Nanotechnology for Energy Storage Applications

Dr. Siny Paul
Professor
MACE
Kothamangalam

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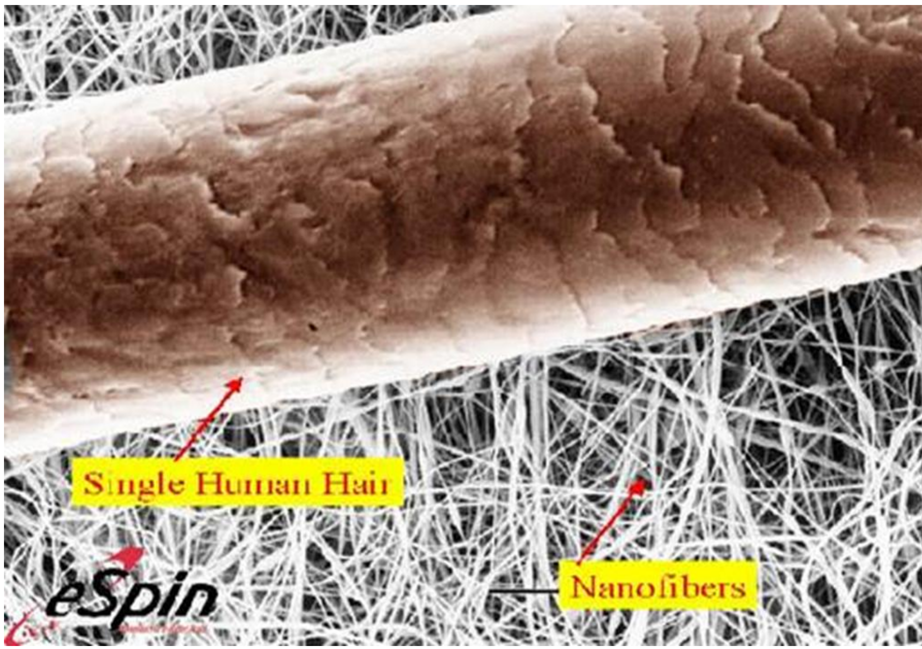
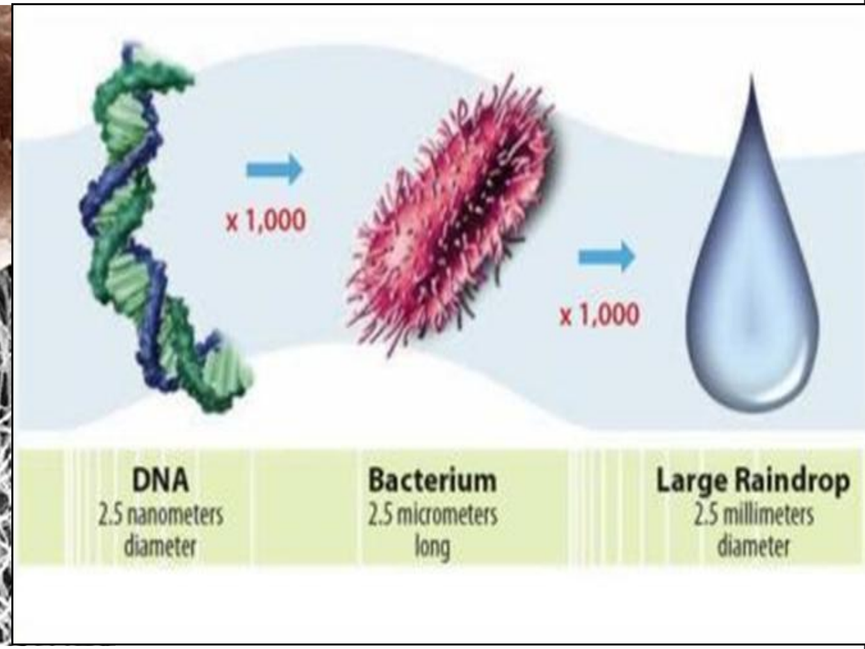
Size Scales

1 nm = 10^{-9} m

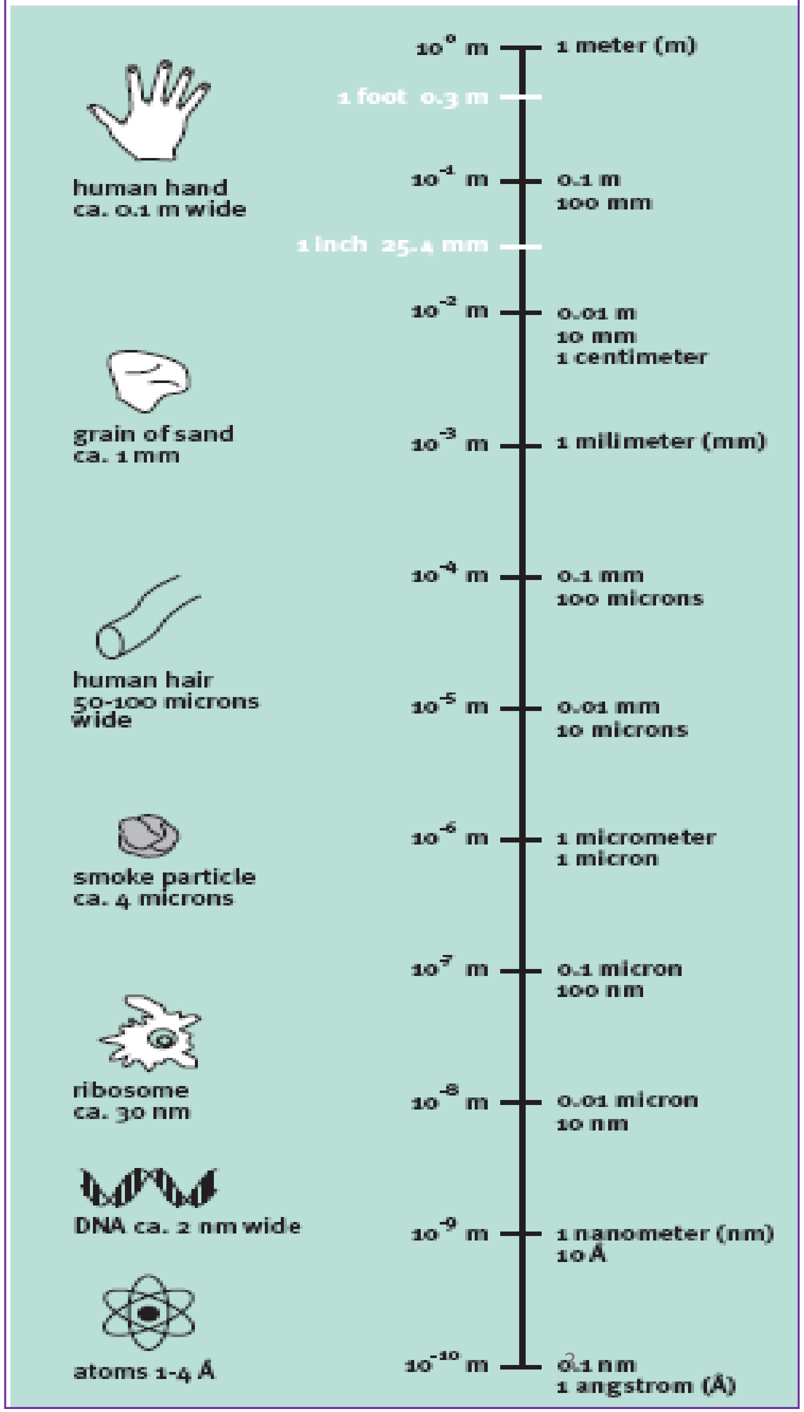
A human hair is of about 100 µm diameter





Nano scale

- **Nano particles are those** whose size is in the range of **1-100 nanometres.**
- Atomic scale in Angstroms (Å)
- Nanometre comes closer to atomic and molecular scales.

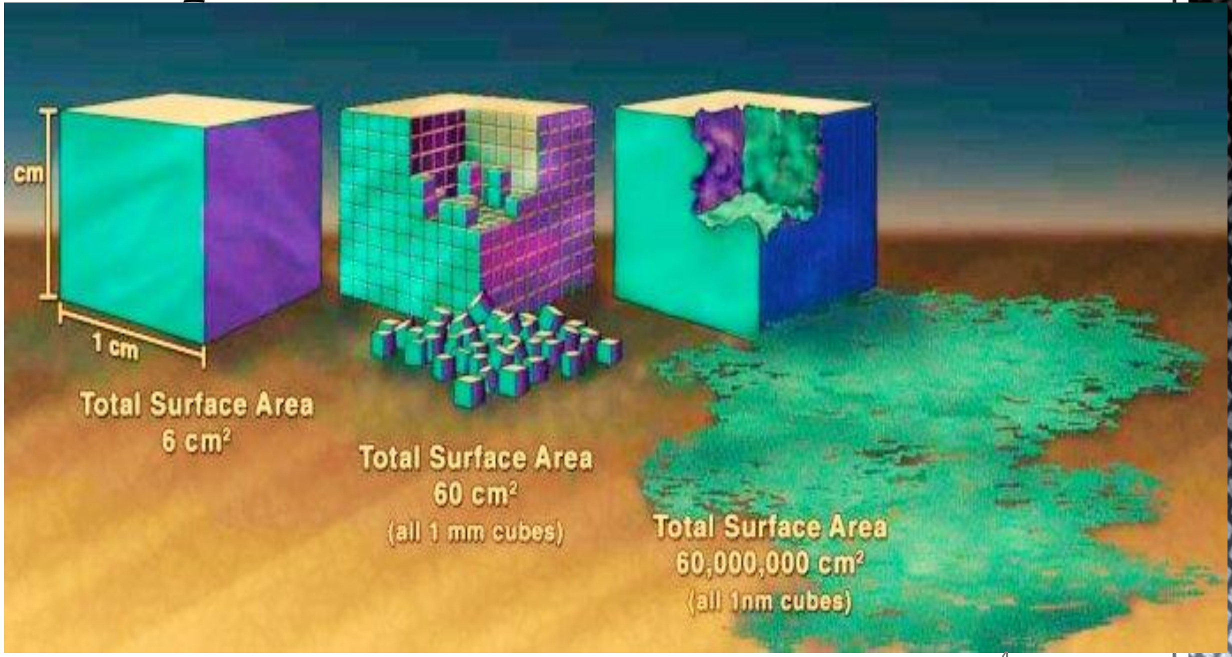


Why new properties

- *Properties of nano materials are very different from those at a larger scale.*

- *As a particle decreases in size, a greater proportion of atoms are found at the surface compared to those inside.*

If a cube is divided into smaller cubes by keeping volume same, there is a increase in surface area and hence the particles on the surface; which gets increases with further reduction in size.



