Developments in Conducting Polymer Composites and Coatings for Bipolar Plates

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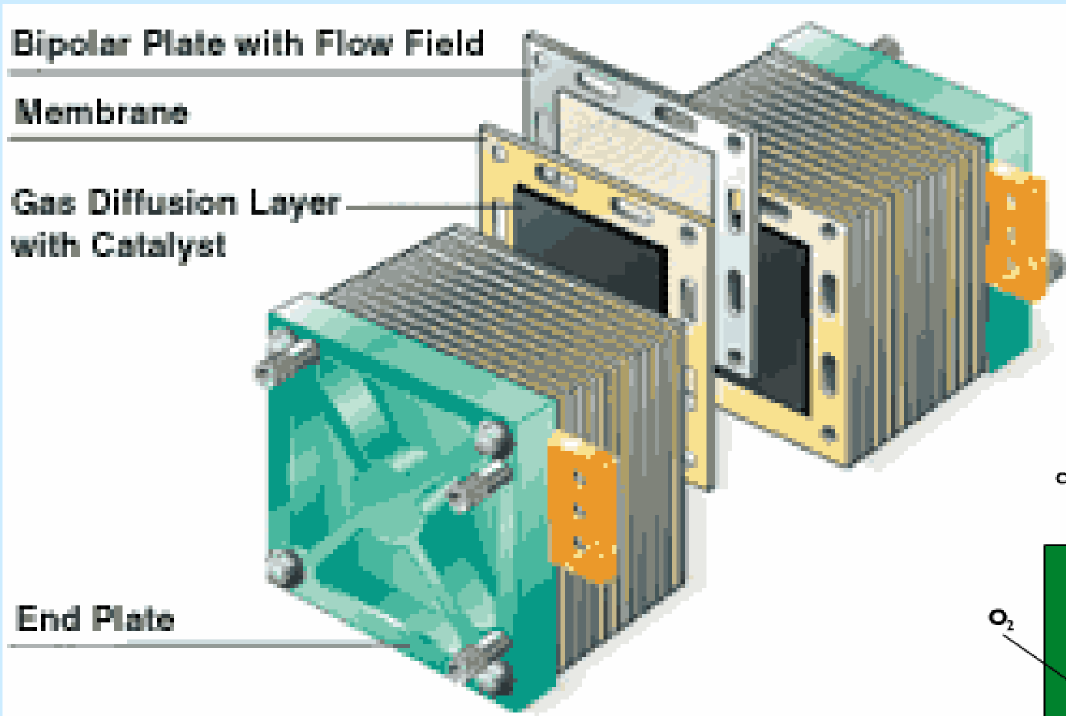
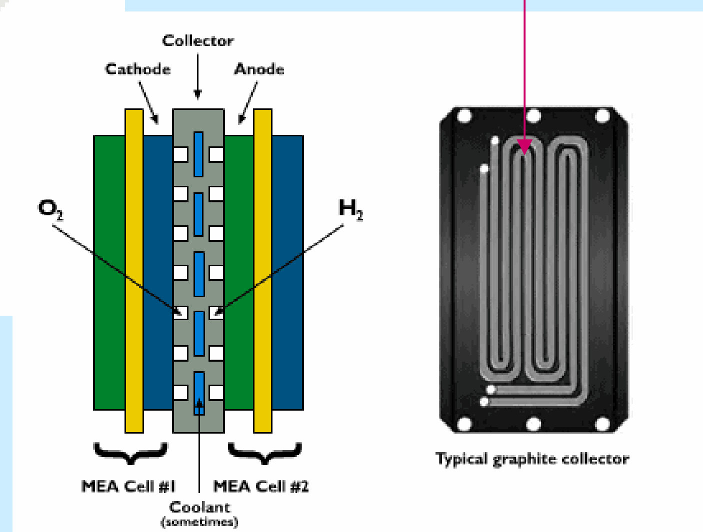
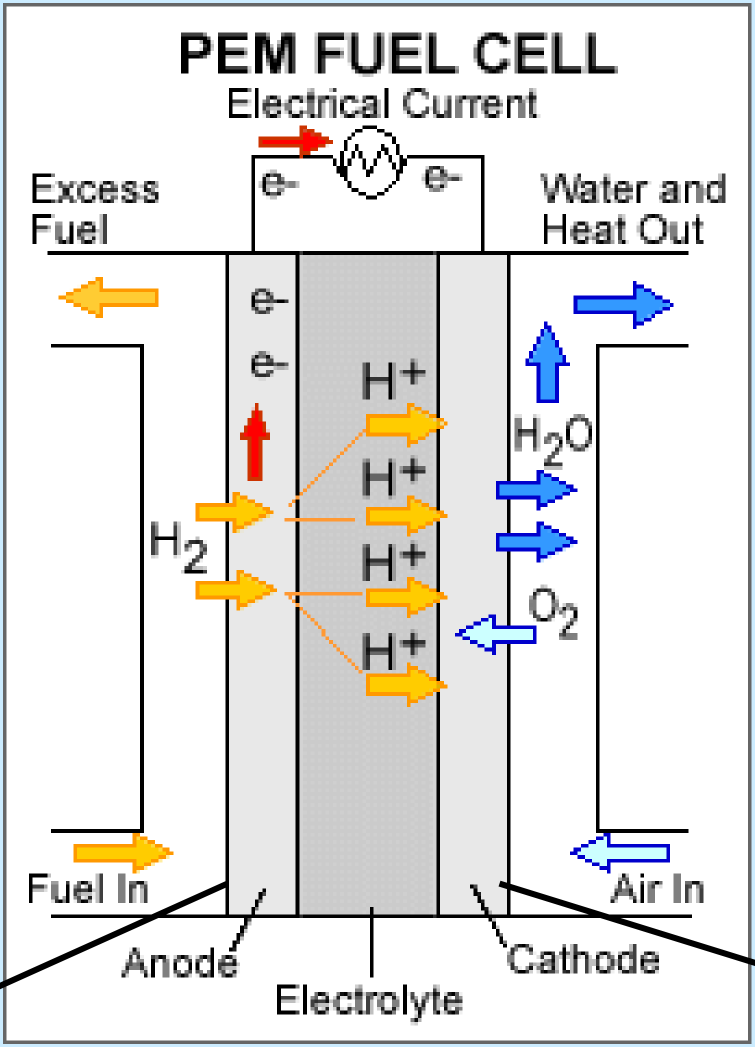
FUEL CELL CONSTRUCTION AND BIPOLAR PLATES



Flow Pattern



FLOW OF GASES / VAPOURS IN FUEL CELLS



Graphite Plate

Graphite Plate

IMPORTANT FUNCTIONS OF BIPOLAR PLATES IN FUEL CELLS

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1. MECHANICAL SUPPORT FOR THE MEMBRANE ASSEMBLY
2. PROVIDE FLOW CHANNELS FOR THE FUEL : HYDROGEN OR METHANOL AS WELL AS COOLANT / WATER
3. SEPARATE INDIVIDUAL CELLS
4. PROVIDE BACK TO BACK ELECTRICAL CONNECTION TO CELLS / STACK AS WELL AS EXTERNAL LEADS/ BUS BARS
5. TRANSFER HEAT AWAY FROM THE CELL

IMPORTANT PROPERTIES OF BIPOLAR PLATES WHICH CONTROL THE PERFORMANCE OF FC :

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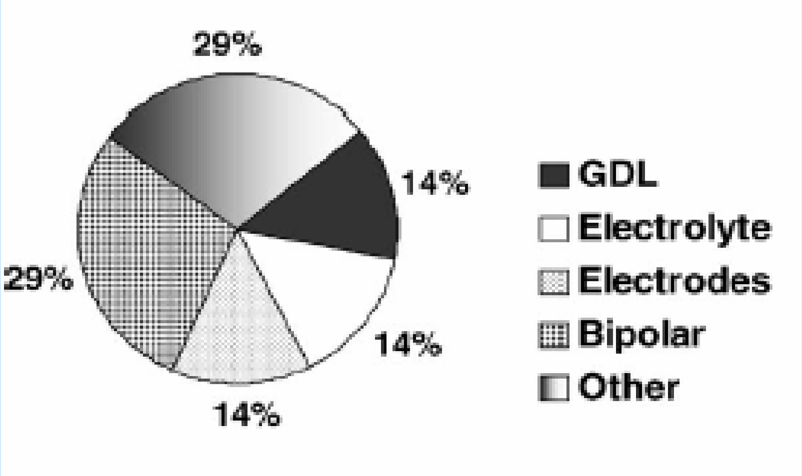
1. HIGH ELECTRICAL CONDUCTIVITY
2. CONTACT RESISTANCE SHOULD BE LOW
3. ROBUST MECHANICAL PROPERTIES WITH SURFACE HARDNESS
4. HIGH THERMAL CONDUCTIVITY
5. FLOW PATTERN UNIFORM AND SMOOTH
6. MACHINABLE / MOLDABLE
7. LOW PERMEABILITY TO GASES
8. LOW WATER ABSORPTION / CORROSION

IMPORTANCE OF BIPOLAR PLATES IN COST AND EFFICIENCY OF FC :

1. BIPOLAR PLATES COMPRISE THE MAXIMUM PORTION OF THE FC : WEIGHT AND VOLUME IS ALMOST 70% OF TOTAL
2. ANY NEW DESIGN OF THE FC HAS TO START FIRST IN THE BIPLOAR PLATES
3. MORE THAN 30% OF THE COST OF THE FC IS IN BIPLOAR PLATES

US GOVT.REPORT 2004 :



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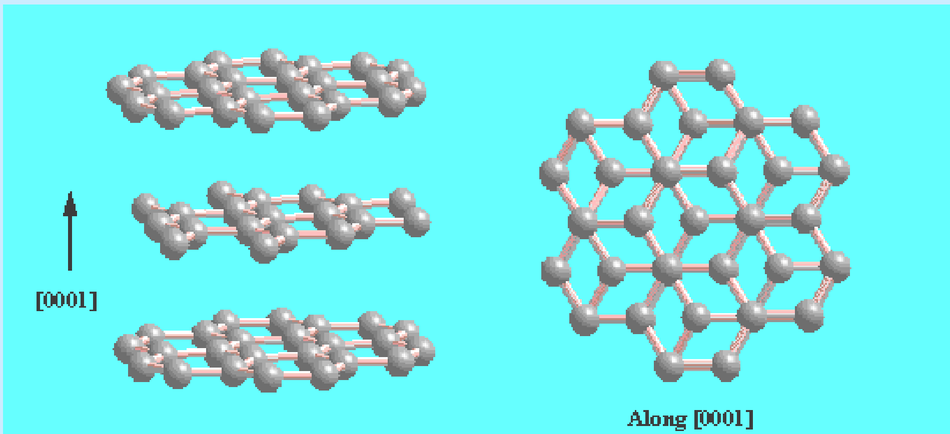
MATERIALS OF BIPOLAR PLATES :

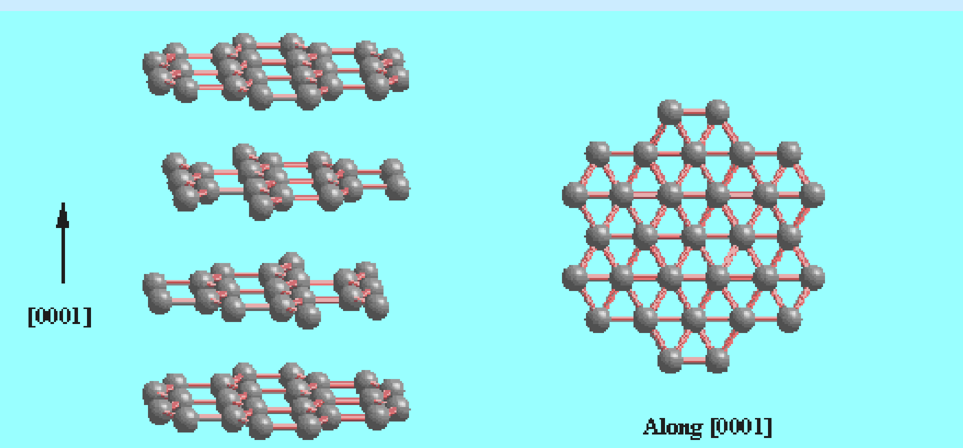
1. PRECIOUS METALS WERE USED IN VERY EARLY DAYS
2. GRAPHITE BECAME VERY POPULAR FOR THIS APPLICATION IN LATER VERSIONS
3. CONDUCTING POLYMER COMPOSITES ARE THE LATEST MATERIALS USED IN THESE PLATES
4. CONDUCTING POLYMER CORROSION RESISTANT COATING FORMULATIONS : FUTURE FUEL CELLS

MATERIALS OF BIPOLAR PLATES : GRAPHITE IS MOST COMMON

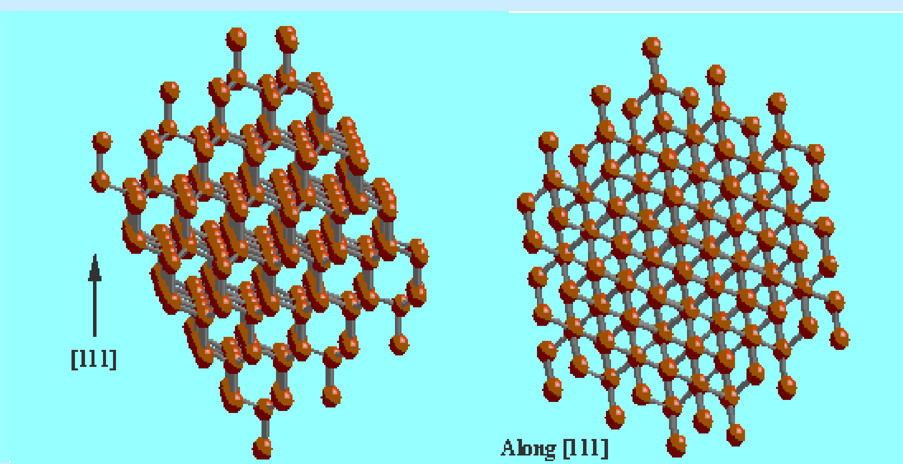
Structure of Graphite :



Hexagonal : Most common



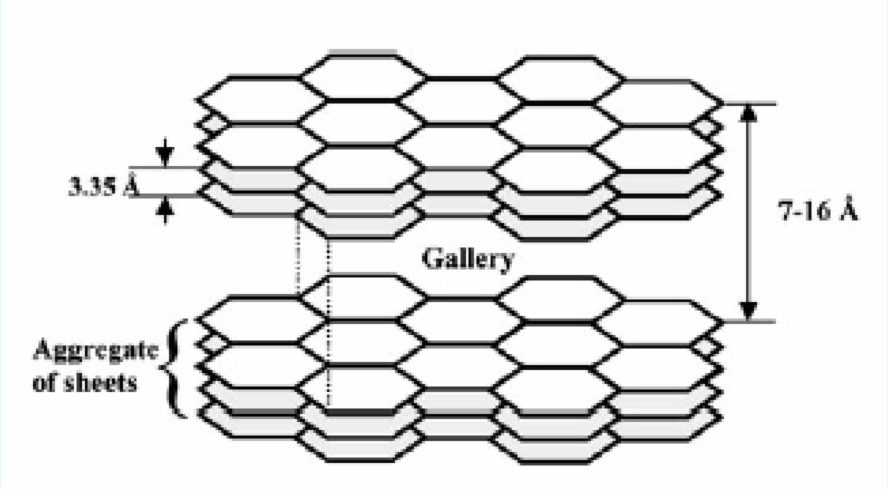
Rhombohedral

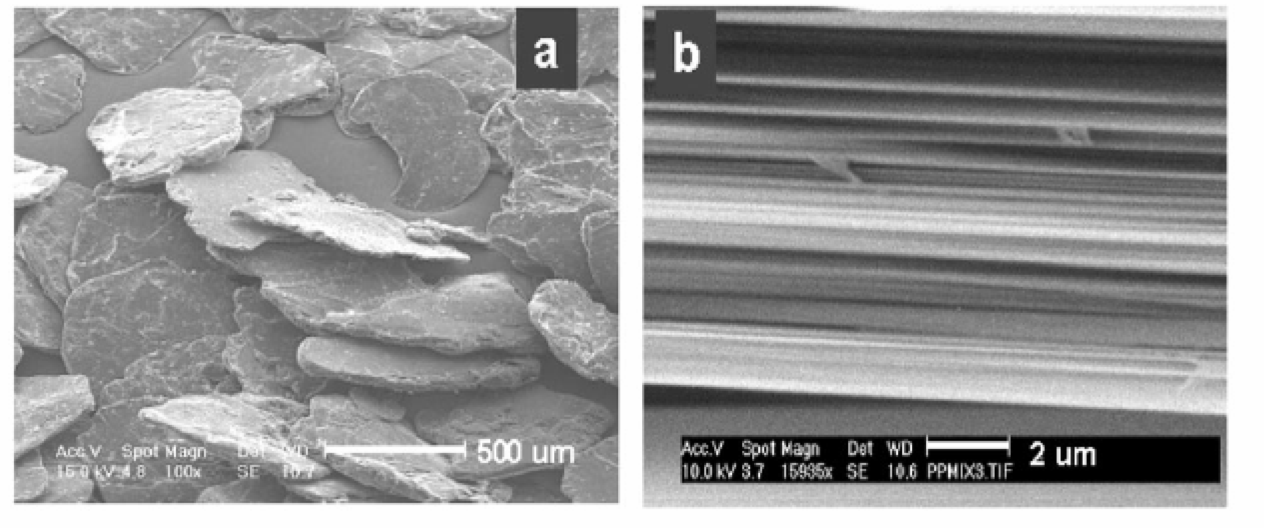


Diamond Cubic

BIPOLAR PLATES MATERIAL : GRAPHITE IS MOST COMMONLY USED

Structure of Natural Graphite :





