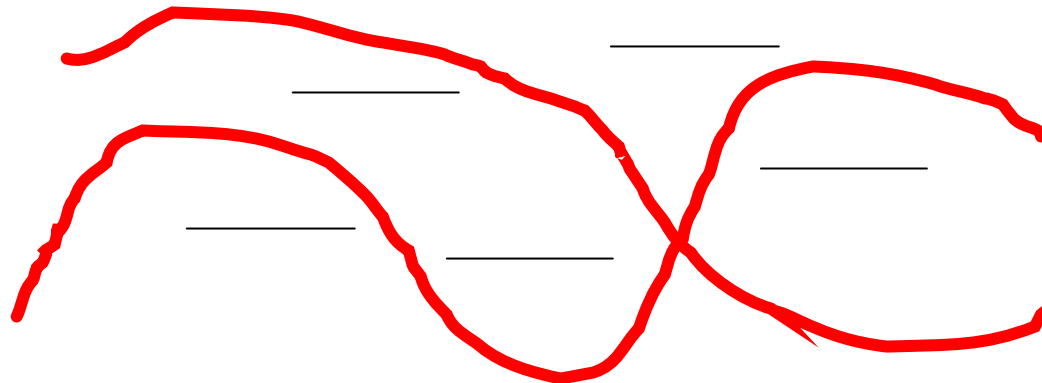
NANO v NORMAL CLAY DISPERSION



NORMAL

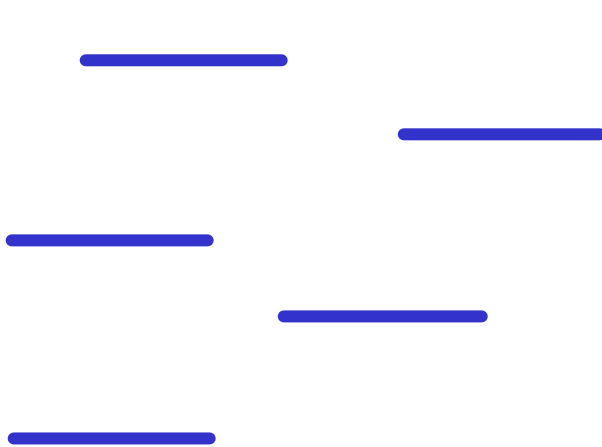


INTERCALATED

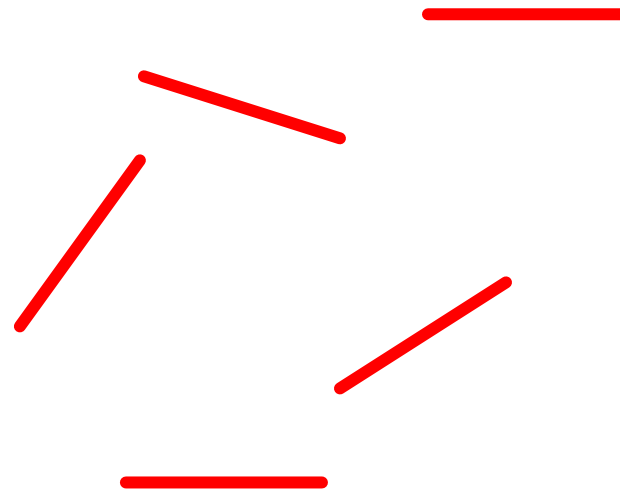


EXFOLIATED

TYPES OF EXFOLIATION



ORIENTED



RANDOM

BENEFITS

LARGE EFFECTS AT LOW LOADINGS

STIFFNESS

HEAT DISTORTION

GAS BARRIER

FIRE RETARDANCY

**e.g. STIFFNESS AND HEAT
DISTORTION IN PA6**

CLAY % w/w	FLEX MODULUS MPa	HDT °C
0	2,840	56
2	4,325	125
4	4,578	131
6	5,388	136

NANO-CLAY HISTORY

- **1950** **National Lead** **Elastomers**
- **1975-85** **ICI** **Vermiculite**
- **mid-1980's** **Toyota** **Polyamides**
- **mid 1990's to date** **Renaissance**