Differences in properties

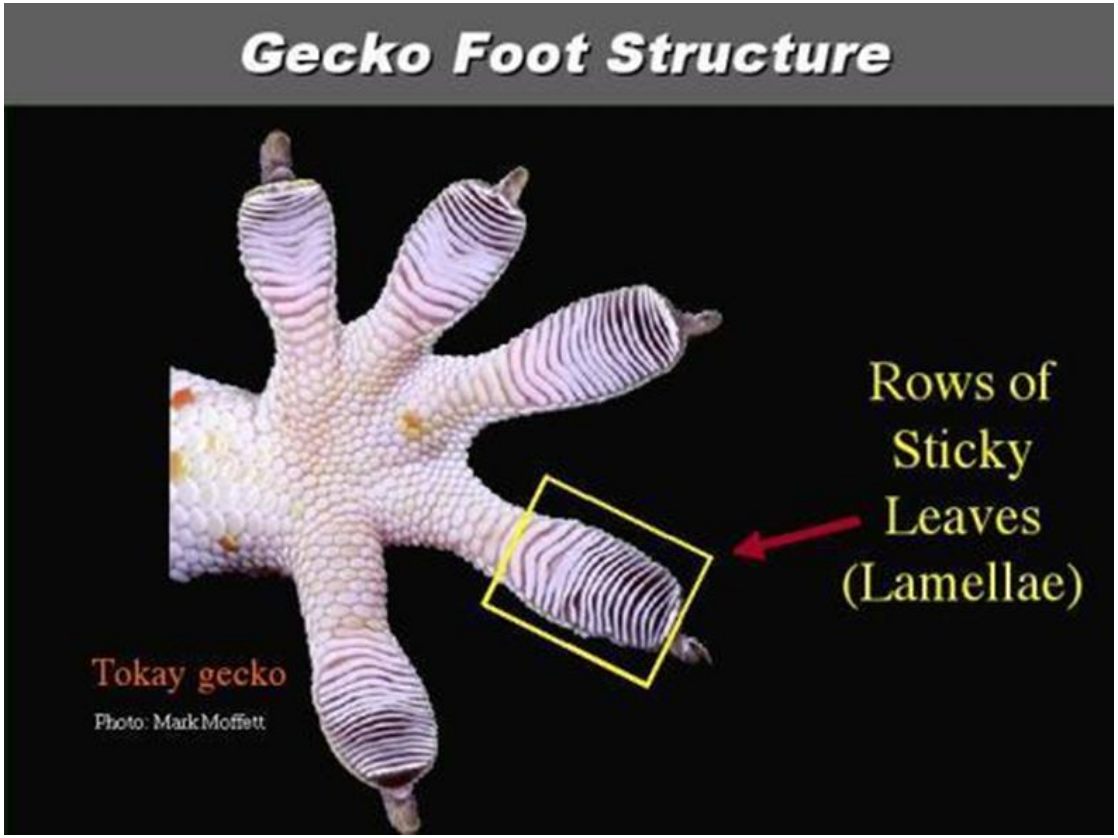
A particle of size 30 nm has 5% of its atoms on its surface
10 nm size particle - 20% of its atoms on the surface
3 nm size particle -50% of its atoms on the surface

- *surface to volume ratio is large.*
- *No of atoms per particle are reduced and almost every atoms reacts in chemical reactions because almost every atom is exposed.*

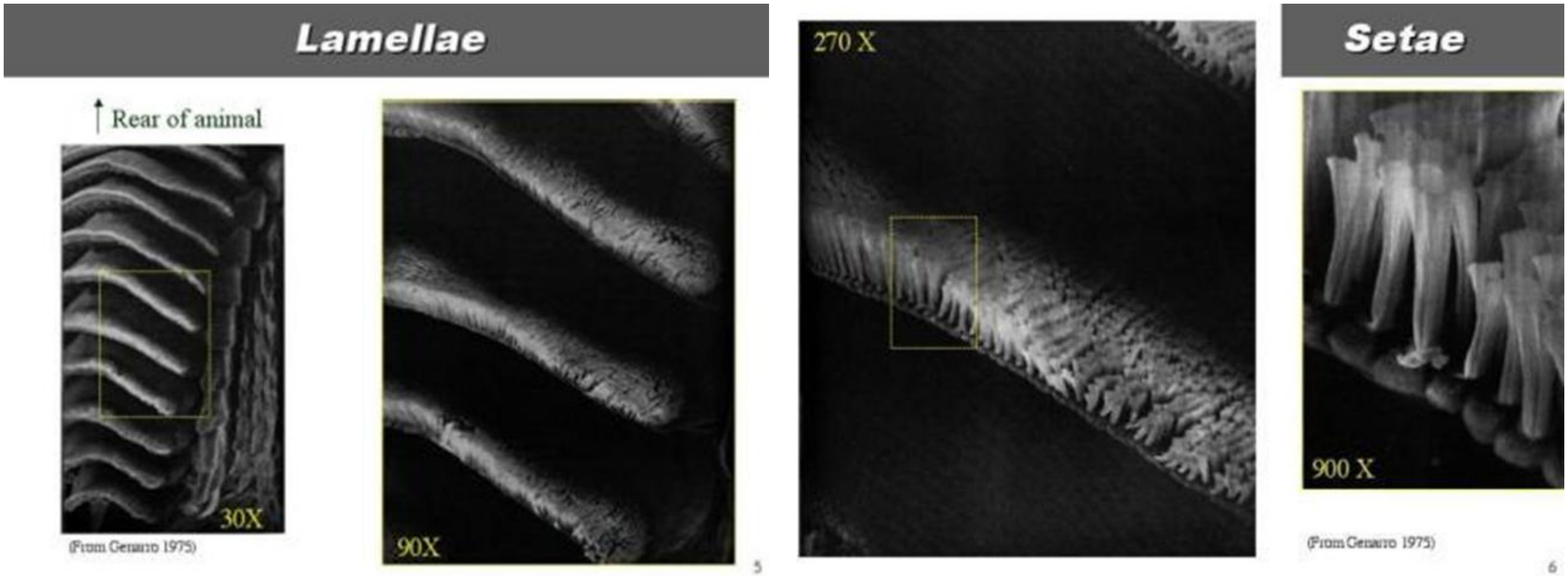
Van der Waals force

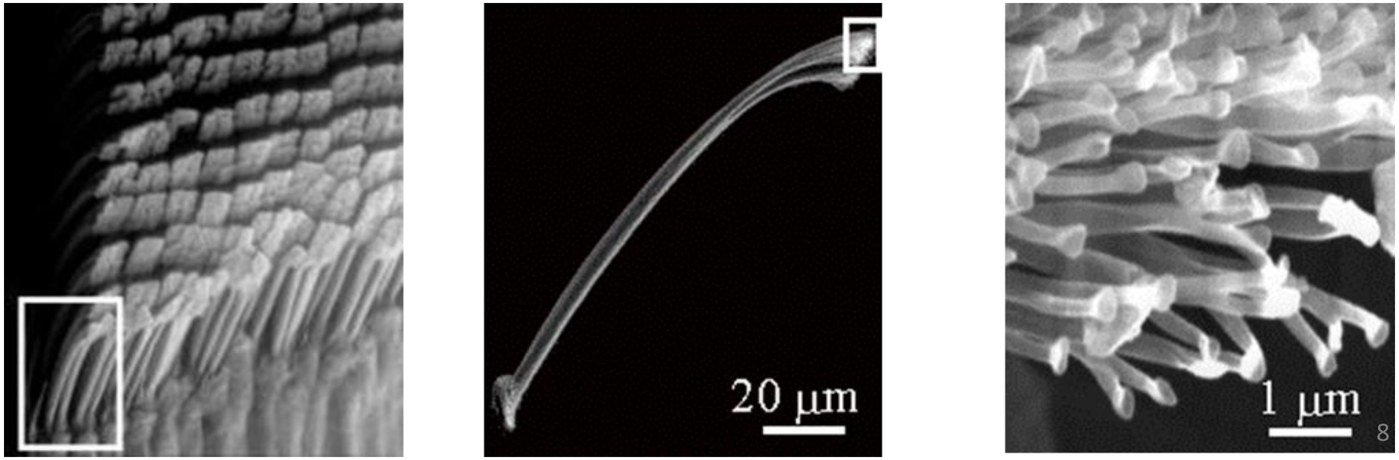
- An attractive force between atoms or molecules.
- Not the result of chemical bond formation, much weaker
- Responsible for some material properties: crystal structure, melting points, boiling points, surface tension, and densities.