BIPOLAR PLATES MATERIAL :
GRAPHITE IS MOST COMMONLY USED

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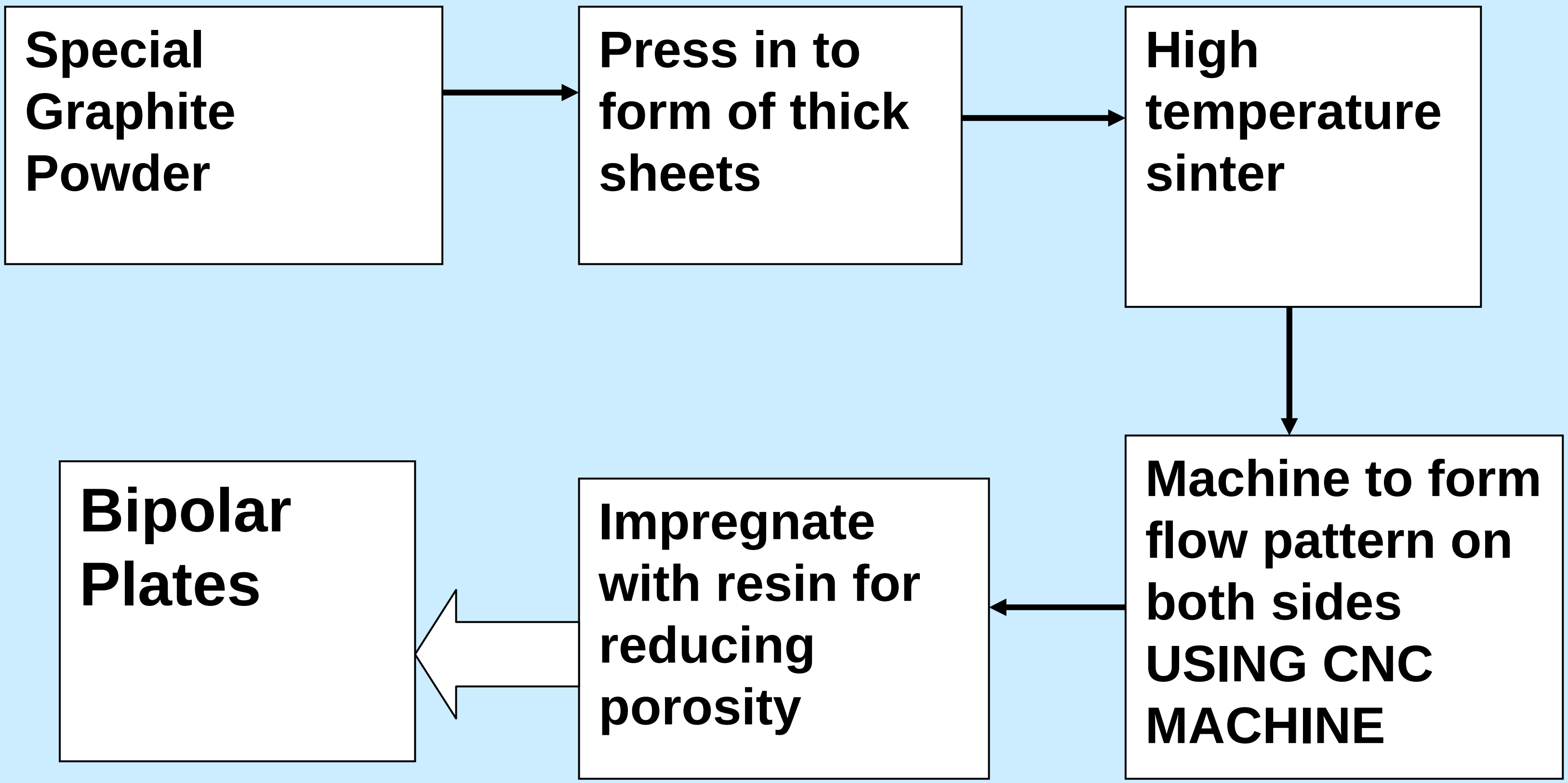
Properties of Graphite : (range of different grades)

Property	Unit	Value
Density	g/cc	1.3 – 1.95
Porosity	%	0.7 - 53
Modulus of Elasticity	GPa	8 - 15
Compressive strength	MPa	20 - 200
Flexural strength	MPa	7 - 100
Thermal conductivity	W/m K	25 - 470
Specific Heat	J/kg K	710 - 830
Thermal exp. Co-efficient	m/m K	2.2 - 6.0 x 10^{-4}
Electrical resistivity	ohm-m	5 to 30 x 10^{-6}

CONVENTIONAL METHOD FOR FARBICATING BIPOLAR PLATES



ROLE OF FLOW FIELD / CHANNELS ON BIPOLAR PLATES:

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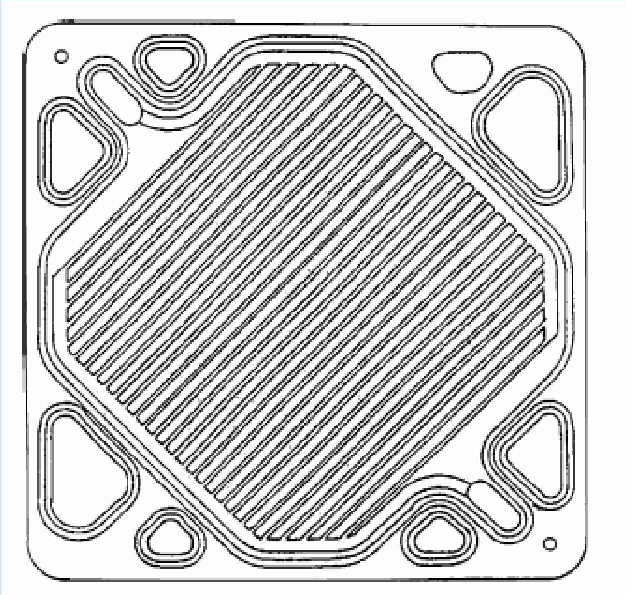
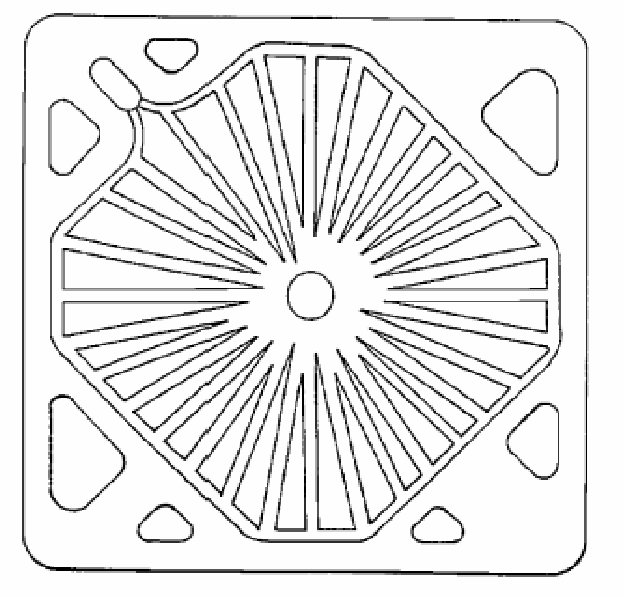
1. ALLOW INPUT OF FUEL AND BRING IT IN CONTACT WITH CATALYST ACTIVATED ELECTRODE
2. ALLOW THE COUNTER PART GAS (OXYGEN) AND BRING IT IN CLOSE PROXIMITY OF MEA
3. DRAIN OFF WATER FORMED
4. CONDUCT AWAY HEAT THROUGH COOLANT FLOW

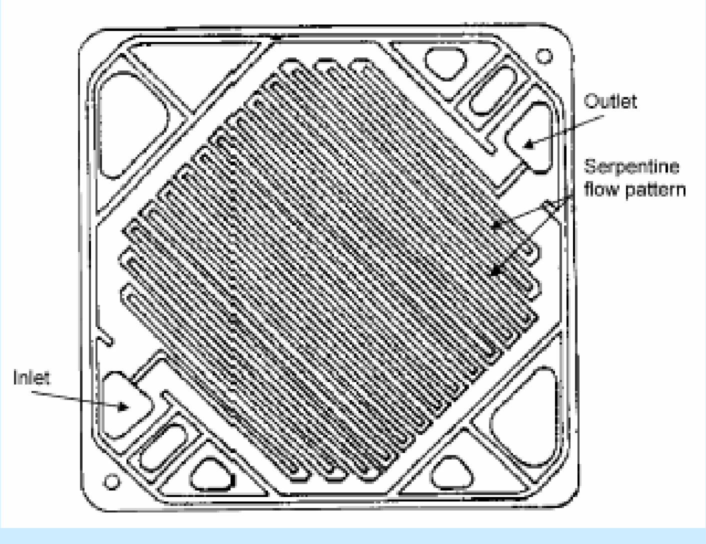
FLOW FIELD DESIGNS:



Straight

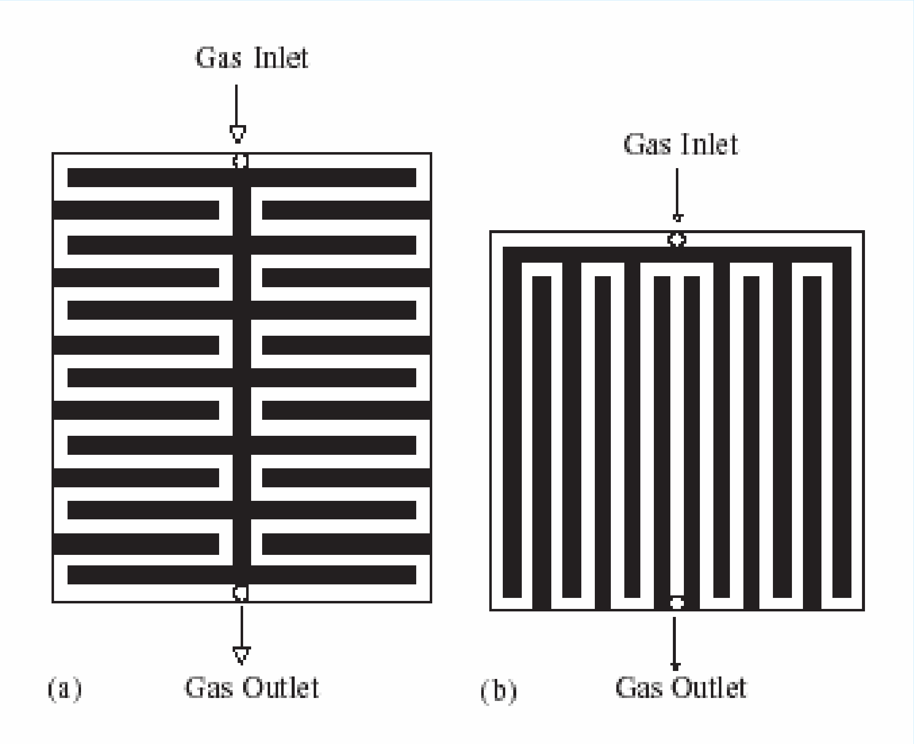


Radial



Serpentine

FLOW FIELD DESIGNS:



Design (a) shows rapid decrease in performance than (b). Flow field design plays a major role in removing the product water and the excess condensed water effectively

FLOW FIELD DESIGNS:

DESIGN IS NEEDED TO BE OPTIMIZED BY TAKING INTO ACCOUNT THE FOLLOWING :

- ACTIVE AREA OF THE PLATE
- GAS FLOW RATE
- PRESSURE DROP
- RESIDENCE TIME REQUIRED FOR CONVERSION
- AMOUNT OF WATER FORMATION

BIPOLAR PLATES MATERIAL :
GRAPHITE IS MOST COMMONLY USED

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Properties of Graphite Bipolar Plates : (Du Pont)

Property	Test Method	Unit	Value
Specific gravity	ASTM D792	g/cc	1.85
Perp. Resistance	DOC A128	Ohm-cm	0.03-0.04
Tensile strength	ASTM D638	MPa	25
Flexural strength	ASTM D790	MPa	53
Compressive creep	ASTM D2990	Strain%	0.02
Impact strength	ASTM D256	Ft;lb/in	0.14
Thermal cond.	Hot Disc	W/m K	43
Max. Use Temp	TMA	C	210

BIPOLAR PLATES MATERIAL :

Oak Ridge Laboratory USA reports Carbon/carbon composite bipolar plates

- Slurry-molded fabrication of carbon/carbon composite material lends itself to low-cost, high-volume production
- Hydrogen/oxygen flowfields can be stamped into the carbon composite preform
- Increased conductivity, lighter weight, and greater corrosion resistance than graphite plates

Porvair Fuel Cell Technology has taken up this for commercialization (it is not yet available)

DRAWBACKS OF EXISTING MATERIAL AND METHODS :

- **High Temperatures / Energy inputs needed : Graphite itself is made by high temperature. Plates have to be sintered at HT**
- **Material is not mechanically sturdy : easily damaged during handling, assembly etc.**
- **Limited in processing : Not easy to shape or machine as required**
- **Large amount of wastage of material (during track machining, moulding etc.)**
- **CONTACT RESISTANCE arises due to limitation on tightening / application of pressure**
- **Batch process hence large scale production difficult**
- **HIGH COST**

ALTERNATIVE MATERIALS AND PROCESSES :

- **Conducting Polymer Composites are most suitable for Bipolar Plates**
- **Injection moulding, compression moulding are employed**
- **Prefabricated Steel with Corrosion resisting coating with conducting polymers**
- **Conducting Polymer Screen Printing the Pattern for micro fuel cells on various substrates**

CONDUCTING POLYMERS:

There are basically three types of conducting polymers :

1. Conducting Polymer Composites (CPC) : Electronic
2. Inherently Conducting Polymers (ICP) : Electronic
3. Solid Polymer Electrolytes (SPE) : Ionic

ALL ARE USEFUL FOR FUEL CELLS

CONDUCTING POLYMER COMPOSITES :

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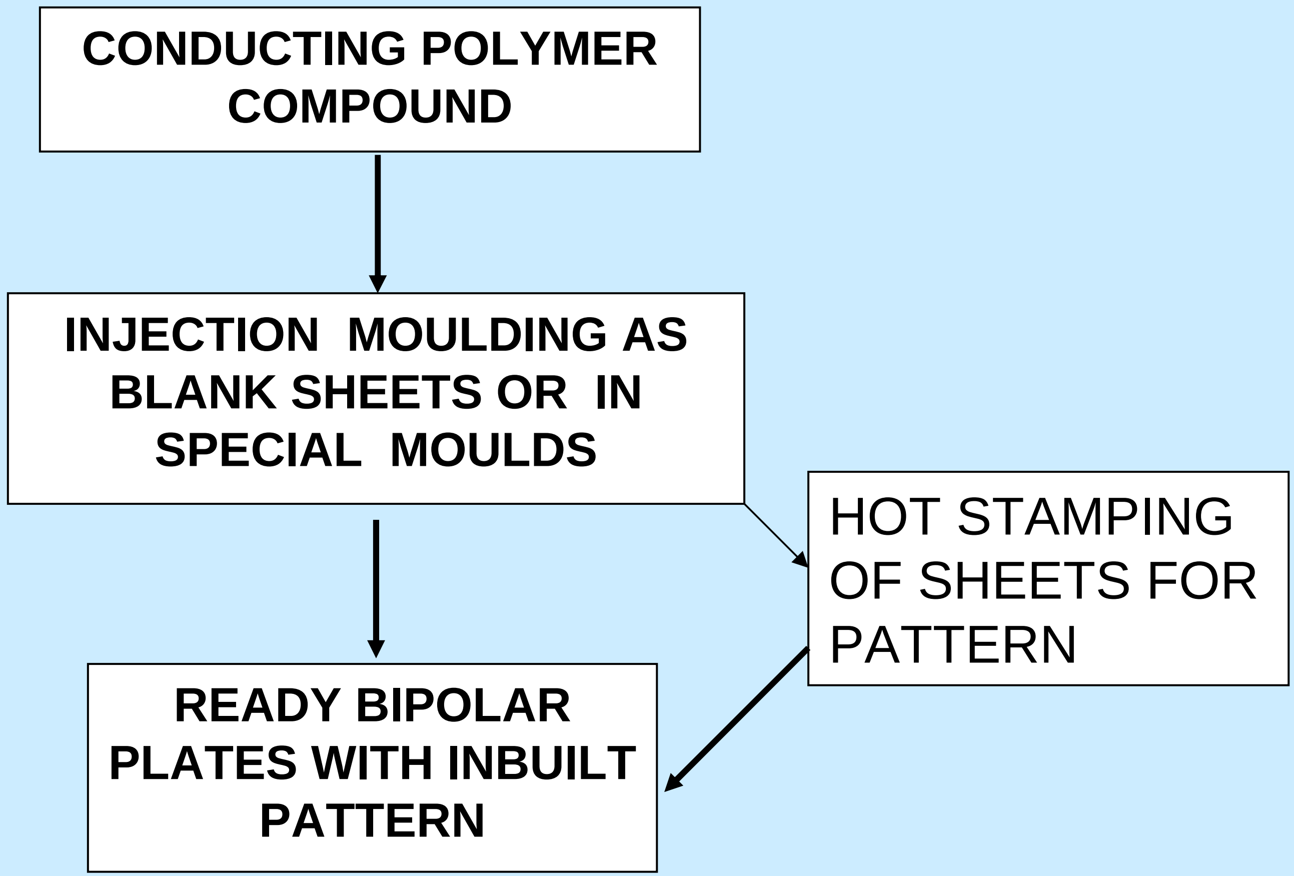
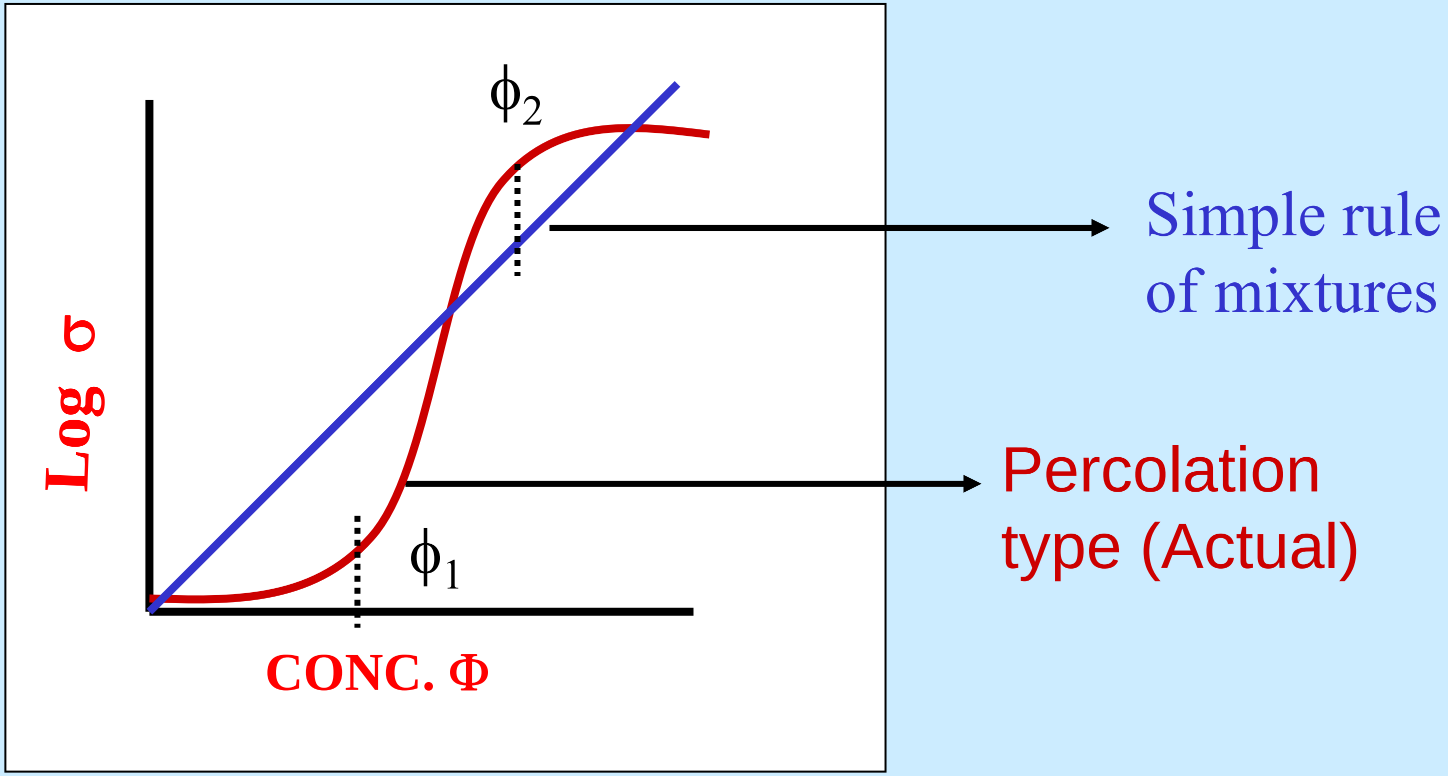
- **Conducting Polymer Composites are made by incorporation of conducting particles in a polymer matrix.**
- **Polymer Matrix : can be thermoplastic or thermosetting**
- **Conducting Particles : can be graphite, carbon black, carbon fiber, metal particles etc.**