MAIN PRODUCERS TODAY

SUD-CHEMIE (Germany)

NANOCOR (USA)

SOUTHERN CLAYS (USA)

VARIOUS JAPANESE (e.g. COOP)

ORIGIN OF THE EFFECTS

- PLATY SHAPE

or

- SURFACE AREA LEADING TO
POLYMER CHANGES

SHAPE ARGUMENT

EFFECTS PREDICTABLE

**USING PLATE MODULUS,
ORIENTATION AND ASPECT RATIO**

SURFACE ARGUMENT

**POLYMERS ARE MODIFIED BY
SURFACES**

**ONLY EFFECT OF SHAPE IS TO
MAXIMISE SURFACE AND AMOUNT OF
MODIFIED POLYMER**

FILLER SURFACE EFFECTS

- **CHANGE IN CRYSTAL FORM**

(eg alpha to beta in PVDF
and to gamma in PA6)

- **CHANGE IN AMORPHOUS FORM**

(e.g. by immobilisation at surface)

**ALTERED POLYMER
5 % FILLER and 10 nm LAYER**

SSA m²/g	ALTERED POLYMER %
30	1.5
300	16
1000	53

RECENT DEVELOPMENTS

**MODULUS OF SINGLE PLATES MUCH
LESS THAN BULK (LIGHT
SCATTERING). IF CORRECT
PREDICTIVE EQUATIONS DON'T
WORK!**

(Gianellis, Cornell University)

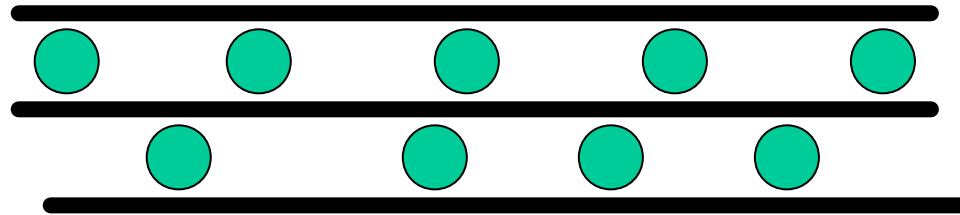
ALSO SAME EFFECTS WITH REGULAR SHAPES

5 % FUMED SILICA IN PMMA

(cf to polymer = 1.0)