Nano-adhesion mechanism of Gecko



Nano-adhesion mechanism of Gecko

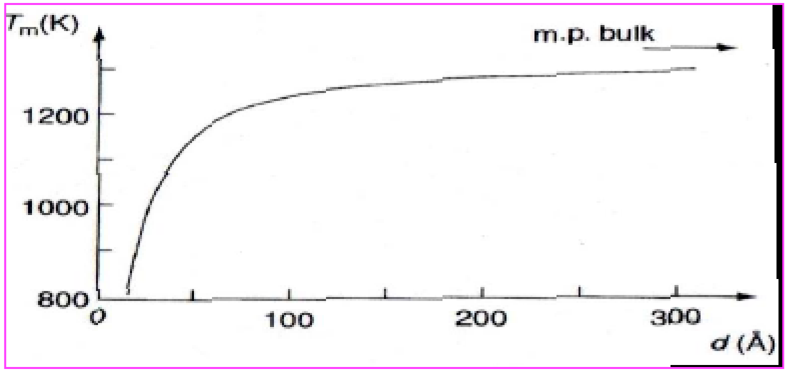




Differences in properties

- **Opaque materials will become transparent – copper**
- **Stable materials will become combustible – aluminum**
- **Insoluble materials will become soluble - gold**

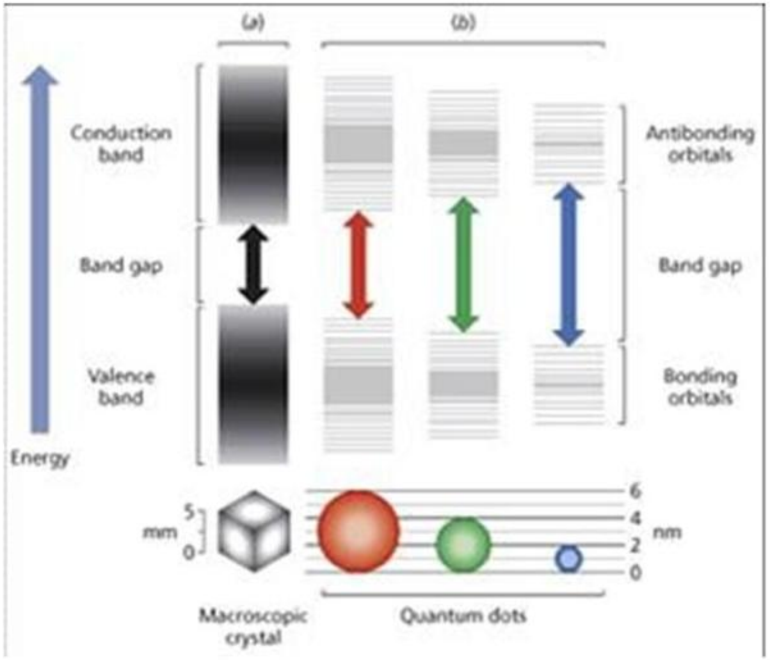
Melting points can be reduced up to 30%



Variation of melting point of copper with size

Properties that have always been considered as material constants inaccessible to engineering, are now subjected to human manipulation.

Differences in properties



Solutions of mono disperse CdSe nanocrystals with increasing diameter (2 to 7 nm) from left to right

Increase in the semiconductor band gap with decreasing semiconductor nano crystal size.

Historical development

The Lycurgus cup (British Museum, London), dating from the 4th century A.D., is made from glass impregnated with gold nanoparticles; seen in transmitted light

Lycurgus chalice

In diffused light In focused light

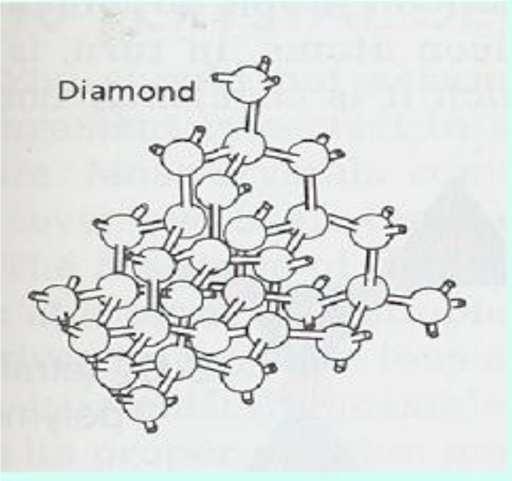
Manipulation of atoms

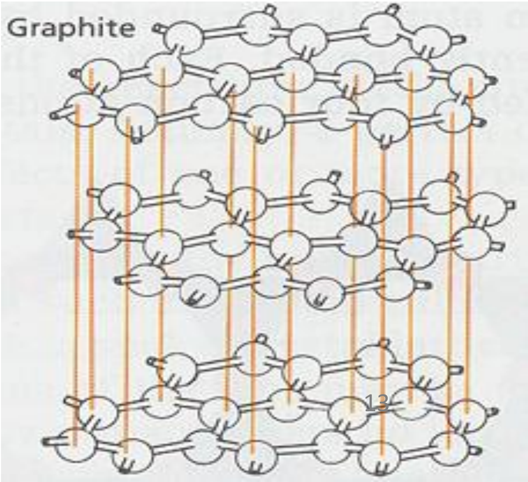
- By manipulating the position of the atoms or substituting one atom for another the properties of the material can be altered in a dramatic fashion
- If we rearrange the atoms in coal we can make diamond.

Carbon nanotube

- Pure carbon takes two forms: diamond and graphite.
- Tubular cylinders of carbon atoms.
- CNT diameter as small as 1nm.

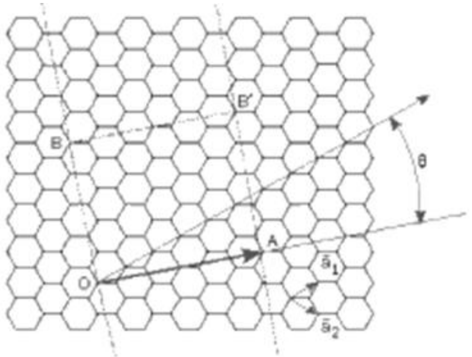
  Length: few nm to microns.
- Thirty times stronger than steel, at one sixth the weight.
- Electrical conductivity is six times that of copper.
- Very high current carrying capacity.

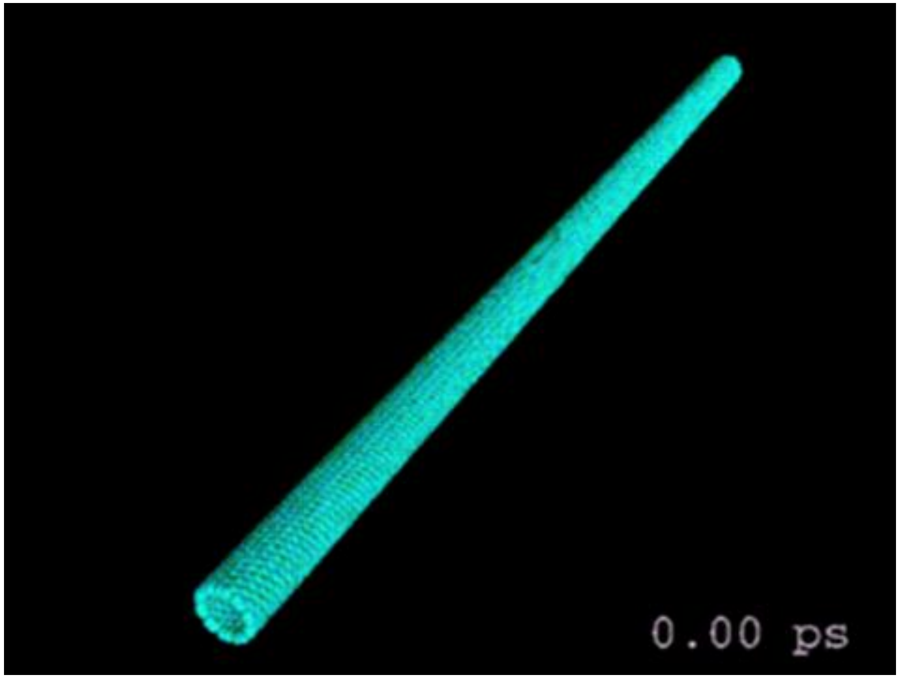


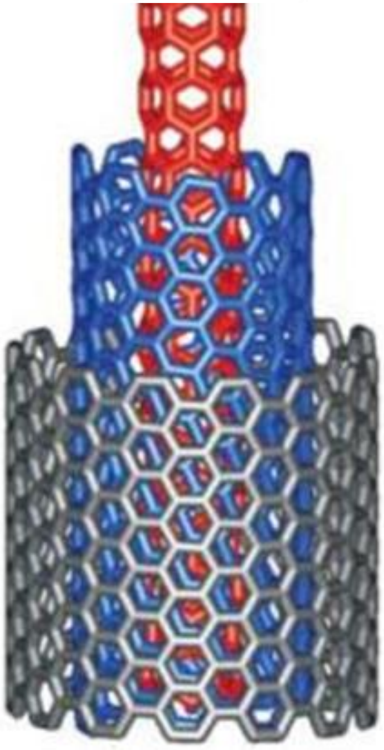


Carbon nanotube

- Hexagonal sheet of carbon atoms (graphene sheet) rolled into 1D cylinder
- “Classes” of nanotubes: SWNTs, MWNTs, and NT ropes or bundles