CONDUCTING POLYMER COMPOSITE BIPOLAR PLATES



COMPOSITIONAL DEPENDENCE OF CONDUCTIVITY

Adding conducting particles to plastics to give CPC



EFFECT OF PARTICLE SHAPE ON RESISTIVITY IN POLYMER COMPOSITES :

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Percolation theory gives :

$$\sigma_m = \sigma_h \left[(\phi - \phi_c) / (1 - \phi_c) \right]^t \quad \text{for } \phi > \phi_c$$

$$\sigma_m = \sigma_1 \left[(\phi_c - \phi) / \phi_c \right]^{-s} \quad \text{for } \phi_c < \phi$$

$$t = (1 - \phi_c) / (1 - L_1) = \phi_c / L_h = 1 / (1 - L_1 + L_h)$$

for oriented ellipsoids

$$t = m_1 (1 - \phi_c) = m_h \phi_c = m_1 m_h / (m_1 + m_h)$$

for randomly dispersed ellipsoids

EFFECT OF PARTICLE SHAPE ON RESISTIVITY IN POLYMER COMPOSITES :

Percolation theory :

Cp = Pc Z

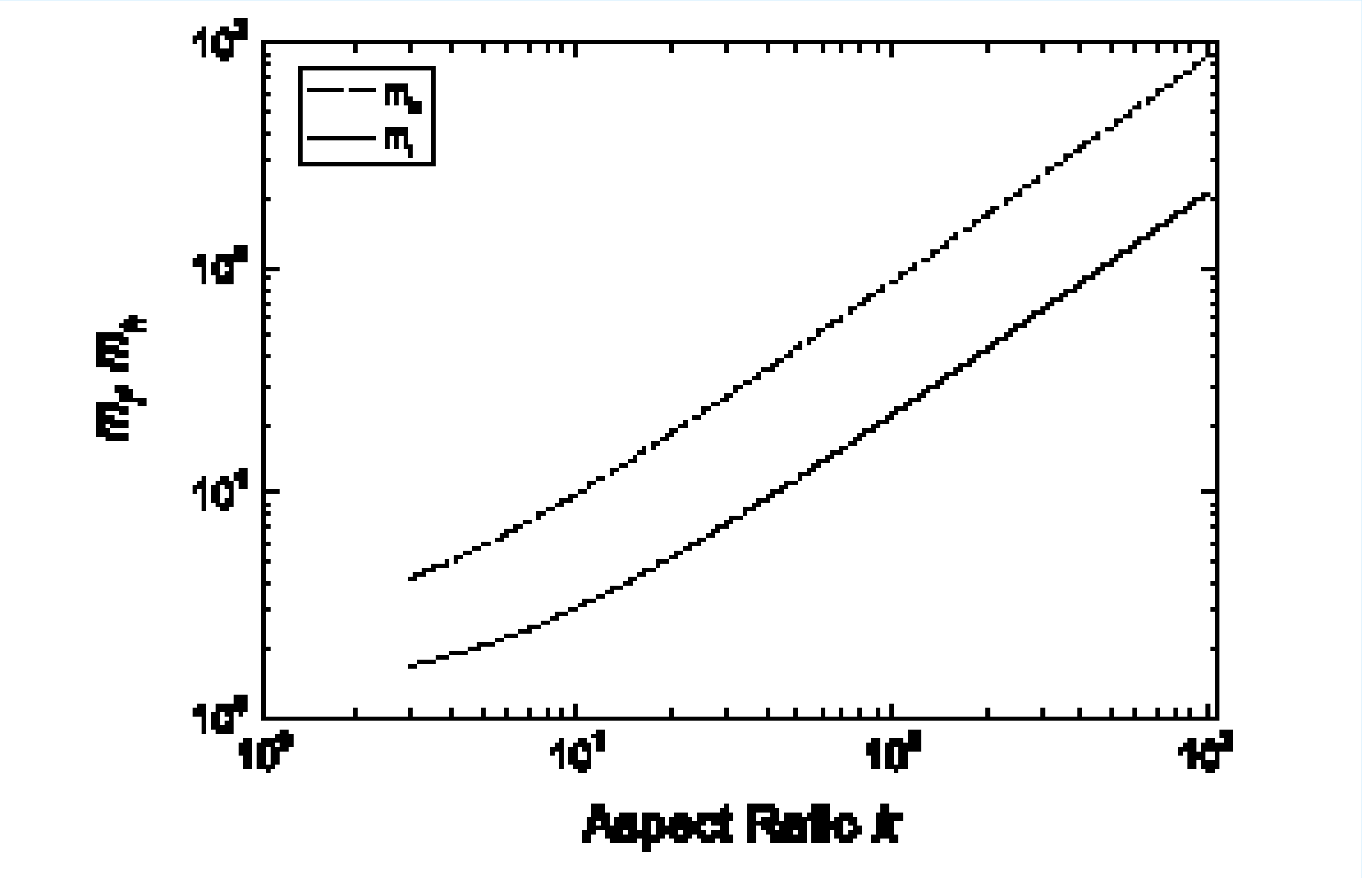
Cp : critical number of contacts / particle

Pc : critical probability of network formation

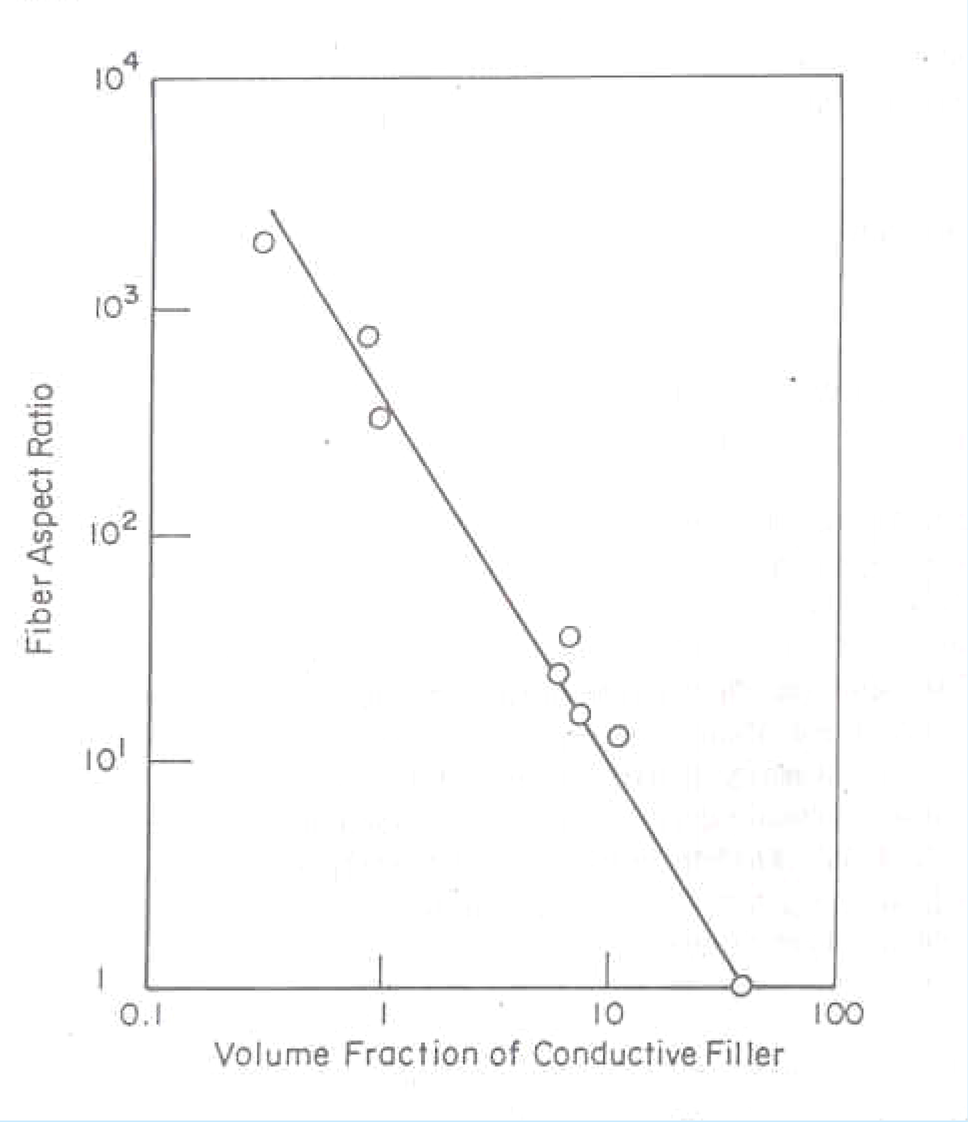
Z : maximum number of contacts possible for the geometry

Lattice	Z	ϕm	Pc	Cp
FCC	12	0.74	0.125	1.5
BCC	8	0.68	0.183	1.46
Simple Cubic	6	0.82	0.254	1.52
Diamond	4	0.34	0.389	1.56
Random	6	o.637		

EFFECT OF PARTICLE SHAPE ON RESISTIVITY IN POLYMER COMPOSITES :



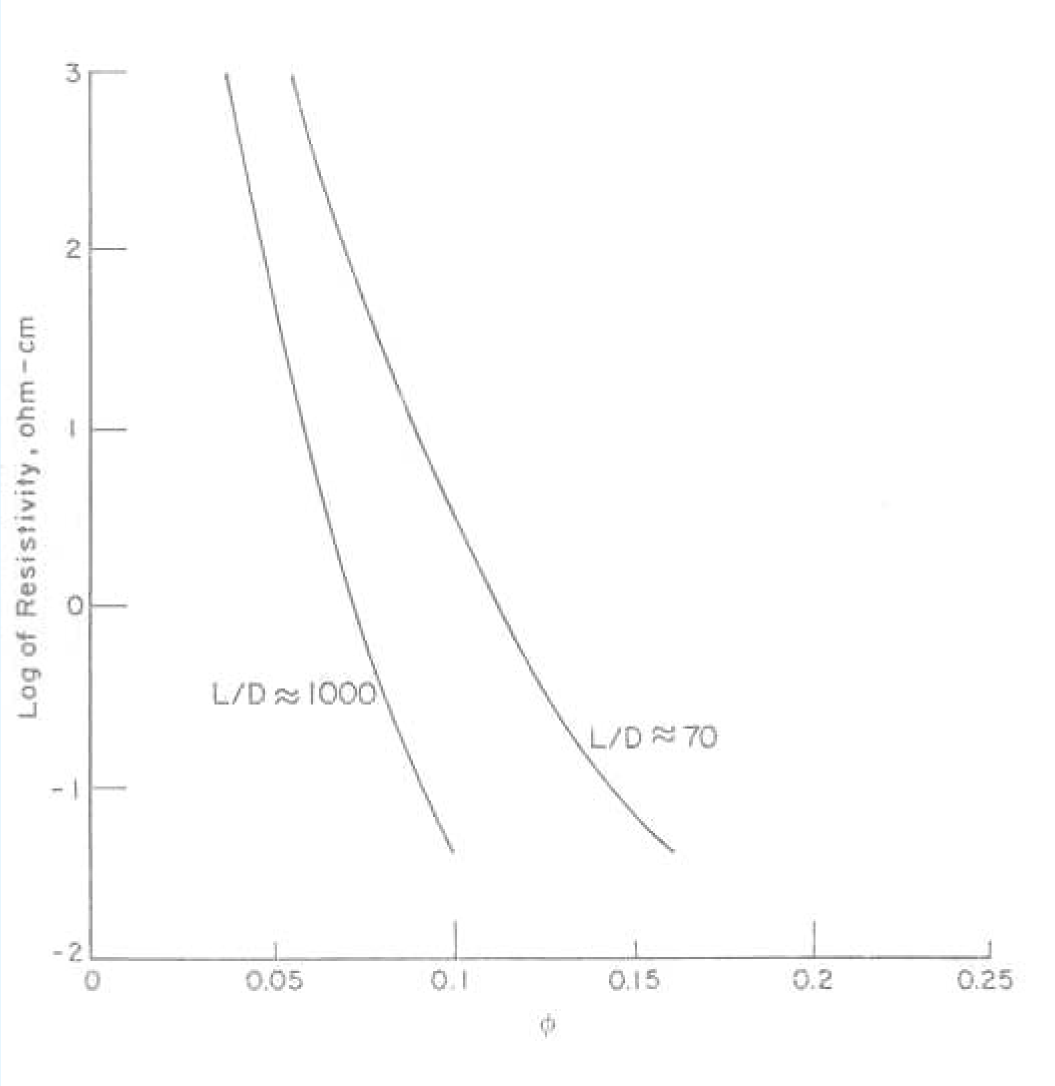
EFFECT OF PARTICLE SHAPE ON RESISTIVITY IN POLYMER COMPOSITES :



Effect of aspect ratio on ϕ_c

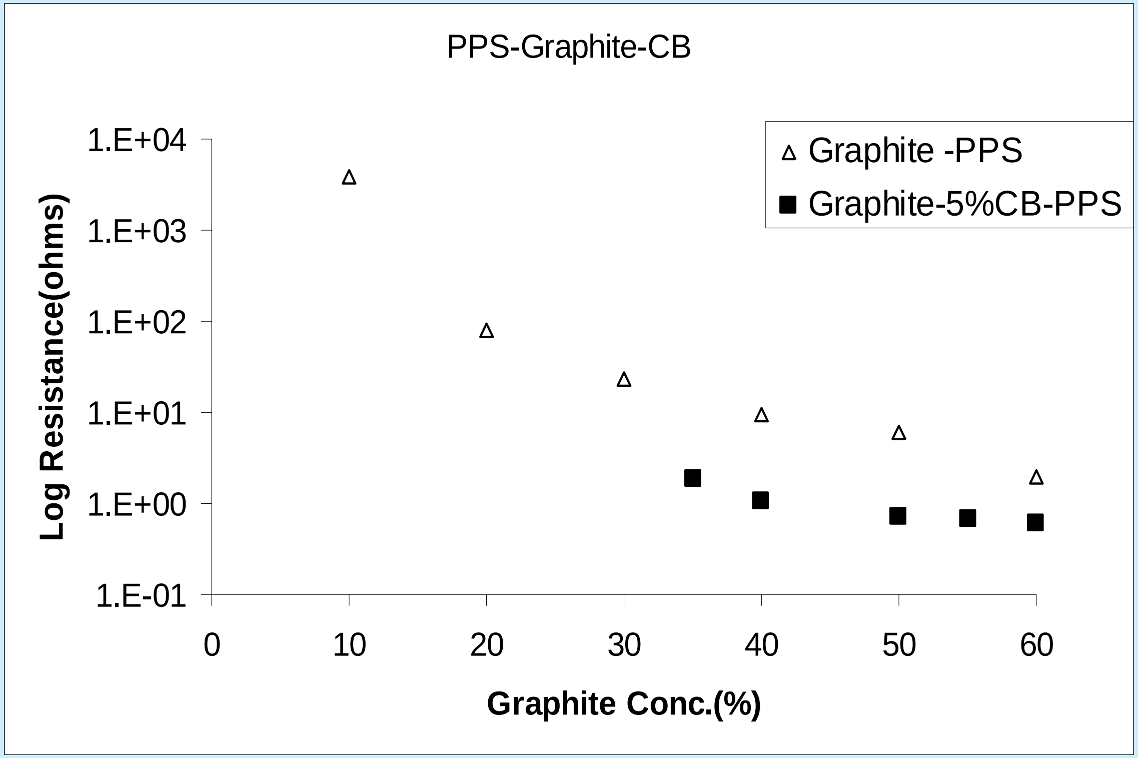
EFFECT OF PARTICLE SHAPE ON RESISTIVITY IN POLYMER COMPOSITES :

NCL



EFFECT OF THIRD COMPONENT ON RESISTIVITY IN POLYMER COMPOSITES :

NCL



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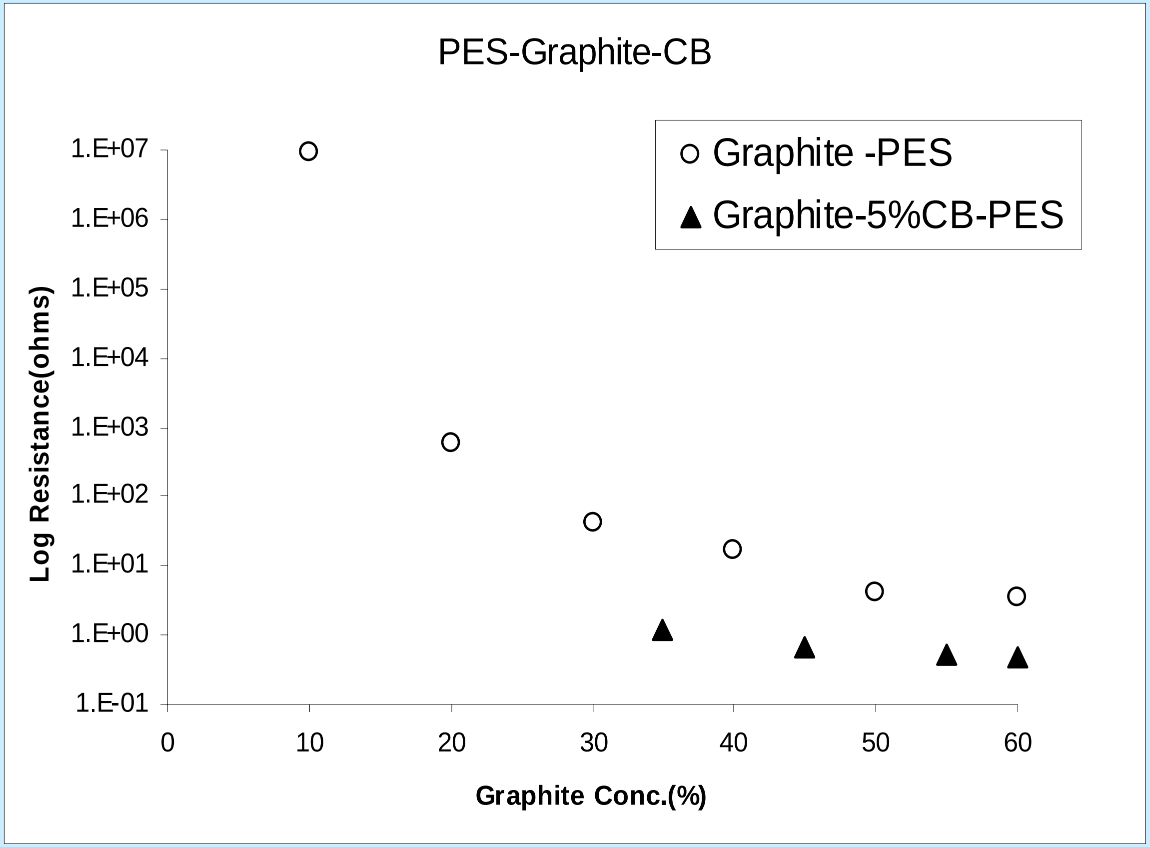