SSA m ² /g	MODULUS	TENSILE
50	1.13	1.5
90	1.45	2.3
300	3.02	3.2

RELEVANT CLAY TECHNOLOGY



**A LAYERED ALUMINO-SILICATE
STRUCTURE WHICH IN SOME TYPES
ALLOWS READY DELAMINATION**

DELAMINATION TECHNOLOGY

ION EXCHANGE

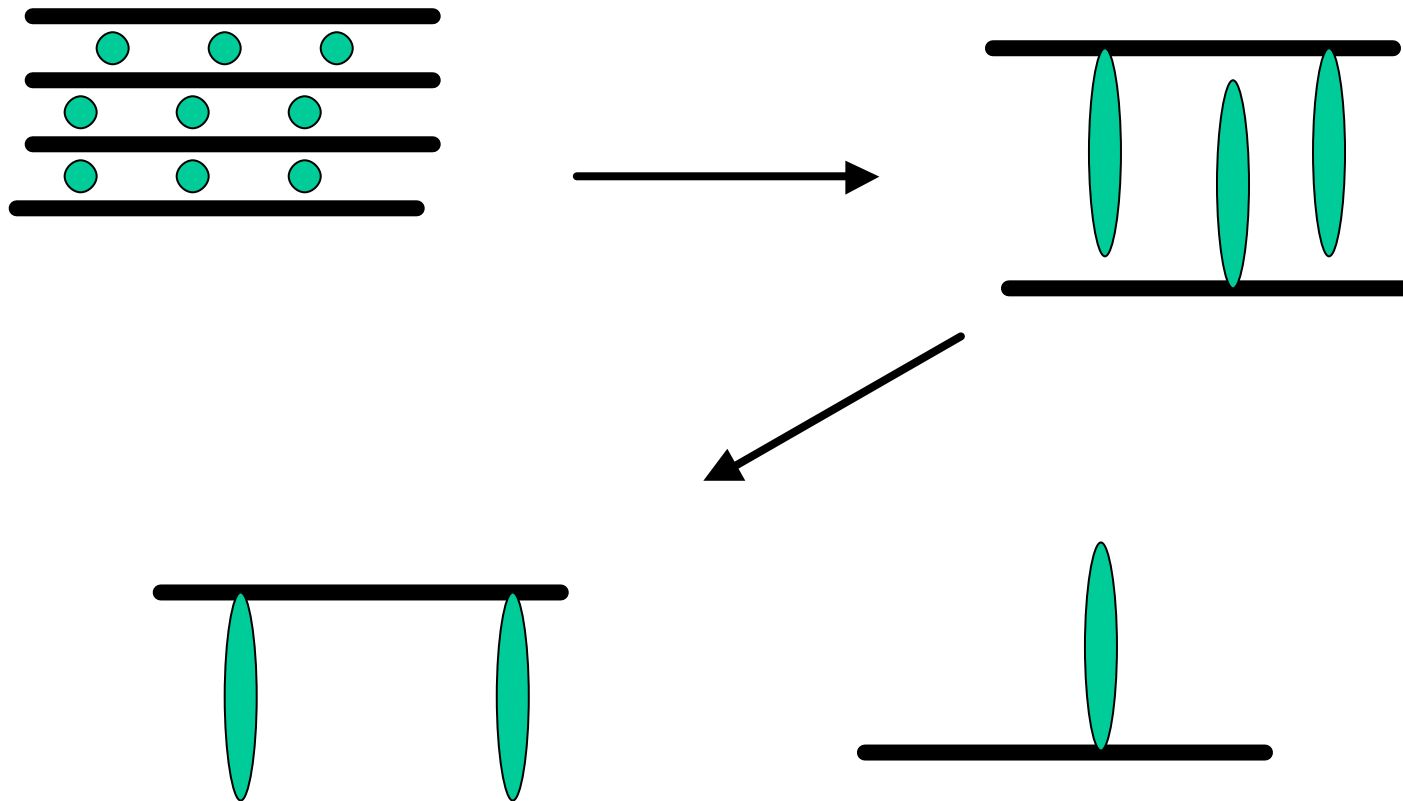
INORGANIC CATIONS

By

LONG CHAIN ORGANICS

(e.g. quaternary ammonium derivatives of
fatty acids)

LAYER SILICATES DELAMINATION



LAYER SILICATES: IMPORTANT VARIABLES

SILICATE LAYER THICKNESS

LAYER MODULUS

LAYER DIAMETER

CATION EXCHANGE CAPACITY

IMPURITIES

NATURAL LAYER SILICATES

	CEC	length
	meq/100g	nm
• MONTMORILLONITE	110	100-150
• HECTORITE	120	200-300
• SAPONITE	87	50-60
• VERMICULITE	?	?

SYNTHETIC LAYER SILICATES

**CLAYS AND MICAS ESPECIALLY
FLUORO-MICAS**

ALLOW

**CONTROL OF ASPECT RATIO, CATION
EXCHANGE CAPACITY , COLOUR AND
PURITY**

**ACHIEVING DISPERSION
AT PLATE SIZE**

**KEY TO GOOD PROPERTIES
BUT IS
NOT EASY IN MANY POLYMERS**

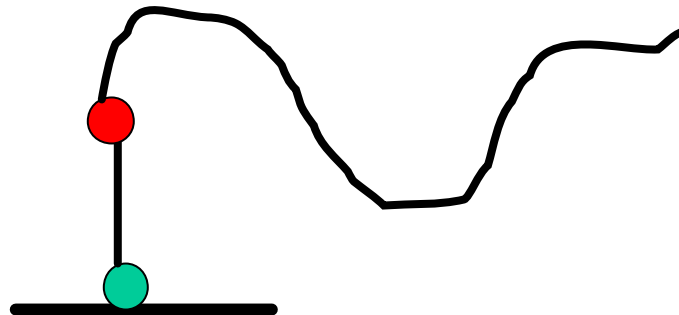
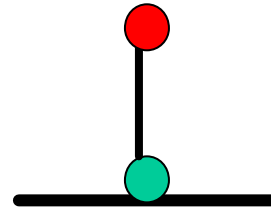
POLYMERISATION FILLING