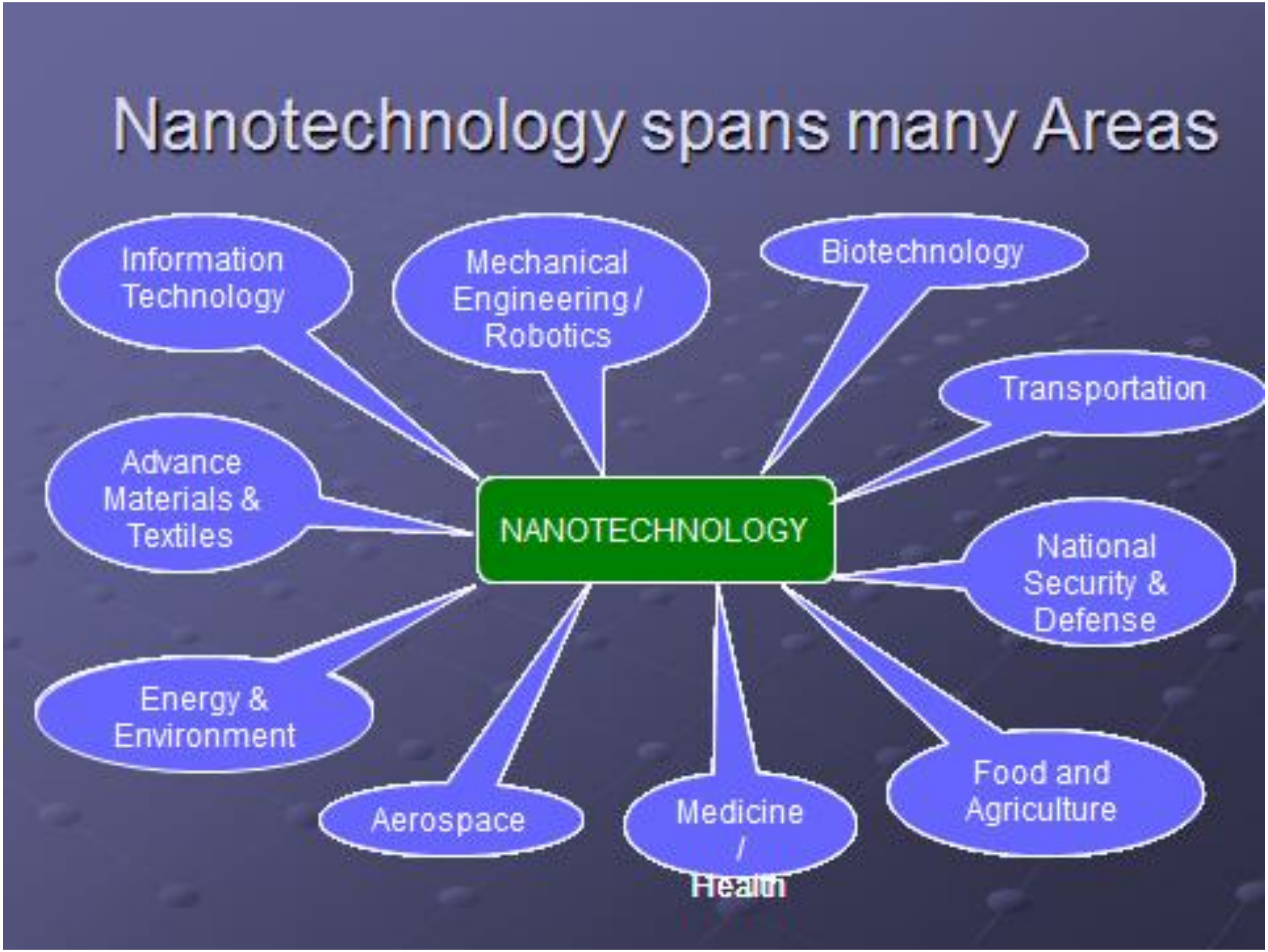


Properties of Carbon Nanotubes

Going to Extremes

PROPERTY	SINGLE-WALLED NANOTUBES	BY COMPARISON
Size	0.6 to 1.8 nanometer in diameter	Electron beam lithography can create lines 50 nm wide, a few nm thick
Density	1.33 to 1.40 grams per cubic centimeter	Aluminum has a density of 2.7 g/cm^3
Tensile Strength	45 billion pascals	High-strength steel alloys break at about 2 billion Pa
Resilience	Can be bent at large angles and restraightened without damage	Metals and carbon fibers fracture at grain boundaries
Current Carrying Capacity	Estimated at 1 billion amps per square centimeter	Copper wires burn out at about 1 million A/cm^2
Field Emission	Can activate phosphors at 1 to 3 volts if electrodes are spaced 1 micron apart	Molybdenum tips require fields of 50 to 100 V/µm and have very limited lifetimes
Heat Transmission	Predicted to be as high as 6,000 watts per meter per kelvin at room temperature	Nearly pure diamond transmits 3,320 W/m-K
Temperature Stability	Stable up to 2,800 degrees Celsius in vacuum, 750 degrees C in air	Metal wires in microchips melt at 600 to 1,000 degrees C
Cost	$1,500 per gram from BuckyUSA in Houston	Gold was selling for about $10/g in October

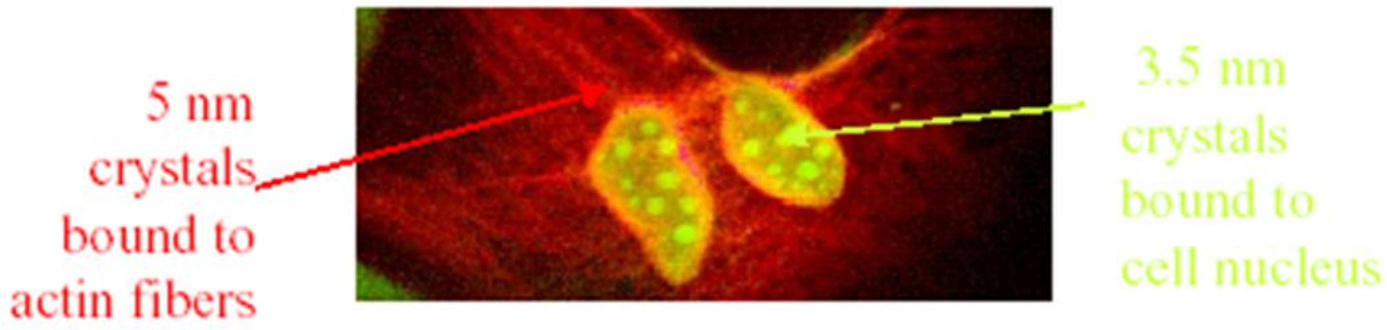
LAURIE GRACE


Nanotechnology spans many Areas
Information Technology
Mechanical Engineering / Robotics
Biotechnology
Transportation
Advance Materials & Textiles
NANOTECHNOLOGY
National Security & Defense
Energy & Environment
Aerospace
Medicine / Health
Food and Agriculture

Medical Applications of Nanotechnology

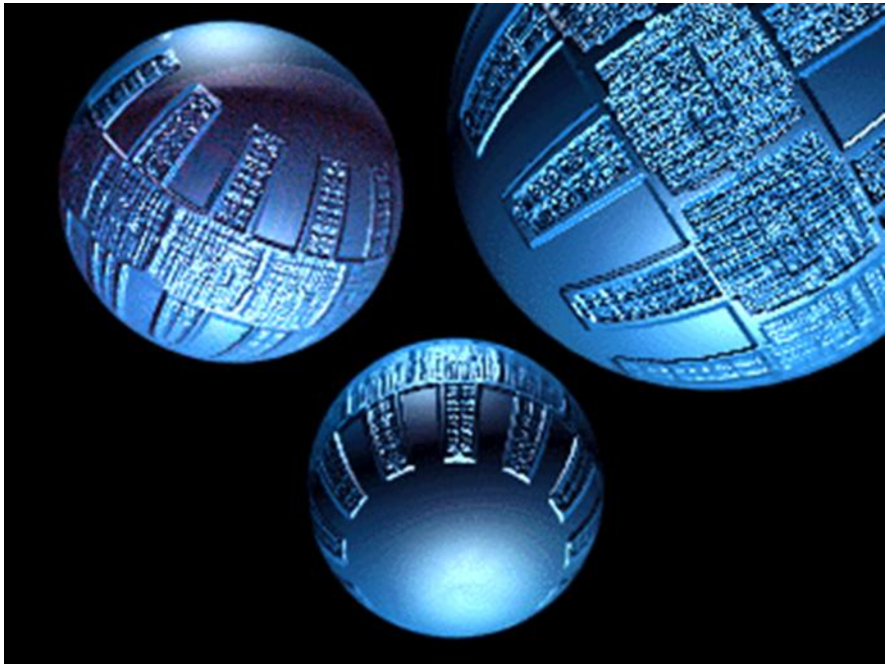
- Current Research
  - Nanocrystals as fluorescent biological labels
  - Magnetic Nanoparticles (scanning)
  - Tissue Engineering
  - DNA Chips
  - Nanorobots, Respirocytes
  - NEMS - Cell Repair Machines

Nanocrystals as Fluorescent Biological Labels



- Significant advantages over conventional dyes:
- Reduced photobleaching
- Multi-color labeling, parallel screening
- Infrared labels, blood diagnostics
- Molecular size nanocrystals are bio-compatible, with many other possible applications

Respirocytes: A Mechanical Artifical Red Blood Cell

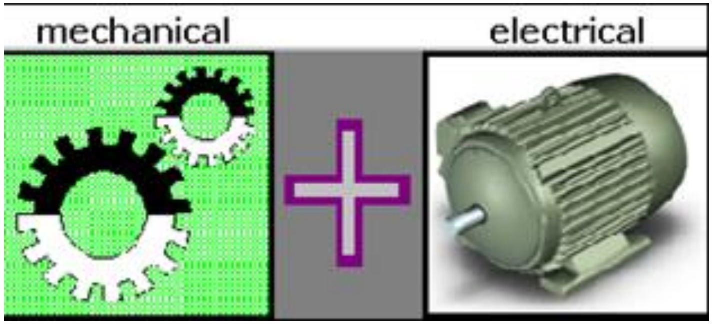


http://bionano.rutgers.edu/mru.html

Able to deliver 236 times more oxygen to the tissues per unit volume than natural red cells.