Conductivity of hybrid conducting composite plates:

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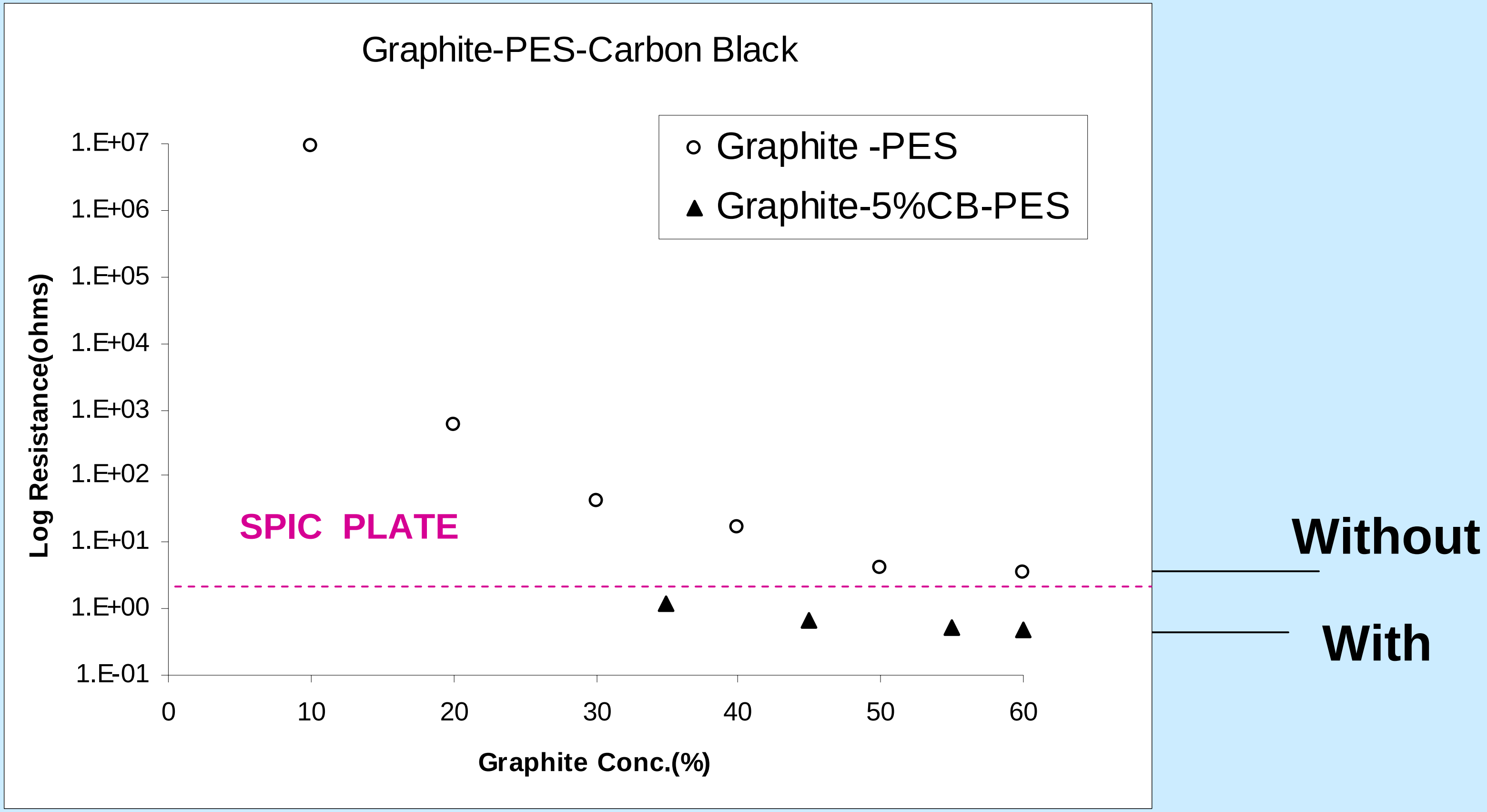
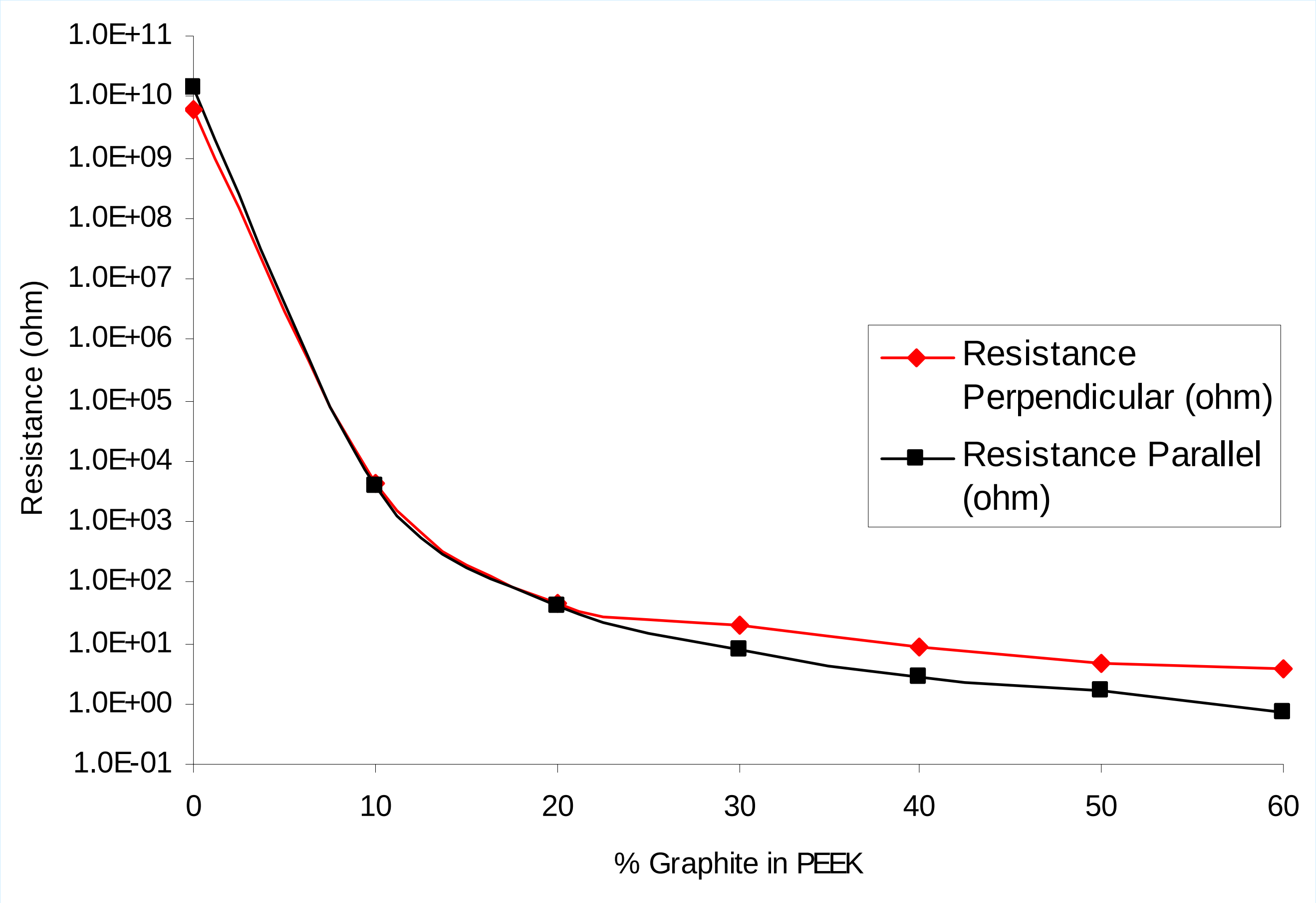
Effect of addition of third component on Conductivity



ANISOTROPY IN RESISTIVITY IN GRAPHITE POLYMER COMPOSITES :



ANISOTROPY IN RESISTIVITY IN GRAPHITE POLYMER COMPOSITES :

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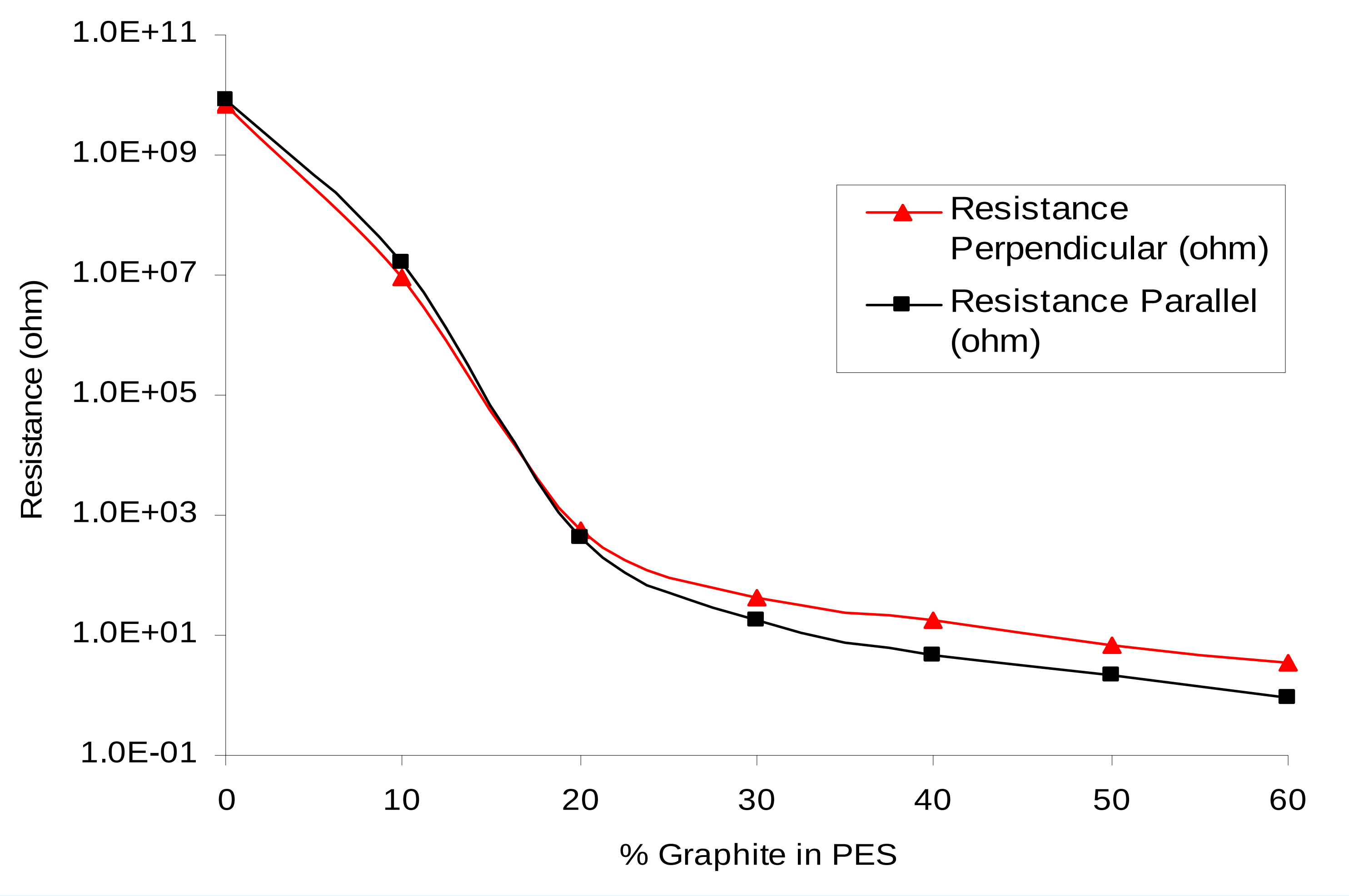

PROCESSING OF BIPOLAR PLATES

TECHNIQUE DEPENDS ON THE NATURE OF POLYMER MATRIX:

Thermoplastic : Injection / Compression Molding

Thermosetting : Hand lay up / Compression ,,

Polymer + Graphite+ additive Mixing :

1. **Powder Processing**
2. **Solution Blending**
3. **Melt extrusion**

PROCESSING OF BIPOLAR PLATES

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POLYMERS USED FOR MAKING COMPOSITES

THERMOPLASTIC POLYMERS :

Polypropylene, TPO, PET,PVDF, PS copolymer for FC operating temperature < 100 C

PPS, PES, PEEK, LCP blends for FC operating at 150 C

Graphite has to be incorporated by melt compounding using sigma mixer and twin screw extruder having high capacity of loading

Melt flow is necessary for the graphite incorporated compound

PROCESSING OF BIPOLAR PLATES

POLYMERS USED FOR MAKING COMPOSITES:

THERMOSETTING POLYMERS / RESINS

Aliphatic polyesters, phenol formaldehyde , epoxies, modified epoxy etc cross-linked with agents

Graphite is incorporated in low molecular weight semi-liquid resin by sigma blender or two roll mill

Cross-linking agent is added and the mix partially cured or directly poured in the moulds

Partially cured mix (B stage cured) is compression moulded at high temperature for fast and final cure

VISCOSITY OF POLYMERS WITH FILLERS

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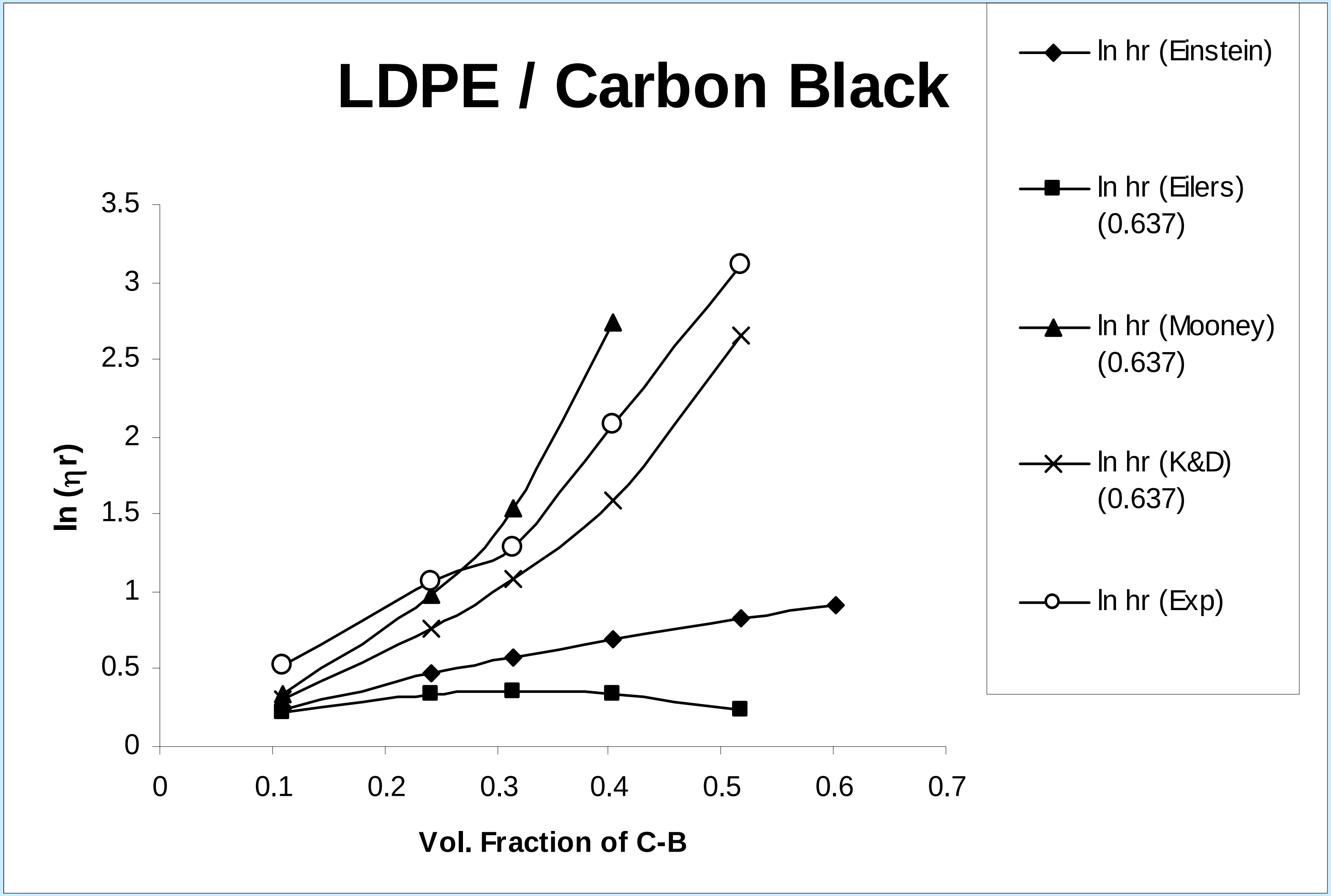
EQUATIONS FOR VISCOSITY