MOST EFFECTIVE WAY

NYLON 6 CLASSIC EXAMPLE

NYLON 6

AMINO-ACID EXCHANGE

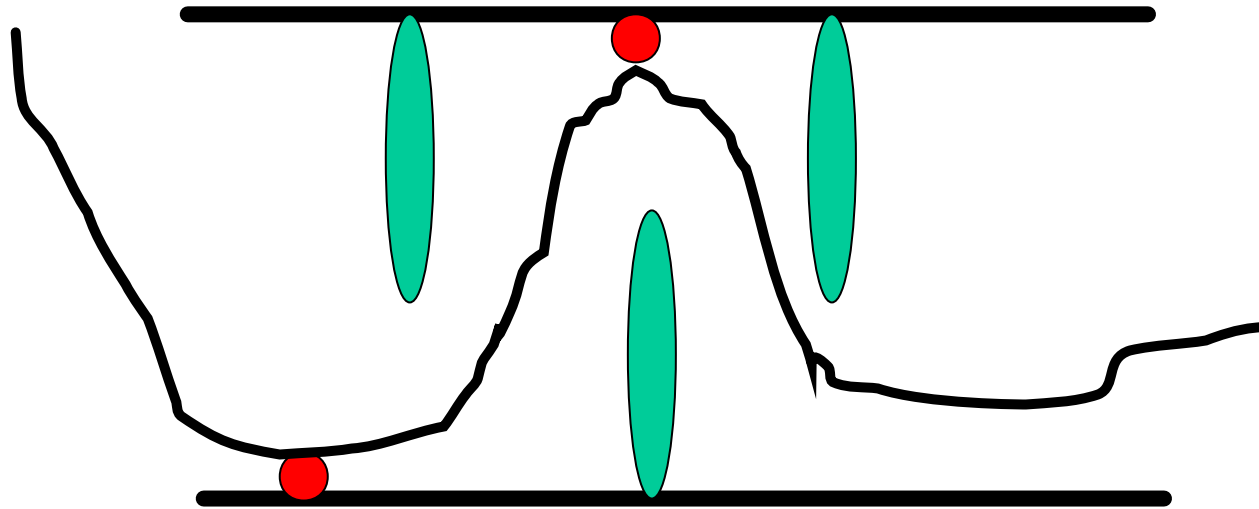


POLYMERISE
WITH
CAPROLACTAM

POLYMER MELT DISPERSION

**MUCH MORE DIFFICULT
COMPATIBILISERS NEEDED
(e.g. MALEATED PP)**

POLYMER INTERCALATION DISPERSION



WHERE ARE WE TODAY?