MEMS/NEMS

- MEMS/NEMS stands for **Micro/ Nano Electro Mechanical Systems**.
- It is a technique of combining Electrical and Mechanical components together on a chip, to produce a system of miniature dimensions .



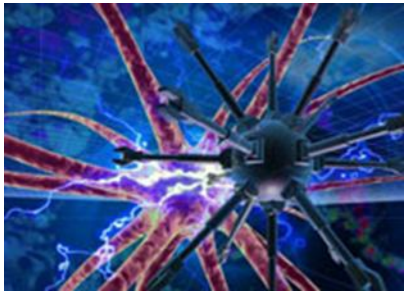
- By miniature, we mean dimensions less than the thickness of human hair !!!!

- ➢ Biomedical MEMS /NEMS
- ➢ Biotelemetry, Drug delivery
- ➢ Precision surgery
- ➢ Biosensors and other physical sensors
- ➢ Diagnostics, gene sequencing, Drug discover
- ➢ Pathogen detection

Micro/Nano Robots

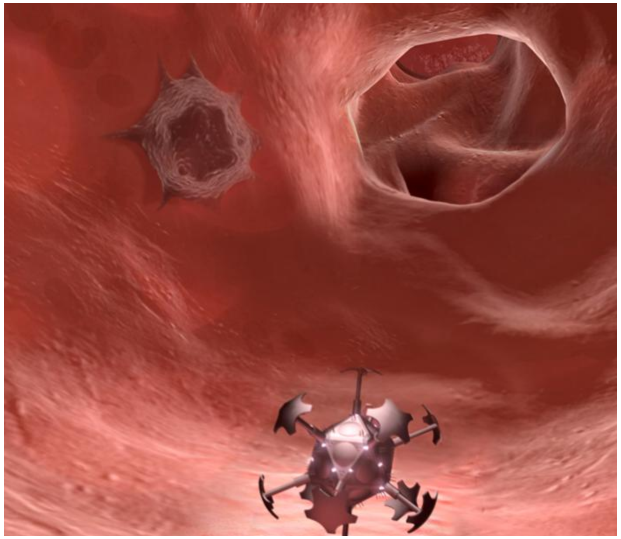
These are micro/nano scale devices capable of treating and eliminating medical problems.

- Such problems may arise due to the accumulation of unwanted organic substances, which interfere with the normal body functions, such as :
  - Tumors
  - Life threatening blood clots
  - Accumulation of scar tissue
  - Arterial blockage
  - Localized sites of infection.



Removal of the diseased area/cancerous cells

- Fatty material deposited on the arterial walls causing artery blockage, can be physically removed using nanoblades.



- Physically shredding tumor can pose a great threat. The pieces can be carried to other locations and result in furthering of cancerous cells.

- One effective approach to kill the cancerous cells would be to enclose the entire tumor in a nano box and destroying everything in the box.

Nanotechnology Applications in Civil Engineering

- Nano silica and clinker used to increase densification and hence mechanical properties and durability of cement.
- Service life can be doubled through the use of nano-additive viscosity enhancers which reduce diffusion of harmful agents in concrete.
- Photocatalytic TiO_2 nanoparticles added to concrete to reduce harmful gas emissions.

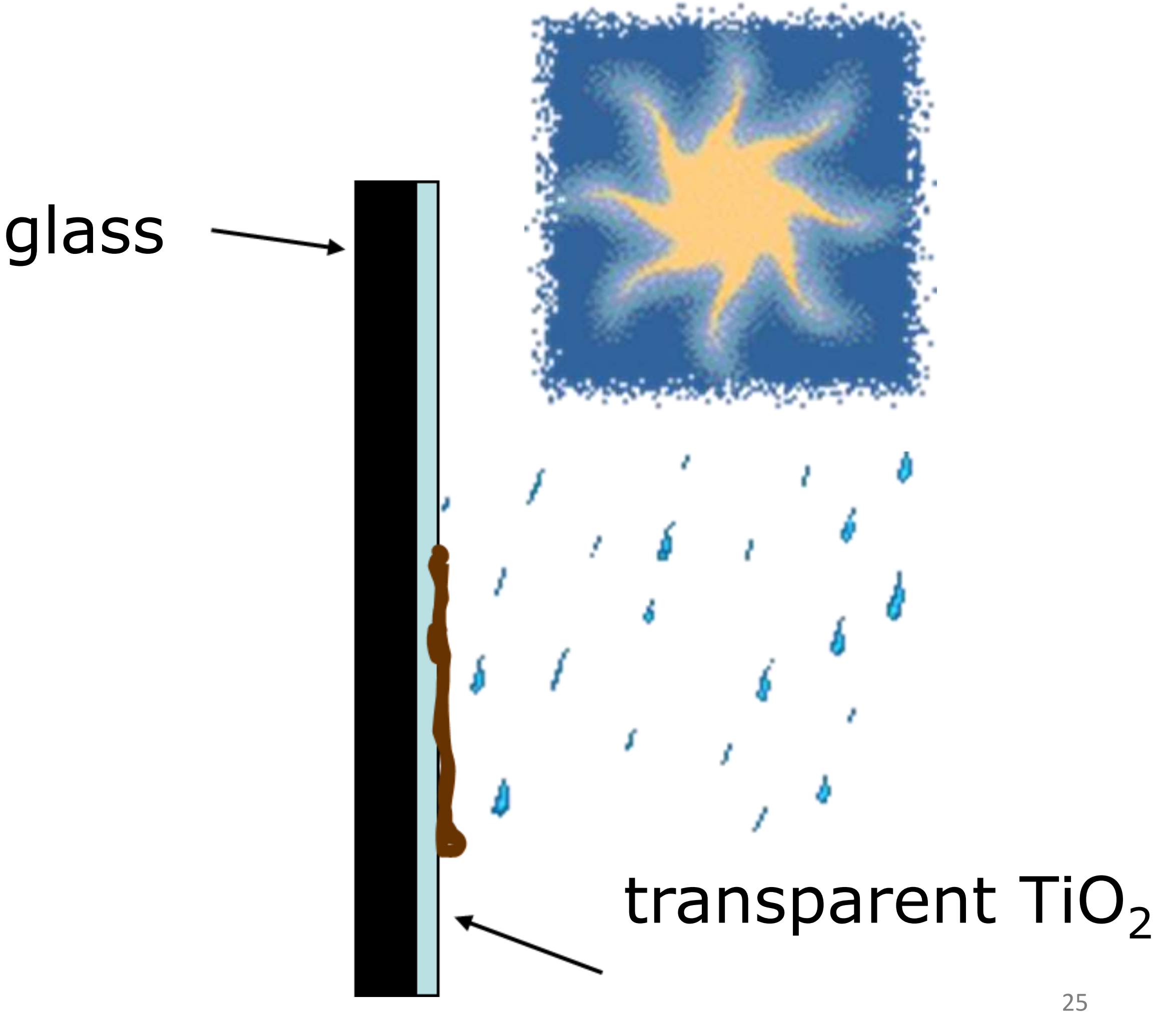
Coatings

- Thin film, clear nanocomposites for improved scratch and mark properties.
- Antimicrobial, self-cleaning surfaces.
- Smart coatings: Sense pressure, impact, damage, chemicals, heat, light, etc.

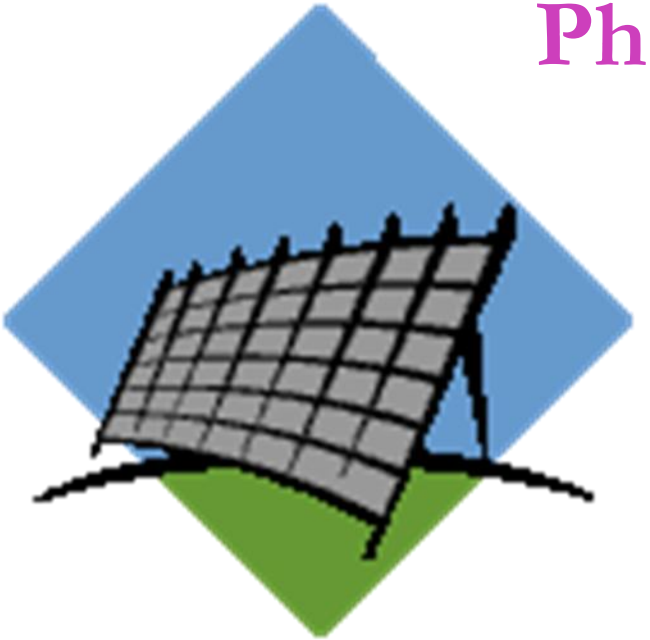
Nano-TiO_2 coated Self-cleaning glass

conventional glass

self-cleaning glass

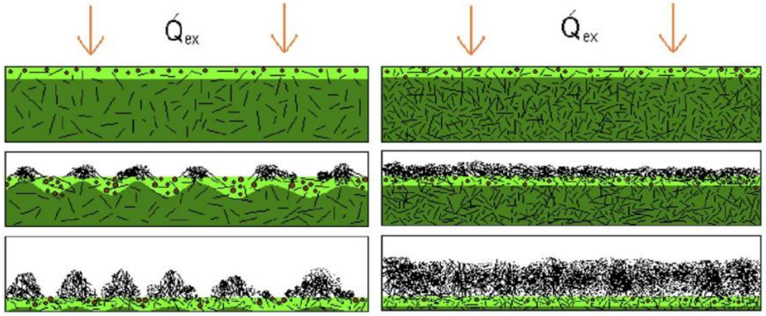


Photovoltaics



- Predominant photovoltaic material is silicon, but an emerging technology involves the use of dye-sensitized nano-TiO_2.
- Large surface area of nano TiO_2 greatly increases photovoltaic efficiency.
- Also has potential for lower material costs and processing costs relative to conventional solar cells.