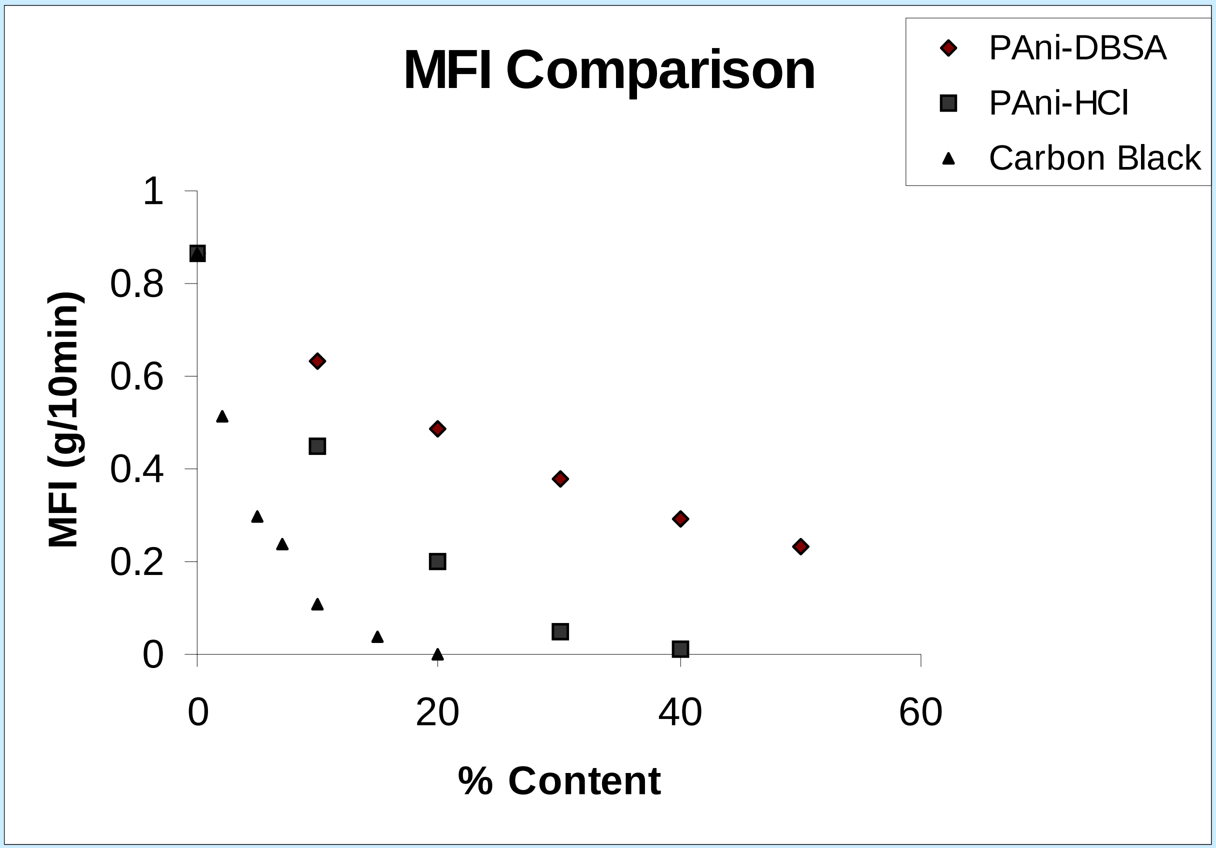
$\eta = \eta_f (1 + 2.5\phi)$	Einstein
$\eta_r = [1 + 1.25\,\phi(1 - \phi/\phi_m)]^{2}$	Eiler
$\eta_r = e^{KE\,\phi\ /\ (1 - \phi\ /\ \phi m\ )}$	Mooney
$\eta_r = (1 - \phi/\phi_m)^{-[K_E]\,\phi\ m}$	Krieger and Dougherty
$\eta_r = (1 - \phi/\phi_m)^{-2}$	Quemada

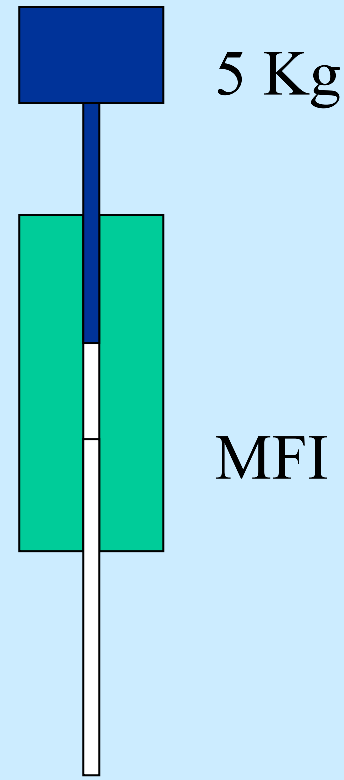
RELATIVE VISCOSITY OF LDPE + CB



RELATIVE VISCOSITY OF POLYMERS WITH FILLERS

$$\eta \ \alpha \ (1/MFI), \quad \eta_r = [\eta_{blend} / \eta_0] = (MFI)_0 / (MFI)_{blend}$$

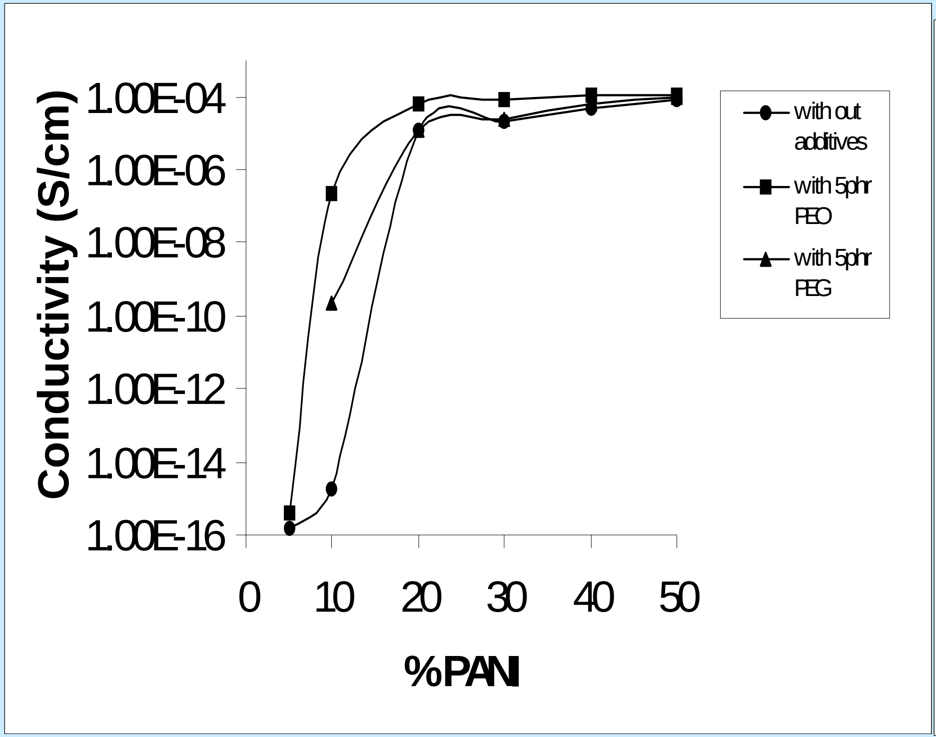


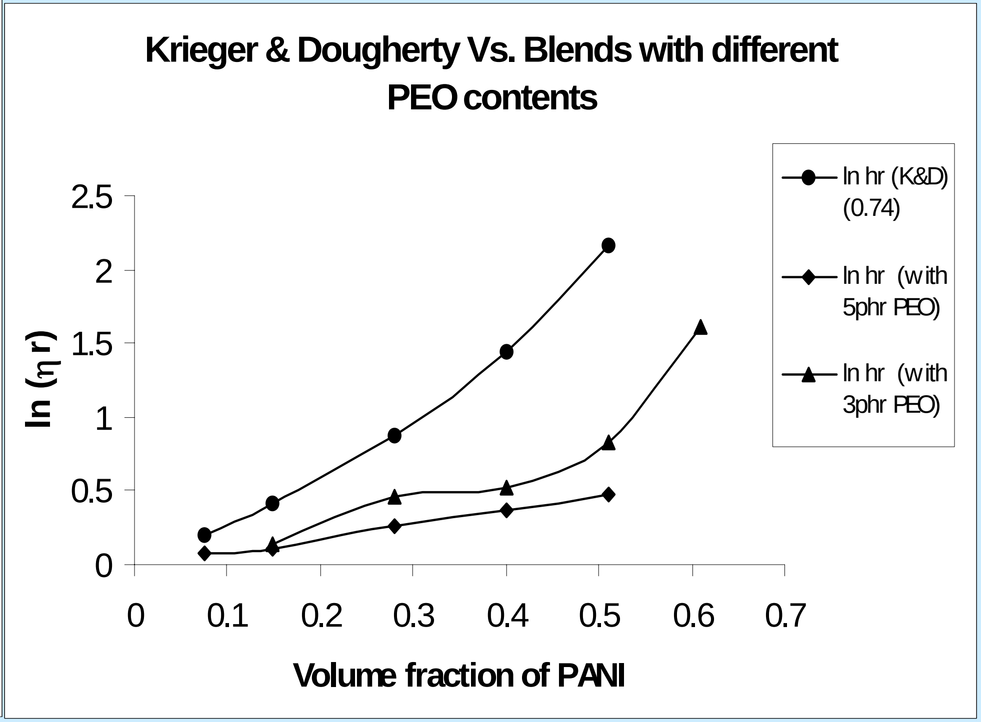


VISCOSITY OF POLYMERS INCREASES TREMENDOUSLY WITH ADDTION OF FILLERS

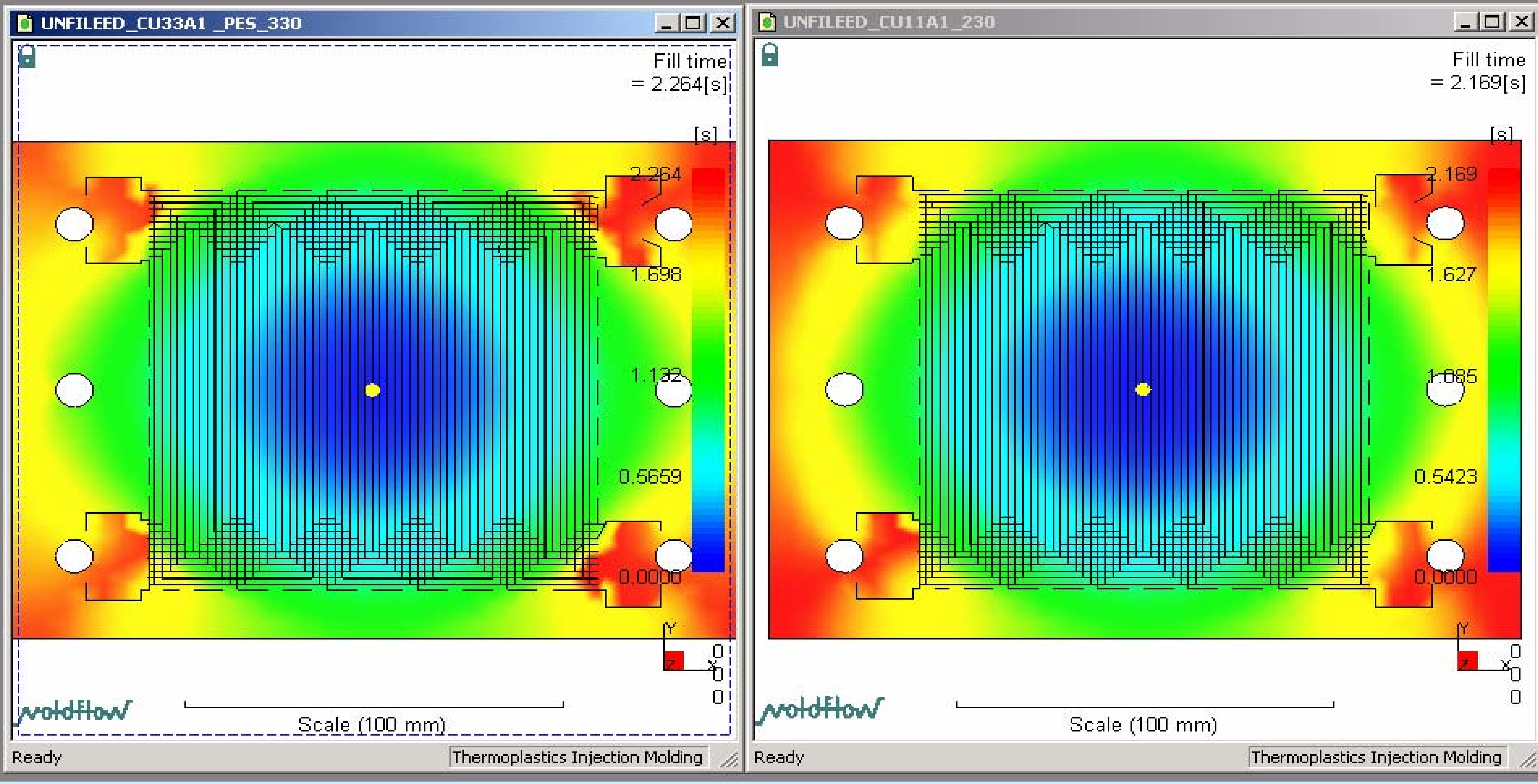
VISCOSITY OF POLYMERS + FILLERS + ADDITIVES

Reduction in percolation threshold + increase in flow by using processing aid (PEO)





TESTING THE MOULD DESIGN USING MOLD FLOW PACKAGE FOR TWO POLYMERS (PES) AND PP



POLYETHER SULFONE GAFONE MELT TEMP 380 C

POLYPROPYLENE REPOL MELT TEMP 230 C

Injection Moulded Bipolar Plate :

Injection Molded samples with PP +carbon black :

Compression Moulded Bipolar Plate :

Compression Molded samples with PP +carbon black

INJECTION MOULDED PLATE :

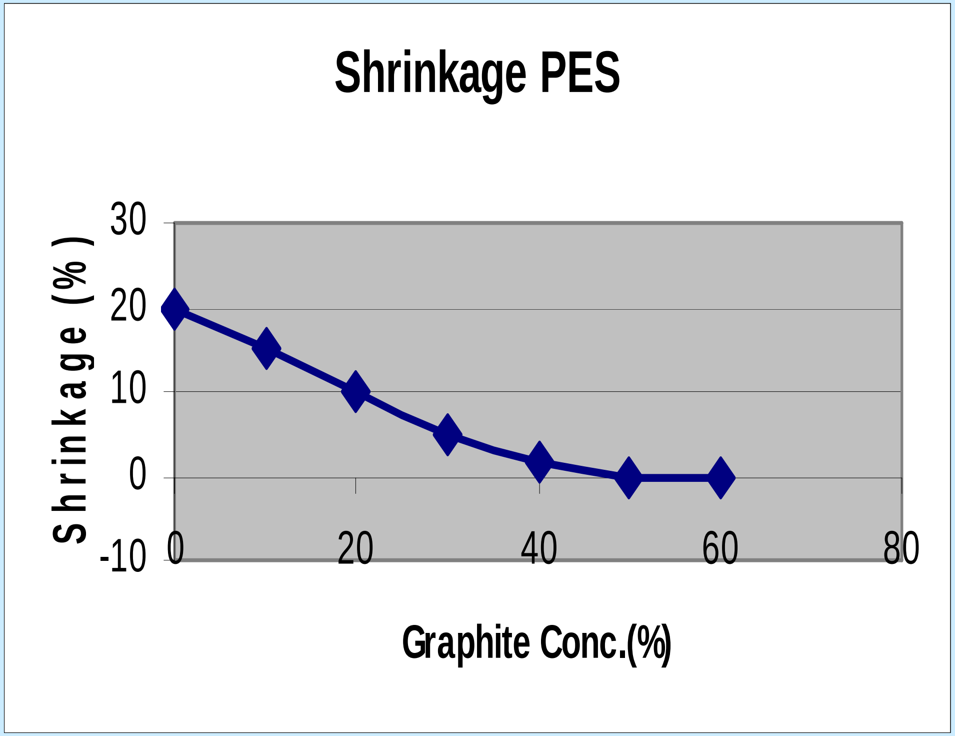
Injection Molded samples with PP +carbon black :

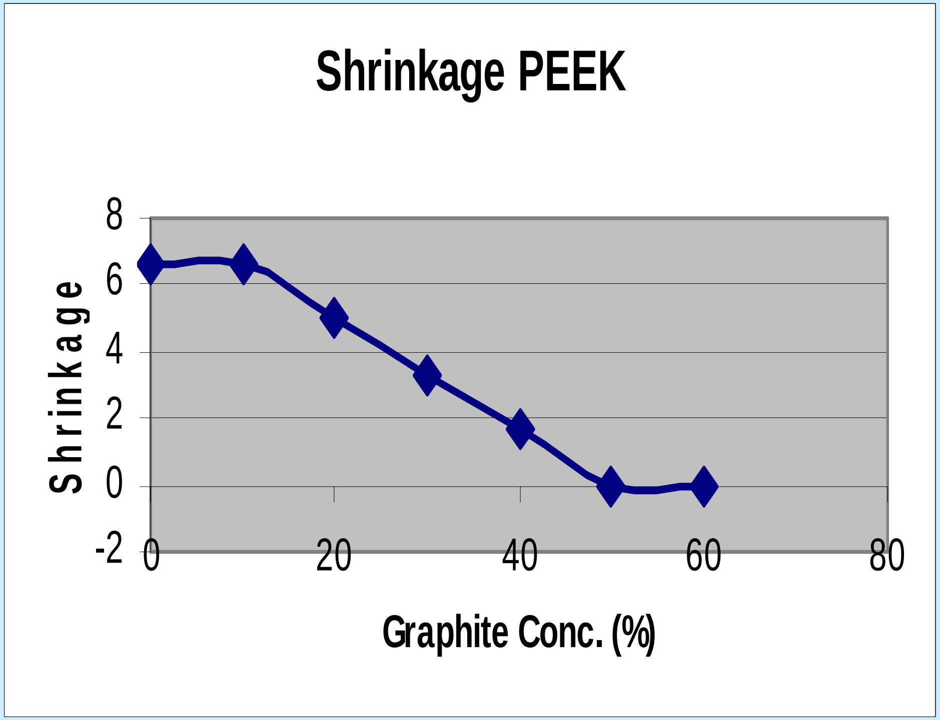
Flow Channel Track depth Variation Pattern

0.53	0.52	0.52	0.52	0.54
0.53	0.55	0.51	0.55	0.61
0.56	0.57	0.52	0.52	0.55

Dimensional changes :