STILL NICHE APPLICATIONS

MAINLY IN THERMOPLASTICS
SOME ALSO IN
THERMOSETS AND ELASTOMERS

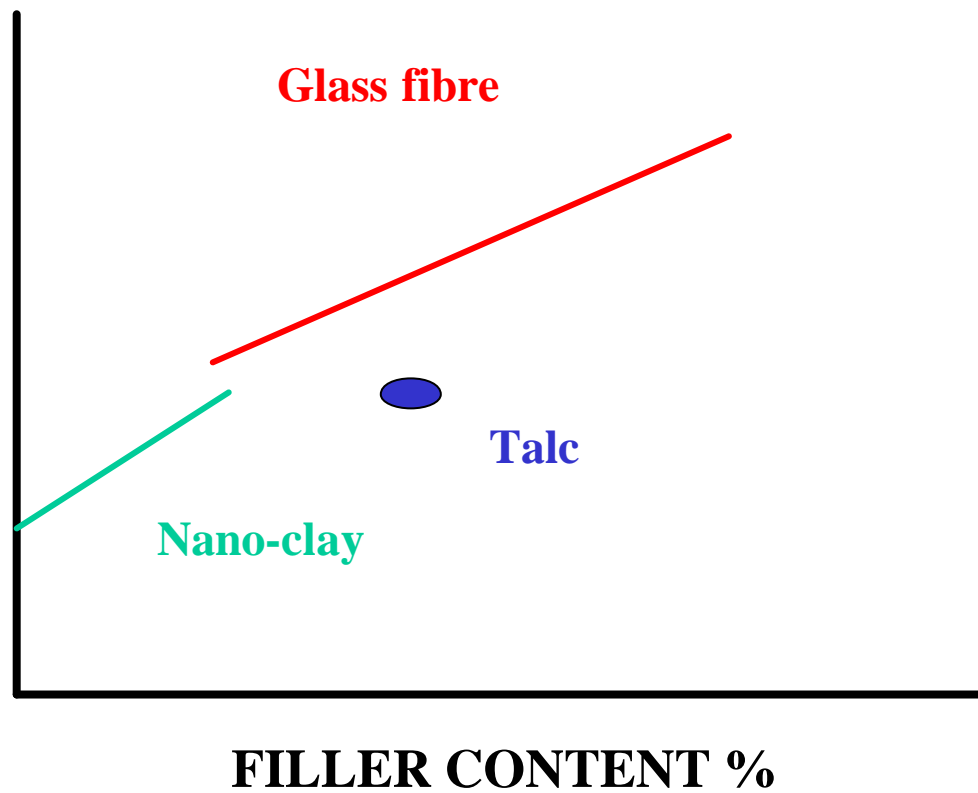
MAIN EXPLOITABLE EFFECTS

- **MODULUS AND HDT**
 - **GAS BARRIER**
- **FIRE RETARDANCY**

LIMITATIONS

- **COST and COST EFFECTIVENESS**
- **LIMITED LOADINGS AND HENCE LIMITED ABSOLUTE EFFECTS**
- **PURITY (COLOUR, HEAT STABILITY)**