Fire retardants



(a) (b)

- Use of nano additive fire retardants prompted by bans on halogenated flame retardants enacted in many states.
- Polymer nanocomposites filled with clay, CNTs, etc., possess improved flammability resistance while maintaining or improving mechanical properties.
- Reduces heat release rate during fire event by formation of surface char which insulates underlying material.

- Carbon nanotubes based membranes for water de-salination and nanoscale sensors to identify contaminants in water system.

Applications in Mechanical Engineering

- NEMS
- Nanorobots
- Nanofluids
- Coolants
- Lubrication oil
- Fuel

Applications in Electronics

Nanoelectronics

- Increasing the density of memory chips - Using nanosized magnetic rings to make Magnetoresistive Random Access Memory (MRAM) which may allow memory density of 100 tera byte per square inch.

- Using carbon nanotubes to direct electrons to illuminate pixels, resulting in a lightweight, flexible, low power, millimeter thick "nanoemmissive" display panel.

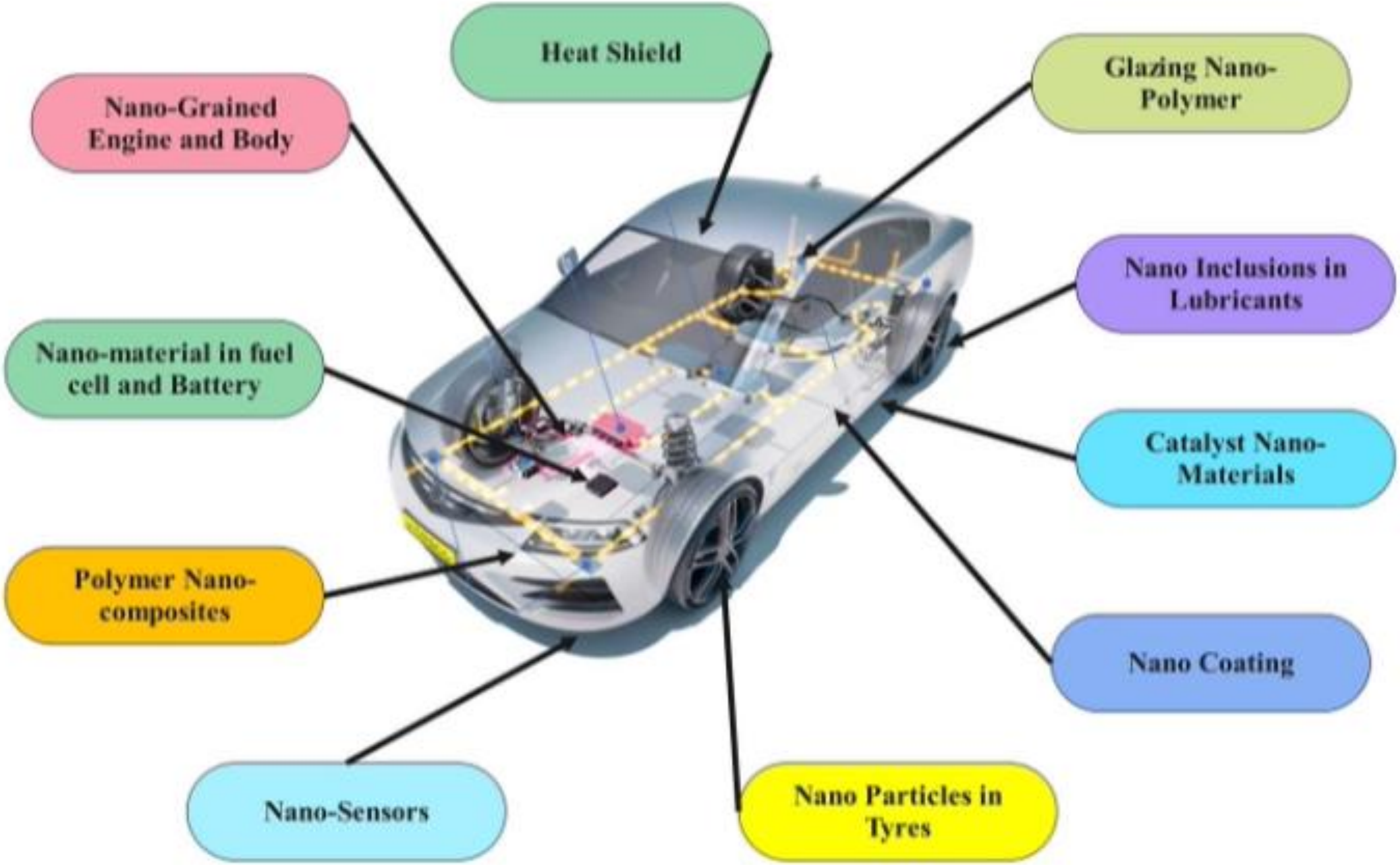
- Developing molecular-sized transistors which may allow us to shrink the width of transistor gates to approximately one nm which will significantly increase transistor density in integrated circuits.

Applications in Electrical Engineering

Nanodielectrics

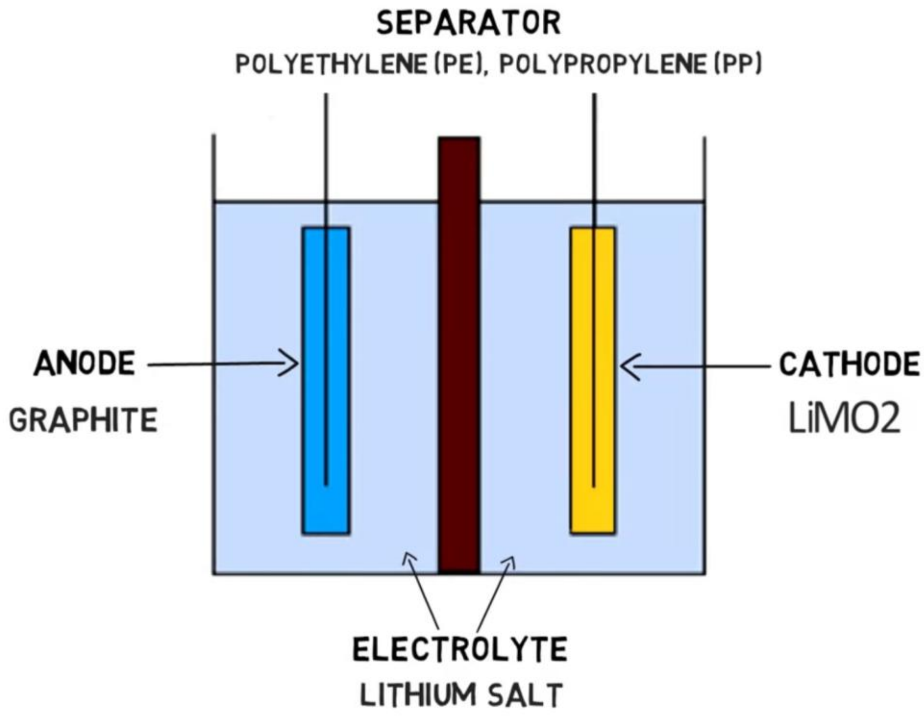
- Pioneering Work of T. J. Lewis In 1994.
- T. J. Lewis first suggested the concept of nanodielectric materials.
- Dielectric materials with nanostructures or nanoparticles embedded.
- Emerging need of power engineers to design new electrical insulation systems that are capable of withstanding higher voltage levels.
- Energy storage applications.