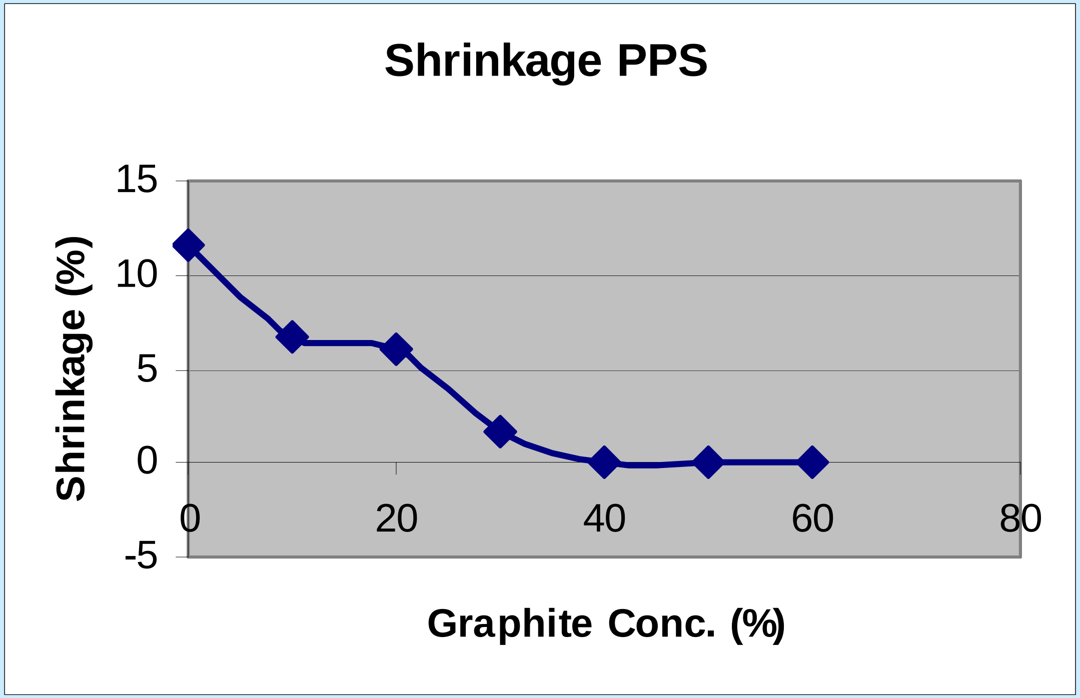
Shrinkage Studies



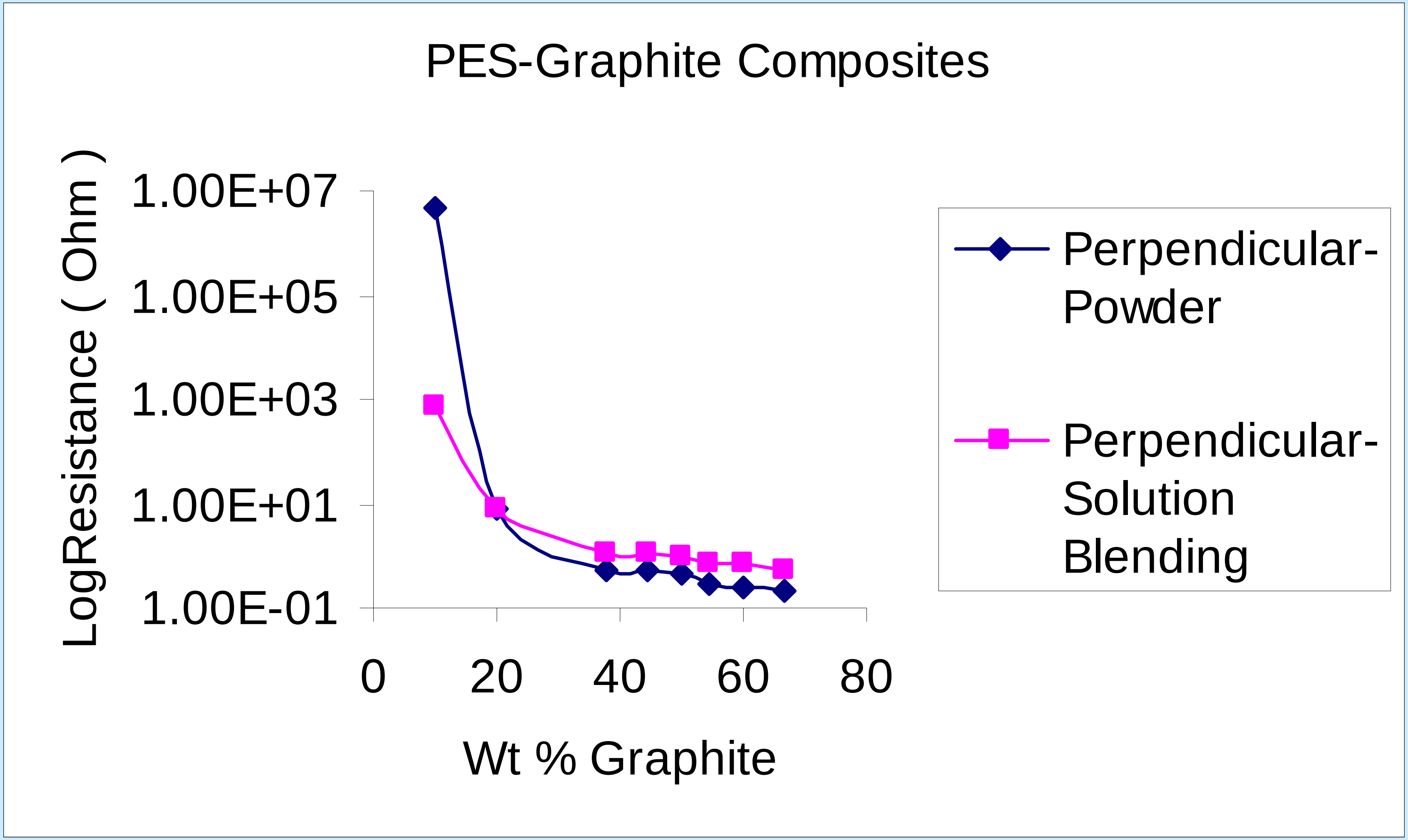


Dimensional changes during processing :

Shrinkage Studies



EFFECT OF BLENDING METHOD ON PROPERTIES :



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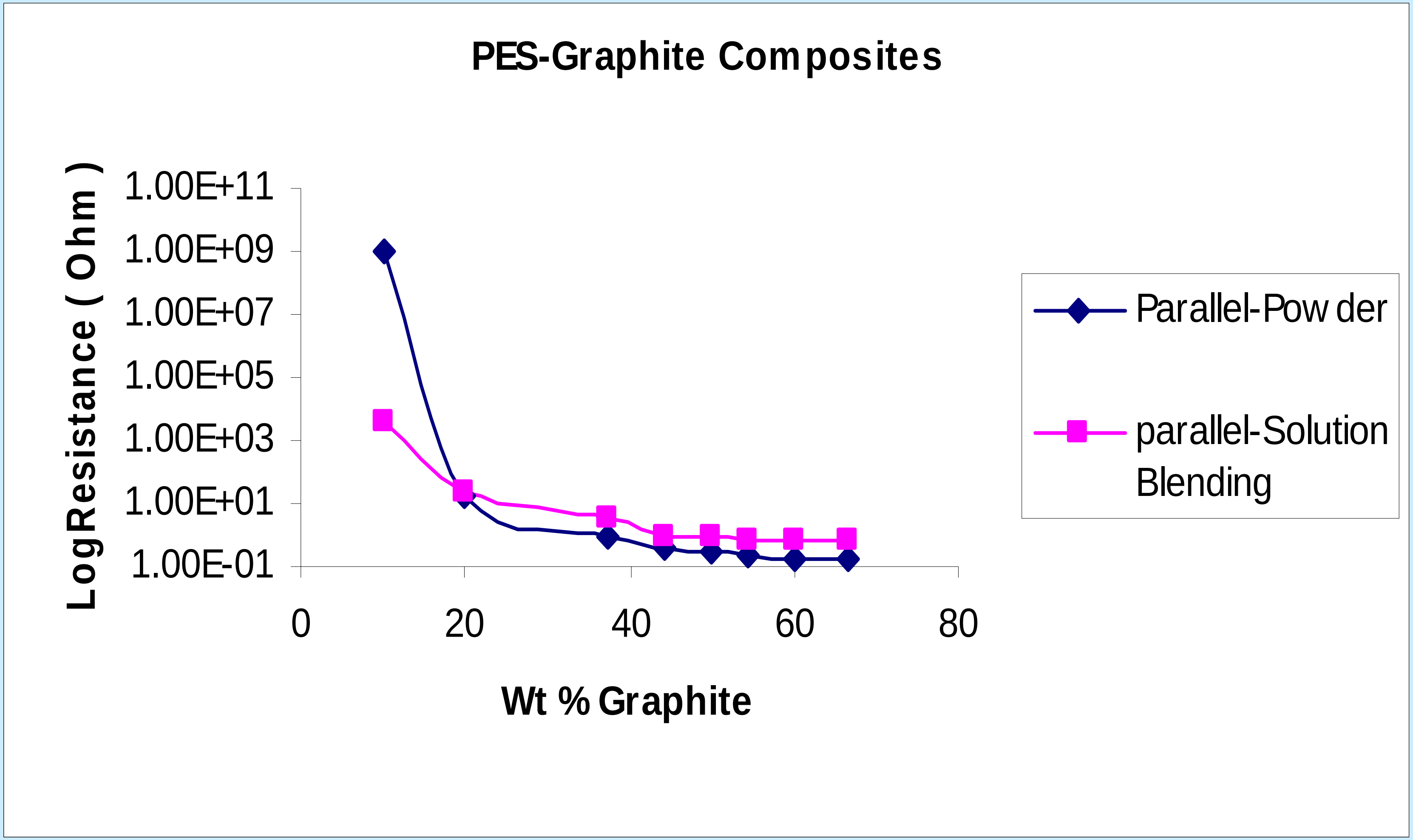

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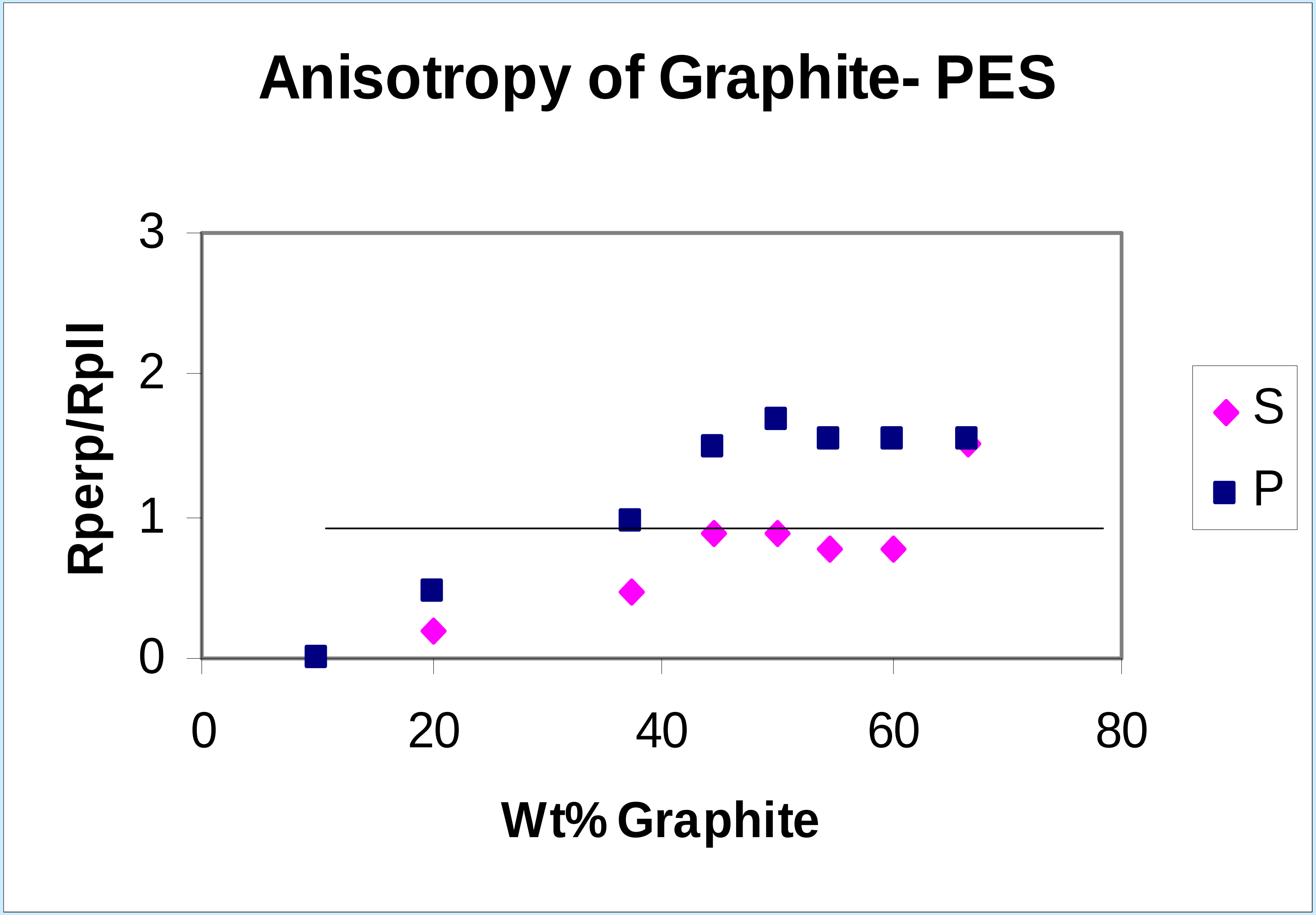
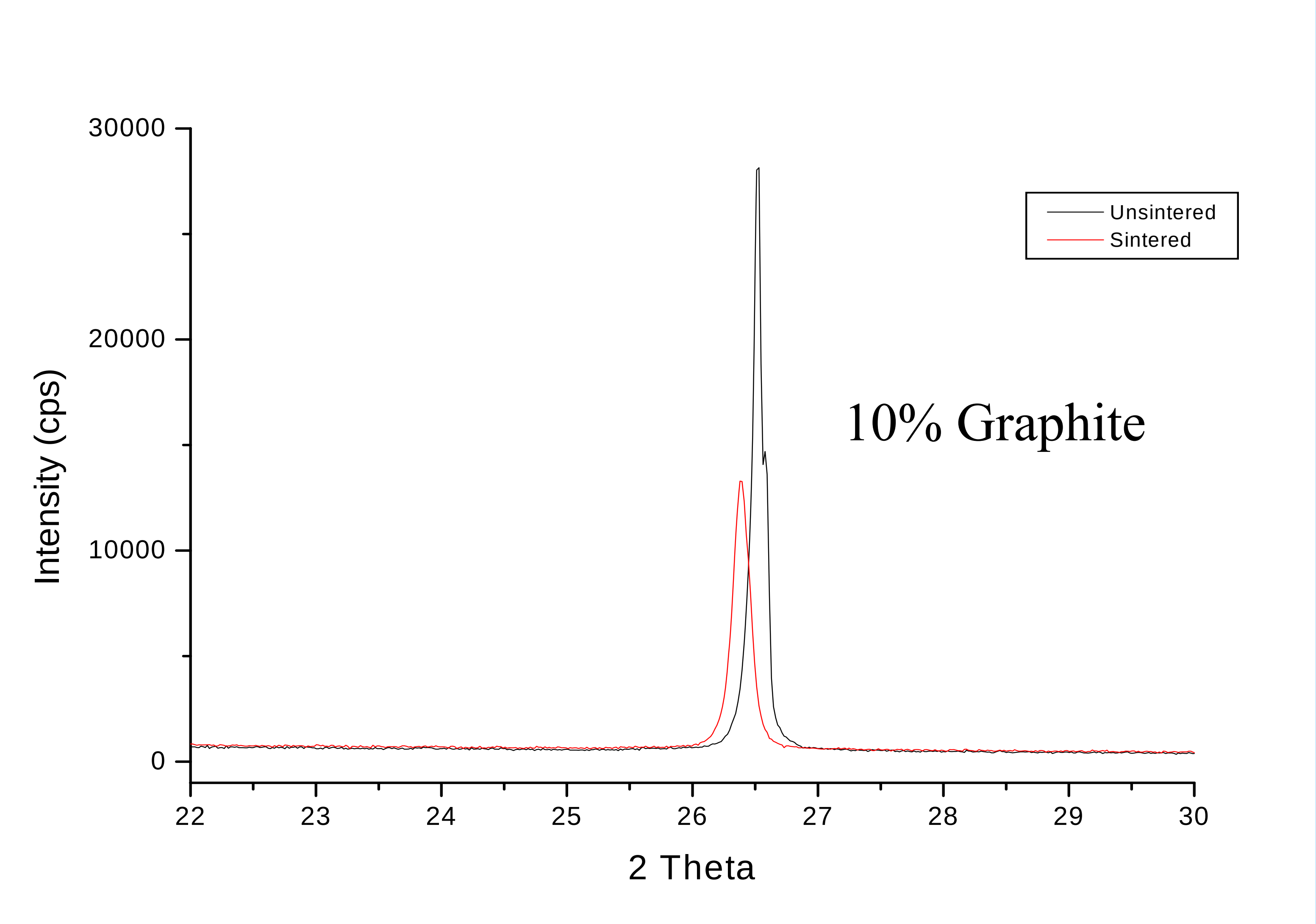
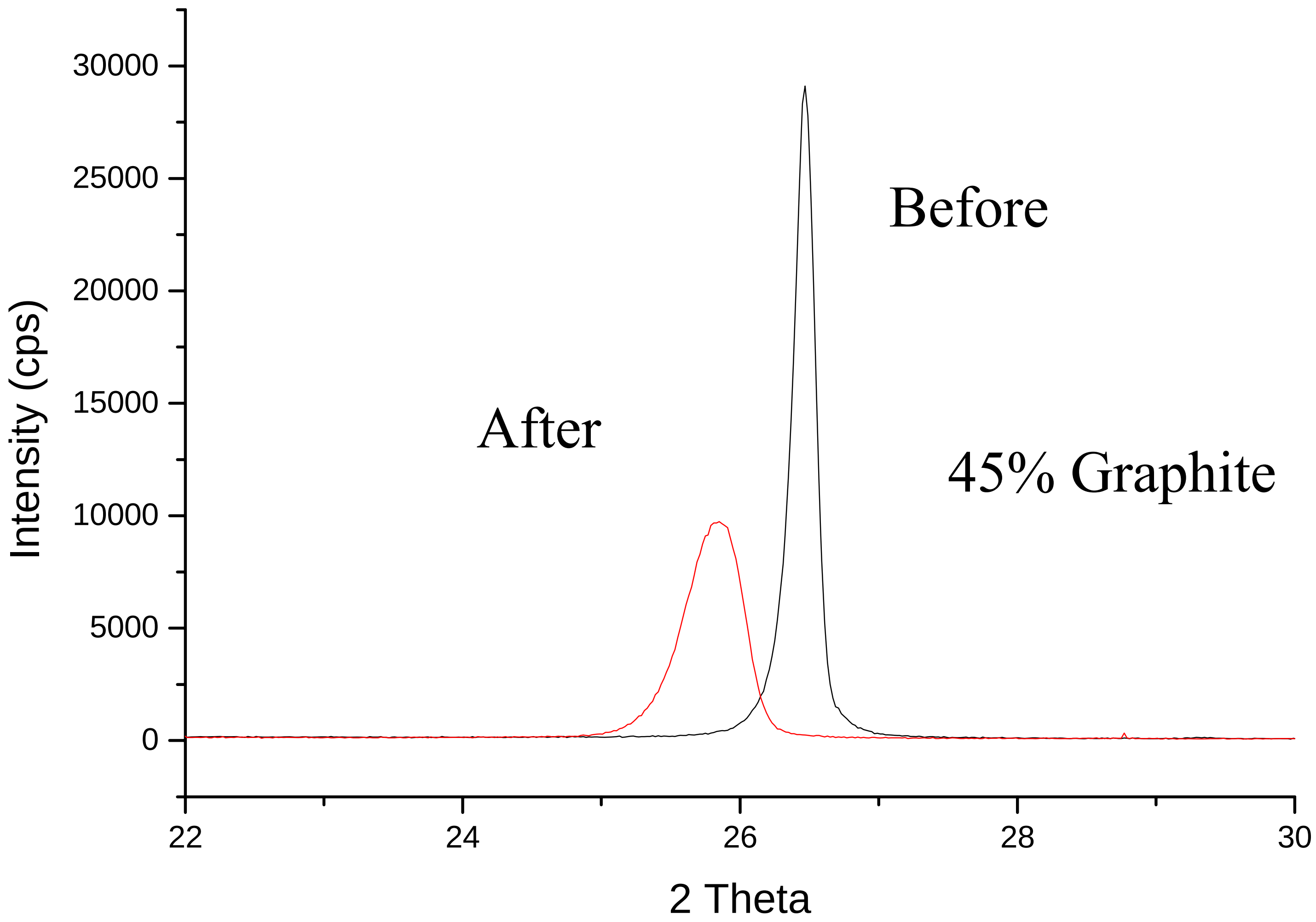