LIMITED MODULUS EFFECT



MODULUS and HDT

- BIG EFFECTS AT LOW LOADINGS

but

- QUESTION OF COST EFFECTIVENESS

NANOCOR CASE STUDIES

PP TRACTOR SEAT

23 % WEIGHT DECREASE

30 FLEX MOD. INCREASE

EPOXY TANK COATINGS

15 –20 C INCREASE IN T_g

GAS BARRIER

PERCOLATION MODEL



PROVEN GAS BARRIER EFFECTS

2% nano-clay added to nylon film

=

40 % reduction in permeability

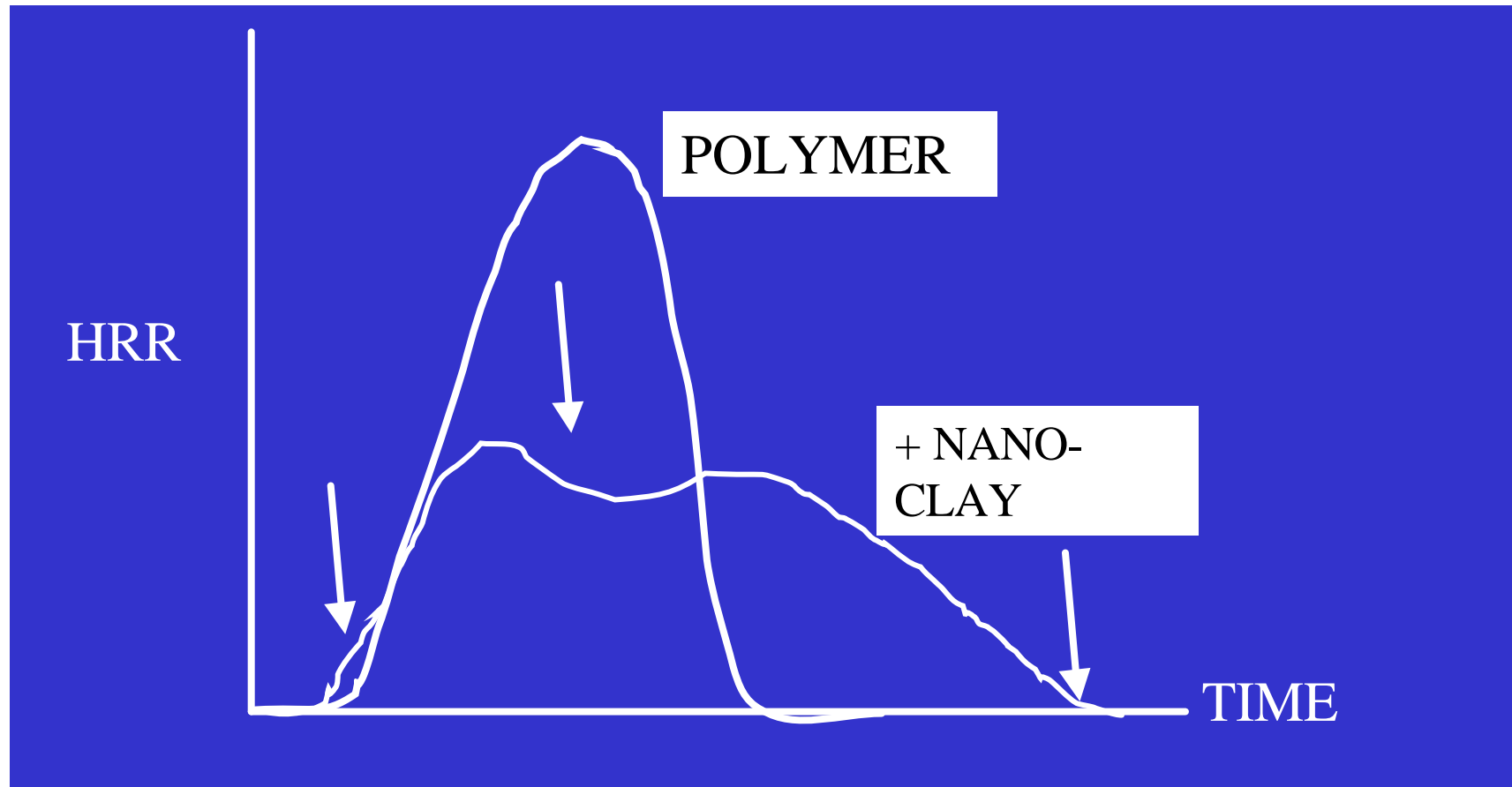
COMMERCIAL GAS BARRRIER PRODUCTS

- **IMPERM™** Nanocor/ Mitsubishi Nylon
- **AEGIS™** Honeywell Nylon
- **DURETHAN™** Bayer Nylon

FIRE RETARDANCY

- **PROVEN EFFECTS**
- **BEST SEEN IN CONE CALORIMETER**
 - **POOR IN SOME OTHER TESTS**
 - **BEST USED WITH OTHER FR**

CONE CALORIMETER



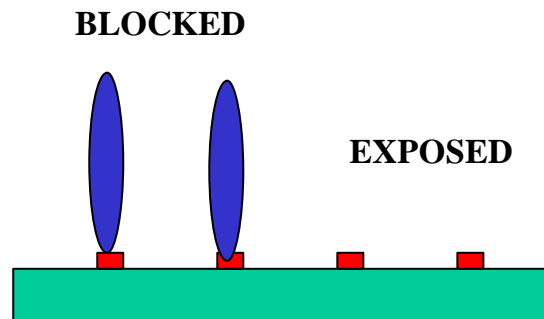
FR MECHANISMS

- **GAS BARRIER EFFECTS**

(slow down ingress of oxygen and
release of fuel)

- **CATALYSIS OF CHAR REACTIONS
BY EXPOSED ACID SITES**

ACID CLAY SITES



**CLAY PARTICLE : ONLY SITES ON
UPPER SURFACE ILLUSTRATED**

NANOCOR CASE STUDY

PP ELECTRICAL UNIT

40 % REDUCTION IN HALOGEN FR

INCREASED MODULUS

20% DECREASE IN SG

MAINTAINED V_0

ALLOWED DOWNGAUGING ALSO

CONCLUSIONS

- **THEORY STILL DEVELOPING**
- **MARKETS STILL DEVELOPING**
- **NOT A PANACEA BUT SOME USEFUL APPLICATIONS**
- **MOST PROMISING APPLICATIONS GAS and FLUID BARRIERS and FIRE RETARDANCY**

THANK YOU