Nanotechnology Applications in Electric Vehicles



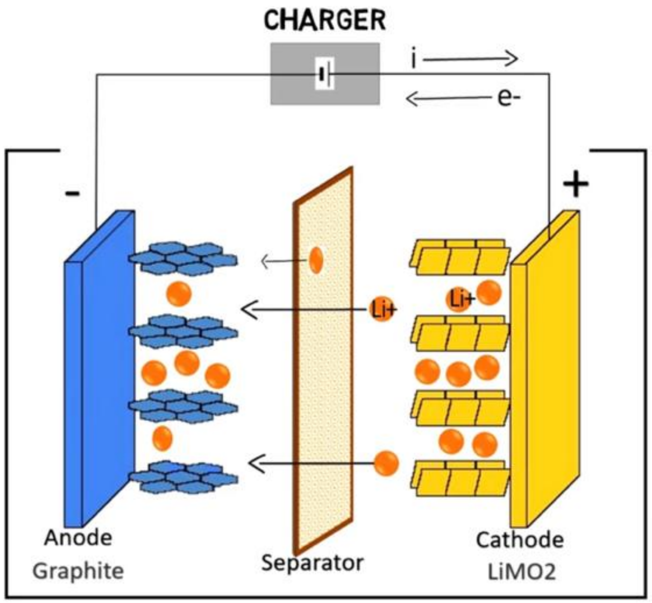
NANO-ENHANCED BATTERIES FOR ELECTRIC VEHICLES

Lithium ion battery



- High Energy density
- Light weight
- Long life span
- Fast charging
- Low self discharge
- Temperature tolerance

Working of Lithium ion battery



AT CATHODE

$$LiMO_2 \rightarrow Li^+ + MO_2 + e^-$$

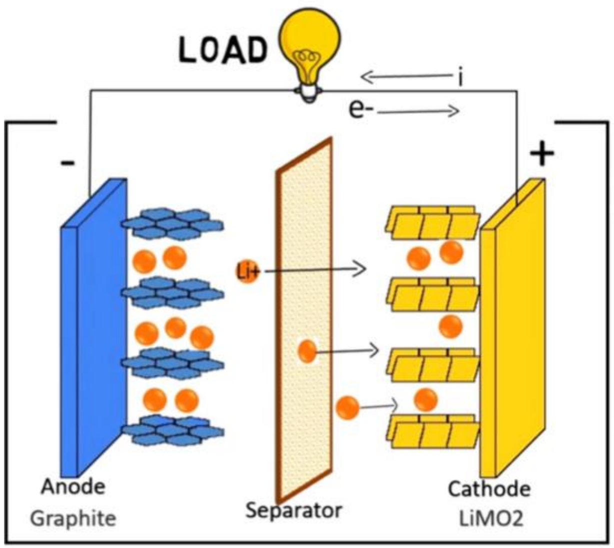
AT ANODE

$$C_6 + Li^+ + e^- \rightarrow LiC_6$$

CELL REACTION:

$$LiMO_2 + C_6 \rightarrow MO_2 + LiC_6$$

Working of Lithium ion battery



AT CATHODE

$$MO_2 + Li^+ + e^- \rightarrow LiMO_2$$

AT ANODE

$$LiC_6 \rightarrow C_6 + Li^+ + e^-$$

CELL REACTION

$$MO_2 + LiC_6 \rightarrow LiMO_2 + C_6$$

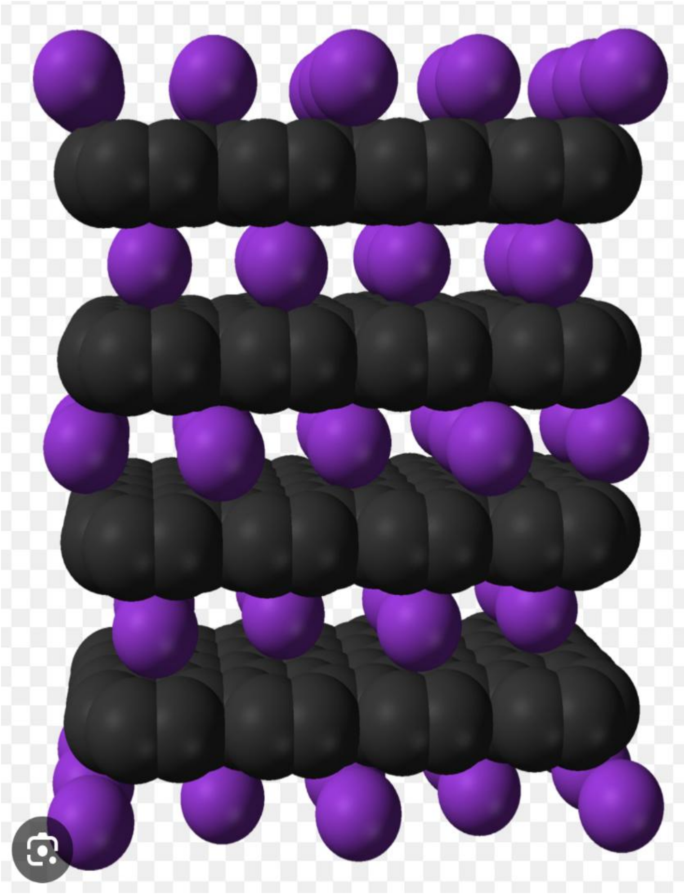
NANOTECHNOLOGY FOR EV BATTERIES

- Nanotechnology modifies battery components at the atomic and molecular levels to enhance performance metrics.

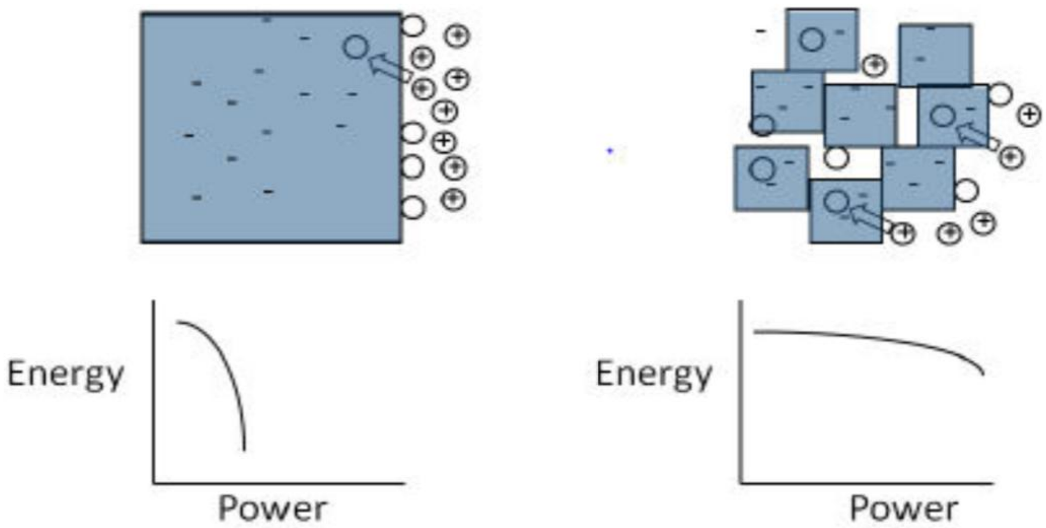
- Key Benefits:
  - **Higher Energy Density**: Nanostructures provide more storage per unit weight
  - **Faster Charging Rates**: Enhanced conductivity reduces charge time.
  - **Improved Durability**: Nanoscale materials reduce degradation over cycles
  - **Safety Improvements**: Reduces risks like overheating and dendrite formation

1. CARBON NANOMATERIALS IN THE ELECTRODES

- For lithium-ion batteries, negative electrode graphite powder has been used as an intercalation material.
- Intercalation is the inclusion or insertion of molecules into layered materials with layered structures.
- If micrometer-sized powder were replaced with carbon nanomaterials (e.g., carbon nanotubes), then the rate of insertion/ removal of lithium can be improved.
- The carbon nanotubes can bind to much higher concentrations of lithium because they have a high surface area.
- The current density and efficiency will be increased



2. NANOPHOSPHATE TECHNOLOGY

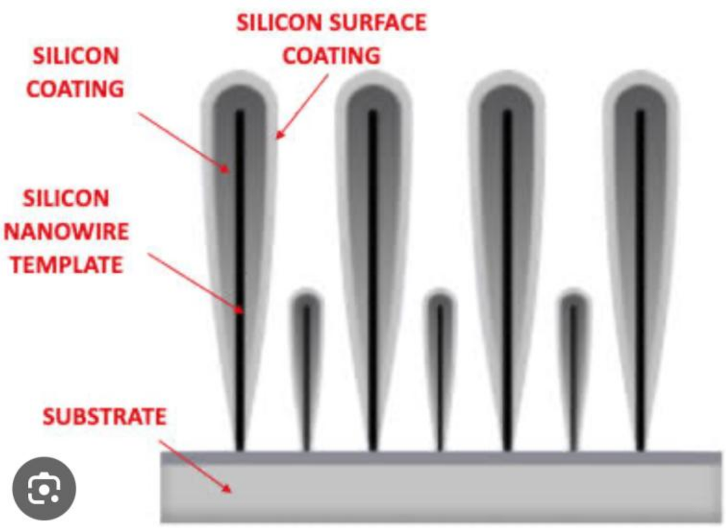


- Nanophosphate technology increases the cathode surface area with the electrolyte, which allows for faster lithium insertion and thus more power.

- In the case of most metal oxide cathode materials, including cobalt and nickel-based materials, only half of the available lithium is transferred during normal operation.