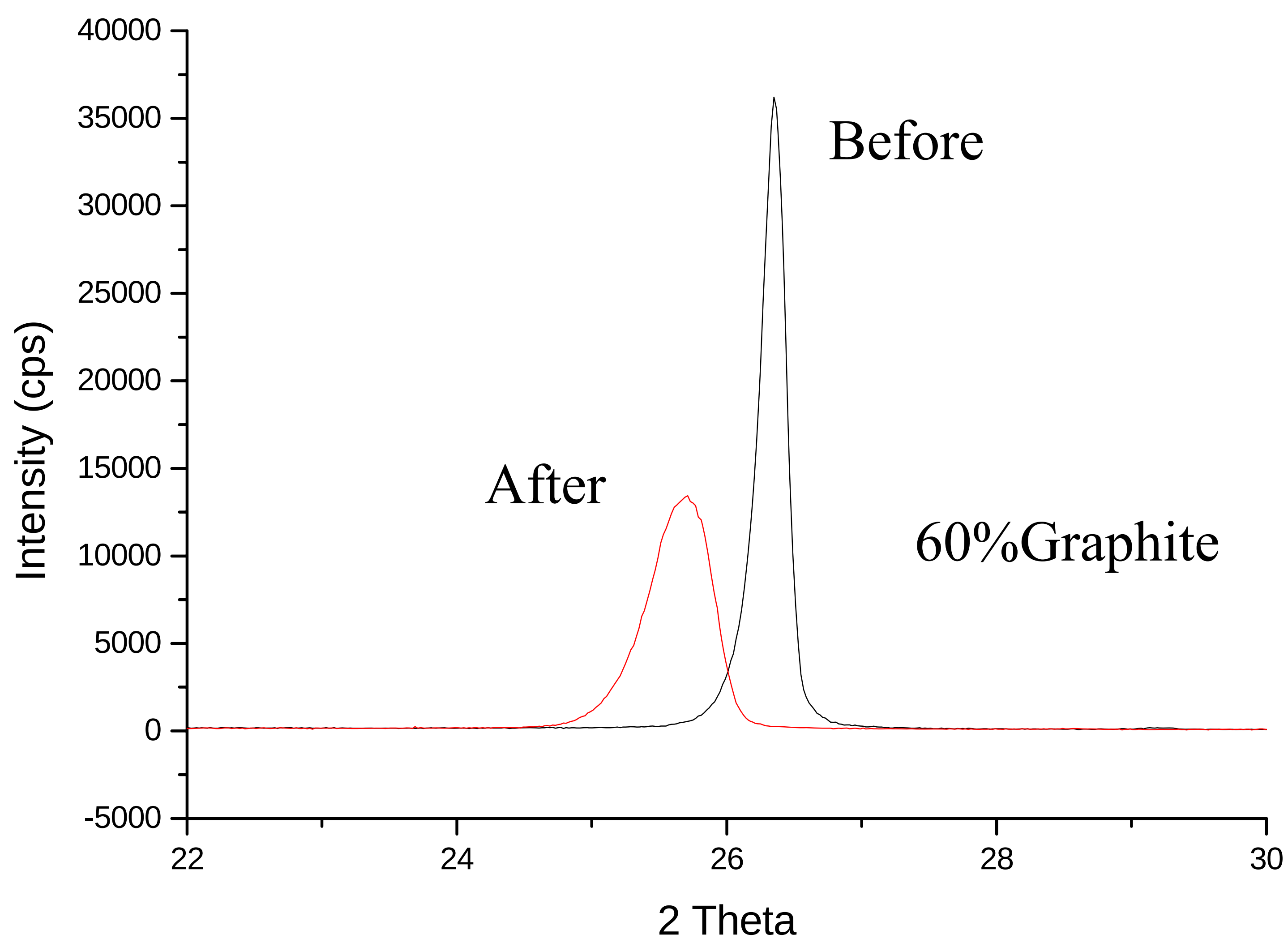
XRD Of PES- Graphite Powder Blended Composite :



XRD of PES-Graphite Solution Blended :



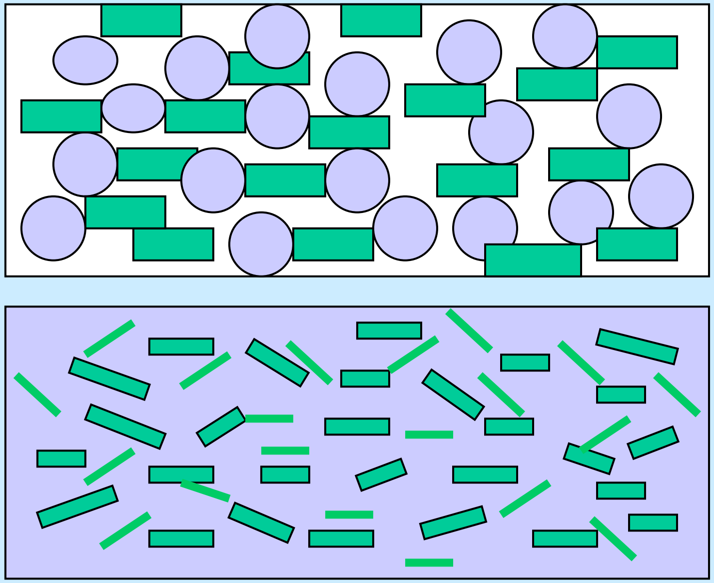
XRD of PES-Graphite Solution Blended :



XRD ANALYSIS :

Wt % Graphite	Crystallite Size (nm)		Interplanar d- spacing (A°)	
	Before sintering	After sintering	Before sintering	After sintering
37.50	46.20	21.92	3.3560	3.3923
44.44	41.67	17.34	3.3646	3.4438
60.00	20.83	13.86	3.3796	3.4623

POSSIBLE REARRANGEMENT OF GRAPHITE PARTICLES :



Powder Processed

Solution Processed

PROPERTIES OF POLYMER COMPOSITE PLATES (BULK MOULING COMPOUND) :

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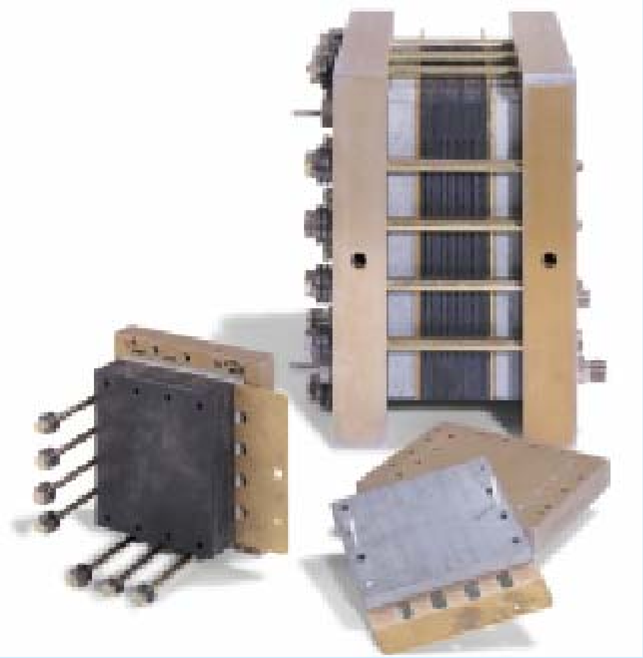
BMCI Vinyl Ester Fuel-Plate Compounds (Compression Molding)		
Grade Filler Application	BMC 940-8596 Graphite (Bipolar Plate)	BMC 845 30% glass (End Plate)
Electrical Conductivity, S/cm Through Plane (Z) In Plane (X-Y)	 70 95	 — —
Specific Gravity Shrinkage, in./in. Flexural Strength, psi Flexural Modulus, 10^6 psi Un-notched Izod, ft-lb/in. Compressive Creep, % 1000 hr@80 C Thermal Conductivity, V/m-K UL Flame Rating	1.82 0.001 6800[a] 1.7 0.5 0.3[c] 16 94V-O	1.8 0.00 12,000[b] 1.6 7.0 2.0[d] — 94V-O

Volume 13 - No. 2 Bulk Molding Compounds, Inc. October, 2001

Injection molding technology has yet to overcome the current preference for compression molding to make thermoset fuel-cell plates.

Quantum's Premtex Vinyl Ester Bipolar Plate Compound (Compression Molding)

Electrical Conductivity, S/cm	
Through Plane (Z)	25
In Plane (X-Y)	96
Specific Gravity	1.8
Shrinkage, in./in.	0-0.0015
Flexural Strength, psi	6500
Fluxural Modulus, 10^6 psi	1.7
Compressive Strength, psi	7800
Glass Transition Temp., C	175
Thermal Conductivity, W/m-K (through plane)	18
UL Flame Rating	94V-O



PROPERTIES OF POLYMER COMPOSITE PLATES (BULK MOULING COMPOUND) :

NCL

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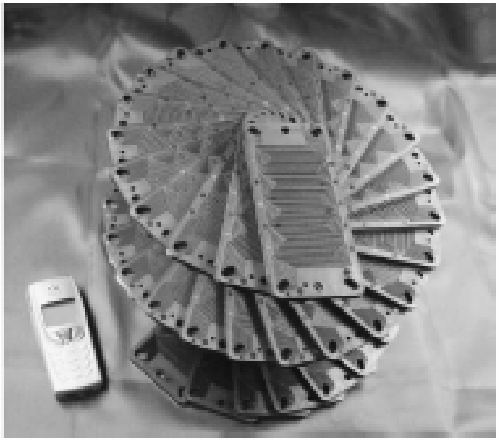
PLASTICS ENGINEERING 2003

Du Pont's new fuel Cells Business is about to launch a graphic-filled LCP compound for injection molded bipolar plates.

POWER 2004 ZBT INJECTION MOLDED PLATES AND STACK

NCL



After injection molding

Granules containing graphite

Properties of Moulded Plate (NCL)

Property	Units	Value with > 90% Gr	Experimental with < 45% Gr
Bulk Density	g/cc	< 1.8	1.3
Flexural Strength	MPa	40	---
Compressive Strength	MPa	50	---
Thermal Conductivity	W/mK	10	5
Electrical Resistivity (with carbon contact at 3.0 Mpa load)	Ohm-cm	5×10^{-2}	4.2×10^{-1}
Roughness variation over 30 x20 (channel depth variation)		0.65 mm	0.55 ±0.02
Maximum Operating Temperature (continuous)	ºC	150	110
Surface hardness	Shore D Scale	62	68

SECOND ROUTE TO MAKE BIPOLAR PLATES :

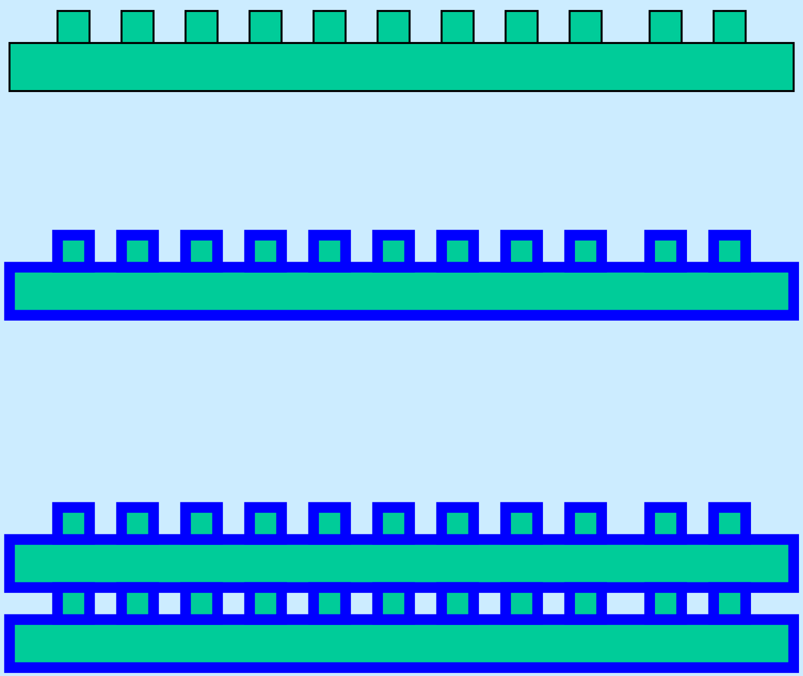
PRE-FABRICATE THIN METAL PLATES WITH PATTERN

↓

DEPOSITE CONDUCTING CARBON OR OTHER HYBRID MATERAL BASED COATING

↓

SANDWICH STRUCTURE



NEW APPROACH TO MAKE THINNER BIPOLAR PLATES

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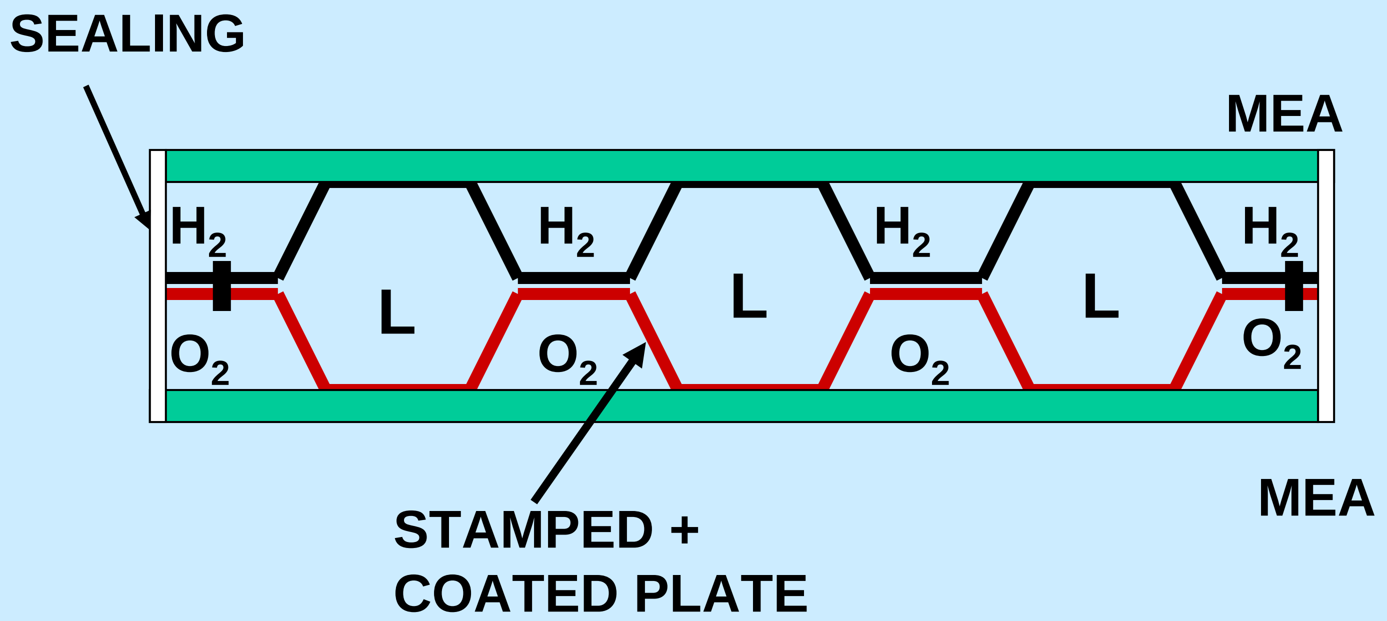
CONDUCTING POLYMER COMPOSITE COATED SS FOILS FOR BIPOLAR PLATES:



TYPICAL SINGLE CELL ASSEMBLY WITH PREFORMED SS FOIL WITH CONDUCTING CORROSION RESISTANT COATING

CONDUCTING POLYMER COMPOSITE COATED STEEL FOILS FOR BIPOLAR PLATES:

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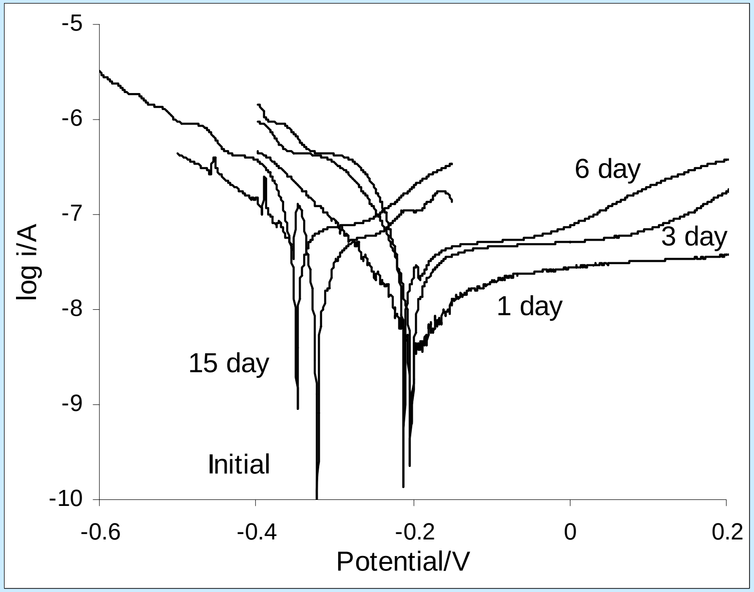
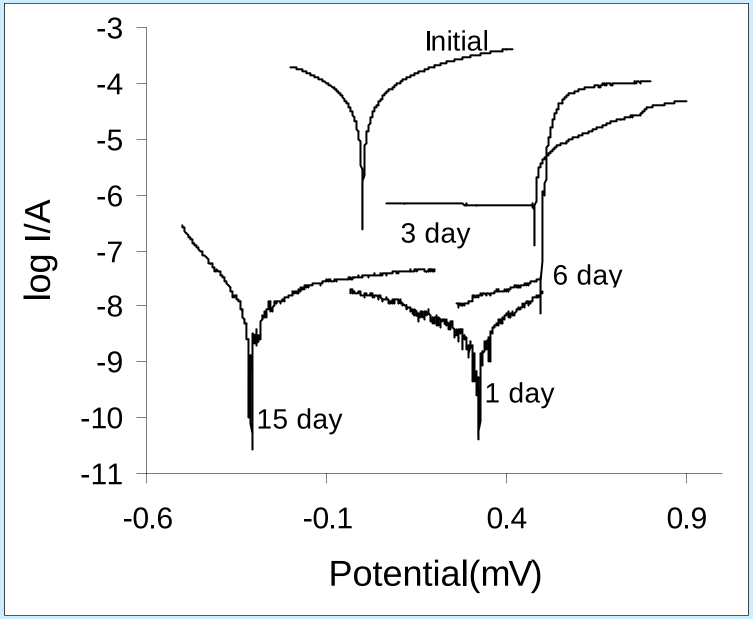
1. CONDUCTING POLYANILINE SYNTHEZED ON BULK SCALE (1 Kg)
2. DISPERSION COATING FORMULATIONS MADE
3. SS PLATES DIP COATED , DRIED, BAKED AT 55-60 C AND TESTED FOR CORROSION
4. TESTING ENVIRONMENT : 60 C, 3.5 Saline

ACCELERATED CORROSION TESTING OF PANI COATINGS :

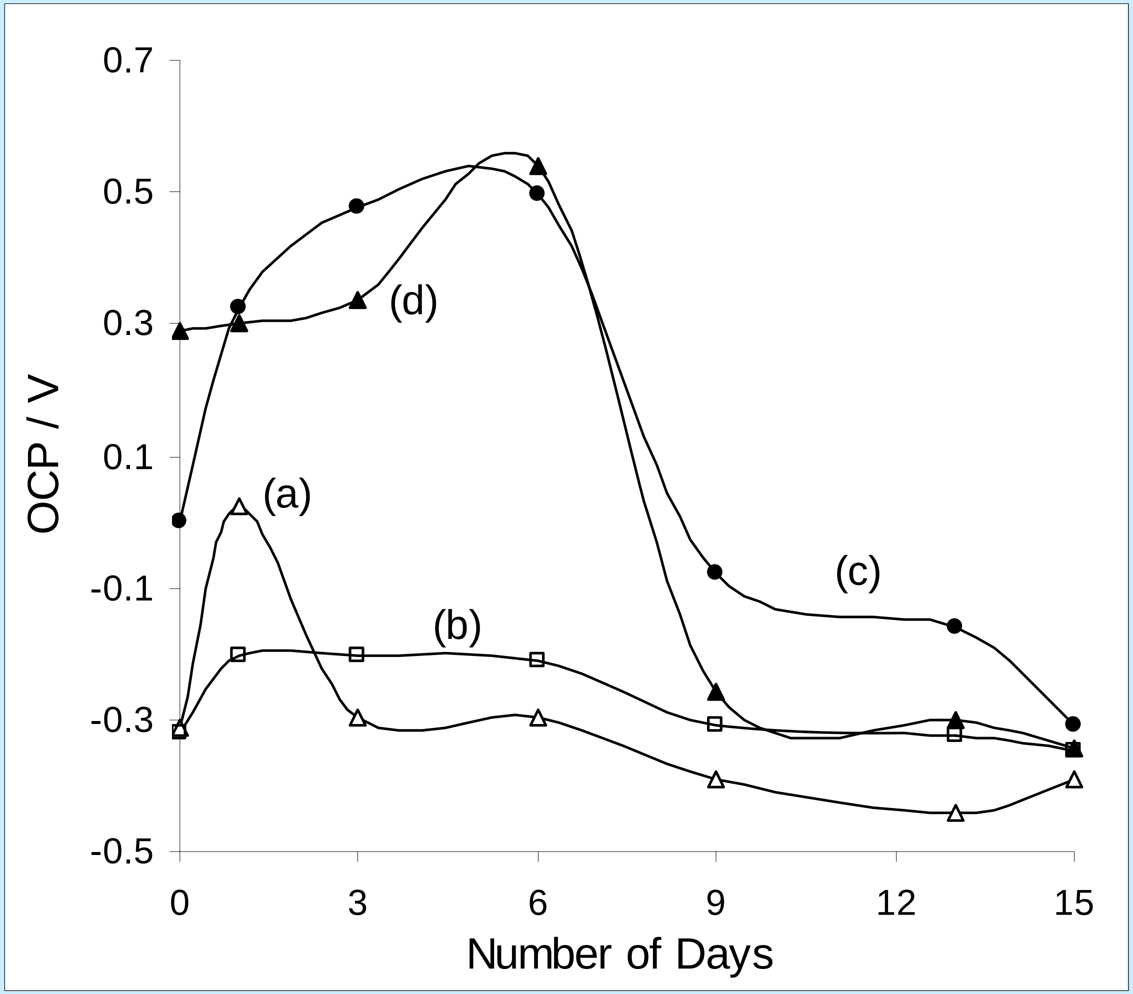


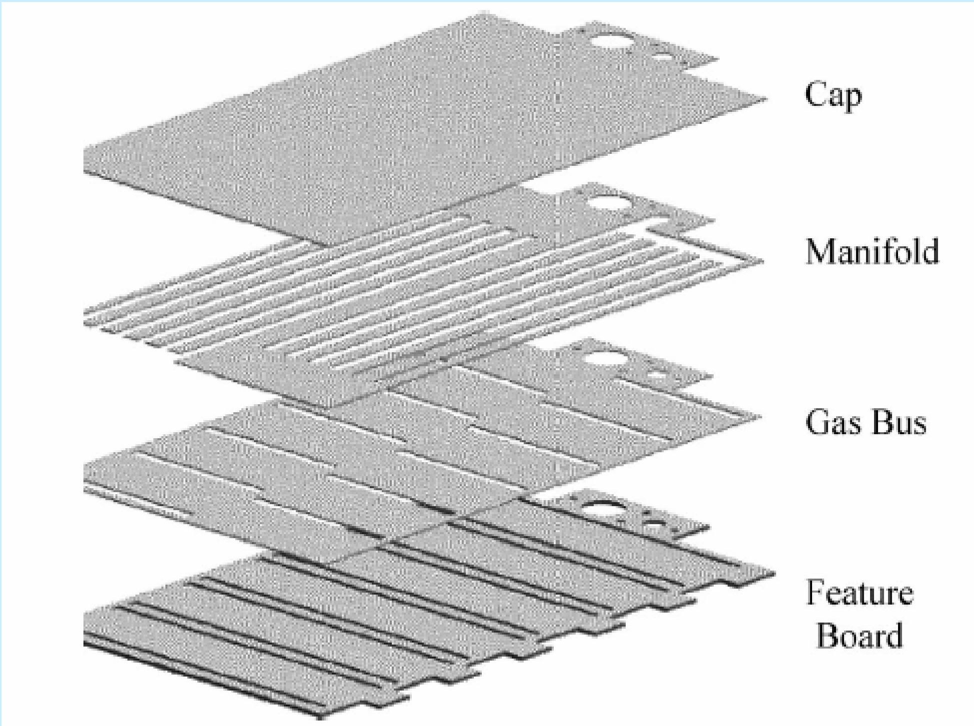


0% PANI +PVAc +ZnO

2% PANI +PVAc + ZnO

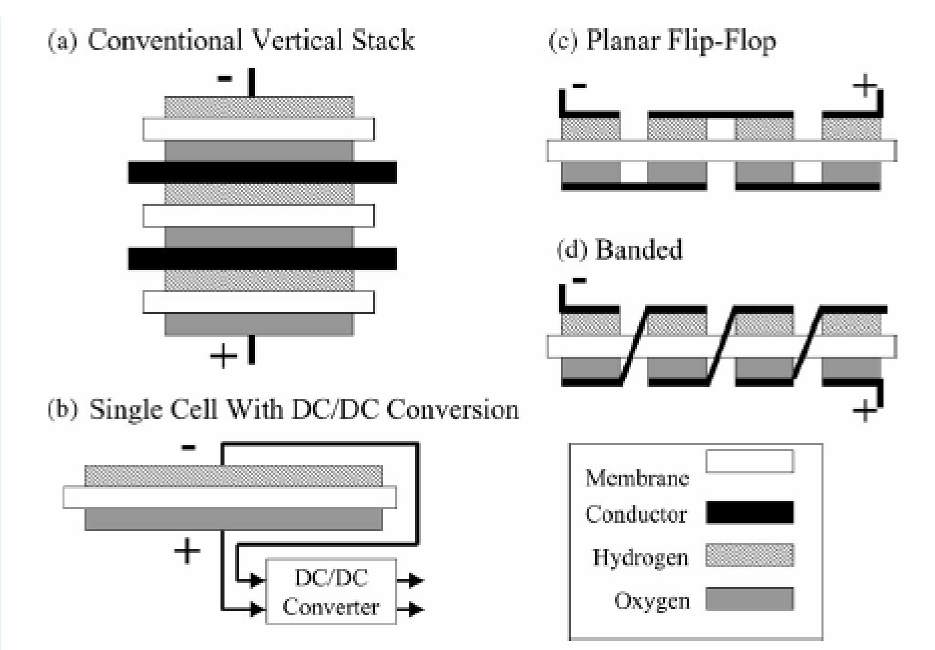
ACCELERATED CORROSION TESTING OF PANI COATINGS ON STEEL :





PCB Type FC stack

INTER CONNECTS
FOR PLANAR FC



Typical Thin Plates Reported for DMFC :

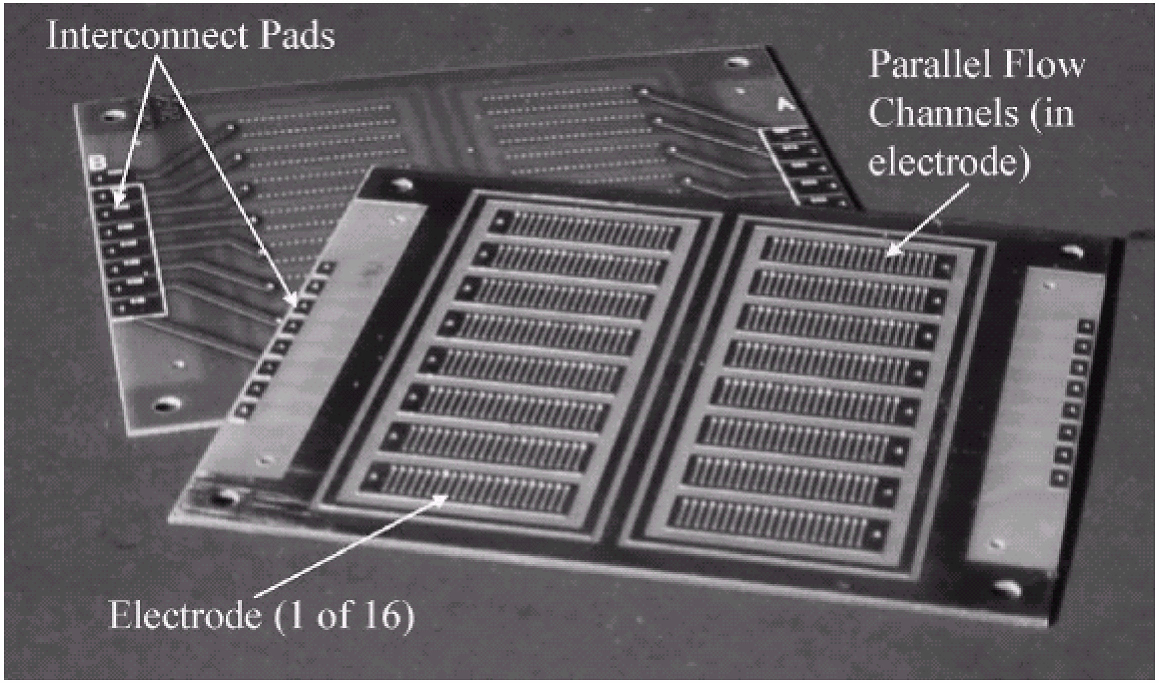
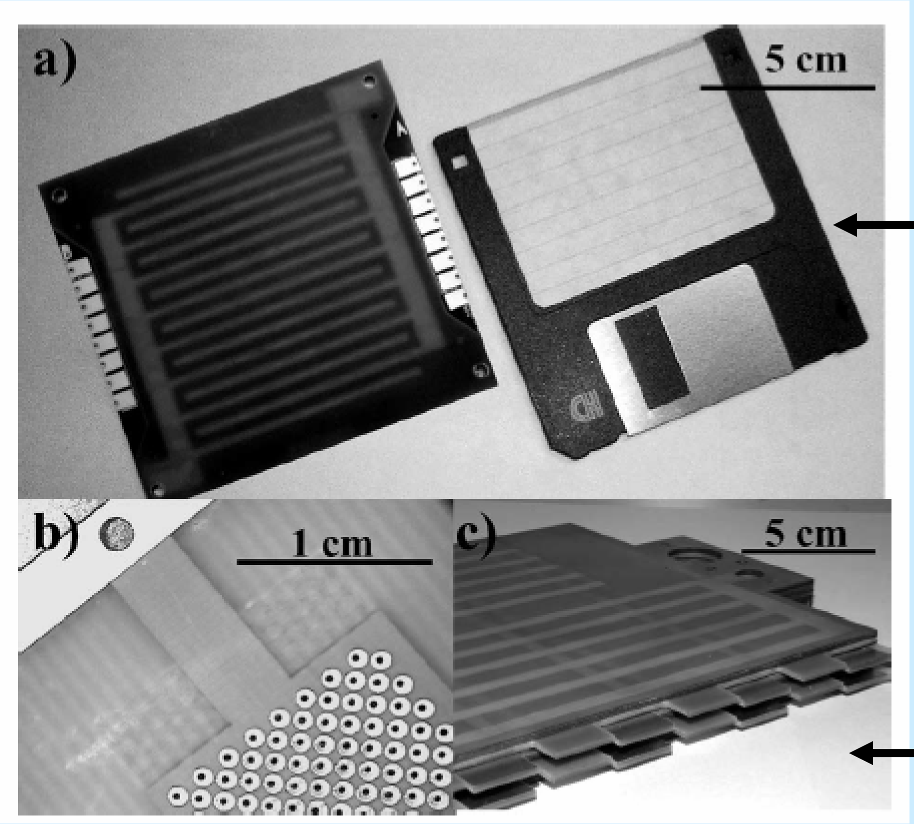


Fig. 3. Inner board detail which shows the array of 16 cell electrode contacts and the 16 perimeter interconnection pads of the third iteration "sea-serpent" PCB-FC prototype.

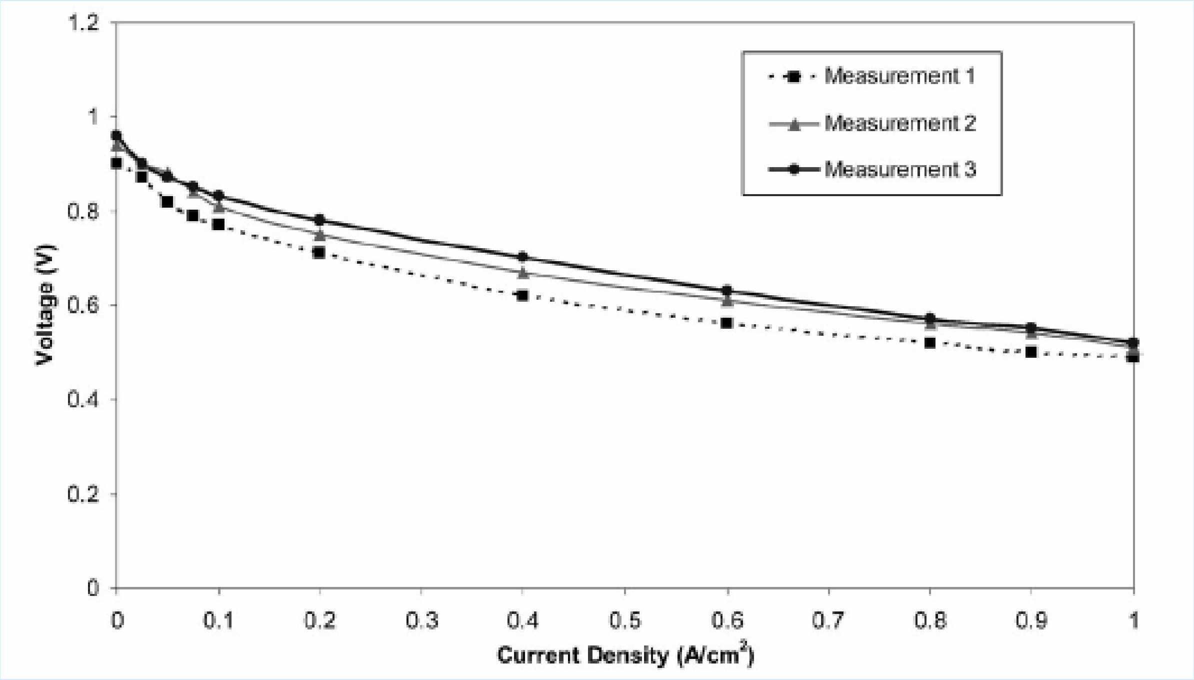
Fuel Cells : As thin as you can get !!



Floppy for comparison

Internal stack

PERFORMANCE OF THIN PCB TYPE FC



Mini and Micro fuel cells require very thin electrodes and bipolar connects

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Portable fuel cells using very thin configuration : screen printing technology

Toshiba announced the DMFC for Laptops

MTI Micro fuel cells- DMFC for Cell phone (Samsung)

ADVANTAGES OF NEW MATERIALS AND TECHNIQUES FOR BIPOLAR PLATES

NCL

- LARGE SCALE PRODUCTION POSSIBLE LEADING TO LOW COST
- HIGH TEMPERATURE (>500C) PROCESSING NOT REQUIRED
- LOW WASTAGE OF MATERIALS
- CONTACT RESISTANCE IS REDUCED (Graphite based plates have problems due to bolts tightening limits)
- MORE FLEXIBILITY FOR DESIGN
- WIDER RANGE OF MATERIALS CAN BE MADE AVAILABLE
- NEW HYBRID MATERIALS WITH MULTIPLE FUNCTIONALITY CAN BE TRIED

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THANK YOU