3. SILICON NANOWIRE ANODES

- Replaces graphite anodes with silicon nanowires to increase lithium capacity
- Silicon anodes can theoretically store up to 10x more lithium than graphite



- Nanowire structures allow silicon to expand/contract without cracking
- Benefits:
  - ➢Dramatic increase in energy density
  - ➢Longer range and/or lighter battery designs possible for EVs

4. LITHIUM-SULFUR BATTERIES WITH NANO-COATINGS

- Coatings like carbon or polymer nanolayers act as barriers to prevent sulfur dissolution
- Nano-coatings on sulfur cathodes to prevent polysulfide leakage, a common issue in lithium-sulfur batteries

Benefits:

- 3–5 times the energy density of lithium-ion batteries
- Potentially lower-cost materials

5. GRAPHENE NANOSHEETS FOR FAST CHARGING

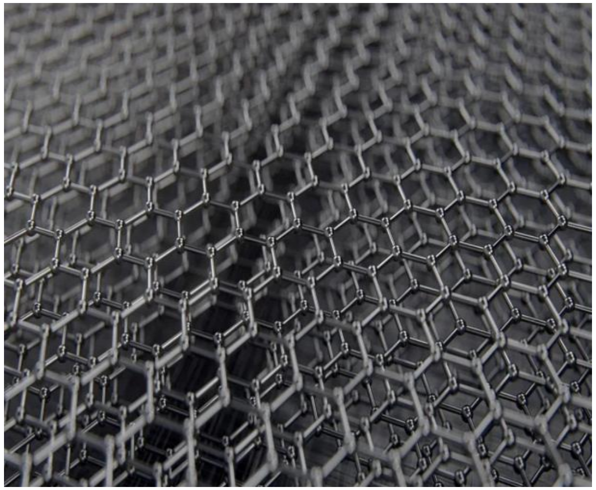
- Graphene nanosheets improve electrode conductivity, enabling faster charging cycles
- Graphene's high electron mobility allows for faster electron transfer
- Thin, flexible sheets prevent overheating during fast charging

Benefits:

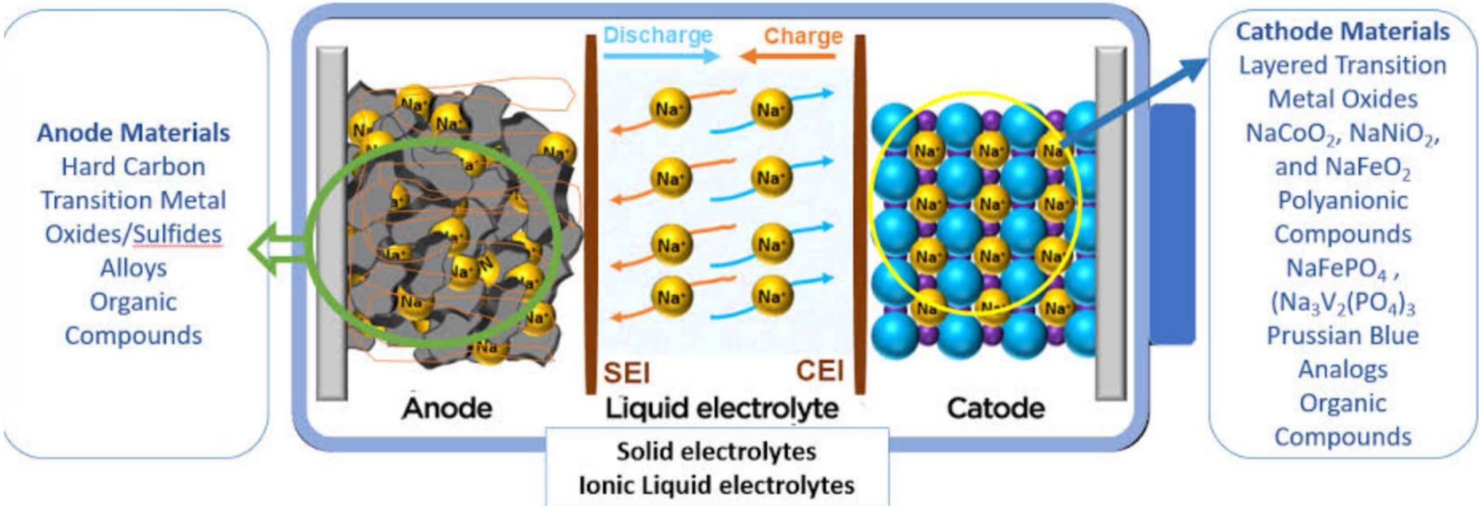
- Drastically reduced charging time (potentially within minutes)
- Improved thermal stability, reduced risk of thermal runaway

Applications:

- High-performance EVs, smartphones, laptops



6. IRON-BASED NANOPARTICLES FOR SODIUM-ION BATTERIES



- Iron and sodium are more abundant and less costly than lithium and cobalt
- Nanoparticles improve sodium-ion battery stability and efficiency

Benefits:

Lower environmental impact and sustainable material sourcing

Reduced production costs, making it accessible for large-scale applications

Advantages:

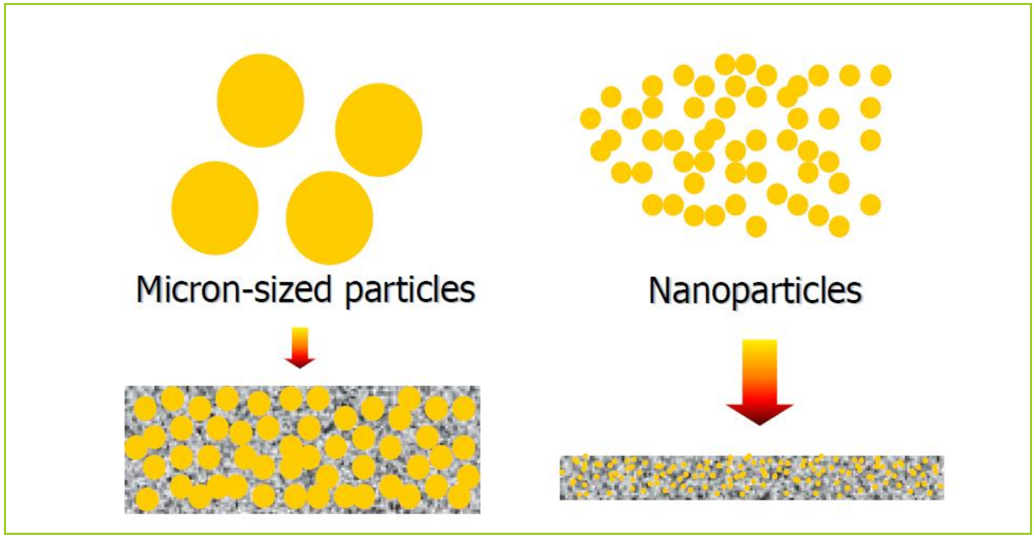
Grid storage, affordable EVs, and applications where cost efficiency is key

ADVANTAGES OF NANO-ENHANCED BATTERIES

- Higher energy density and faster charging for longer range
- More eco-friendly materials, reducing environmental impact
- Safer batteries with less risk of overheating and degradation
- Higher efficiency

POLYMER NANOCOMPOSITES FOR ENERGY STORAGE APPLICATIONS

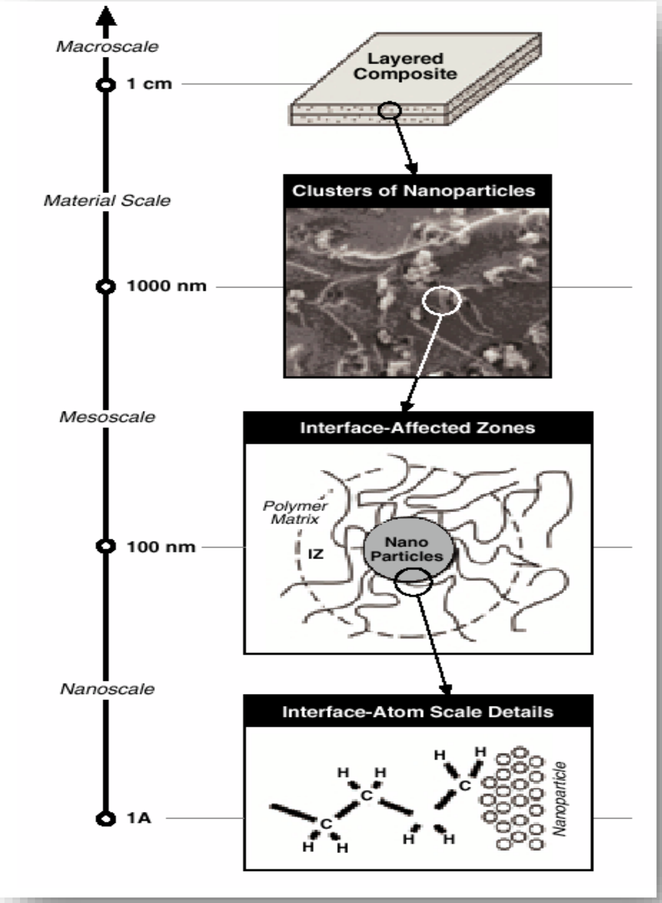
Conventional Composites Vs Nanocomposites



- Nanofillers refer to the particles with less than100 nm size in at least one dimension.
- The advantage for the usage of nanoparticles instead of micron-scale traditional fillers is the effect of nano size on their properties.

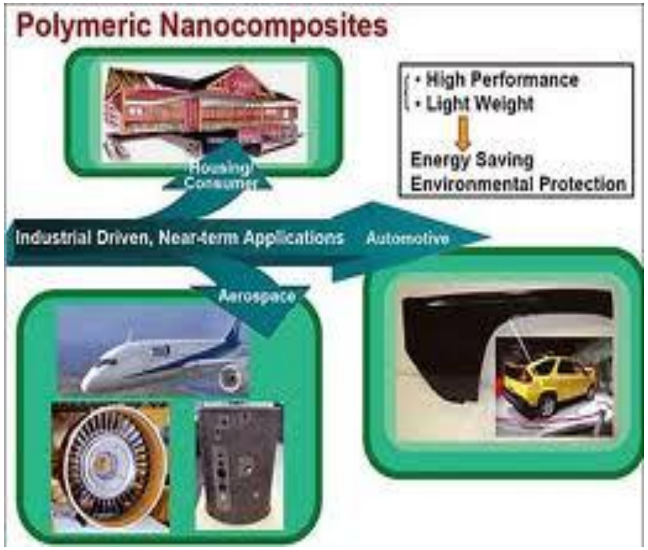
Polymer Nanocomposite

- Polymer nanocomposites (PNC) are polymers that have been reinforced with small quantities of nano-sized particles.
- These materials offer improvements over conventional composites in mechanical, thermal, and electrical properties.
- Addition of few weight percent of nano-fillers has good impact on the electrical properties of polymers.
- Interfacial polarization affects the dielectric properties.

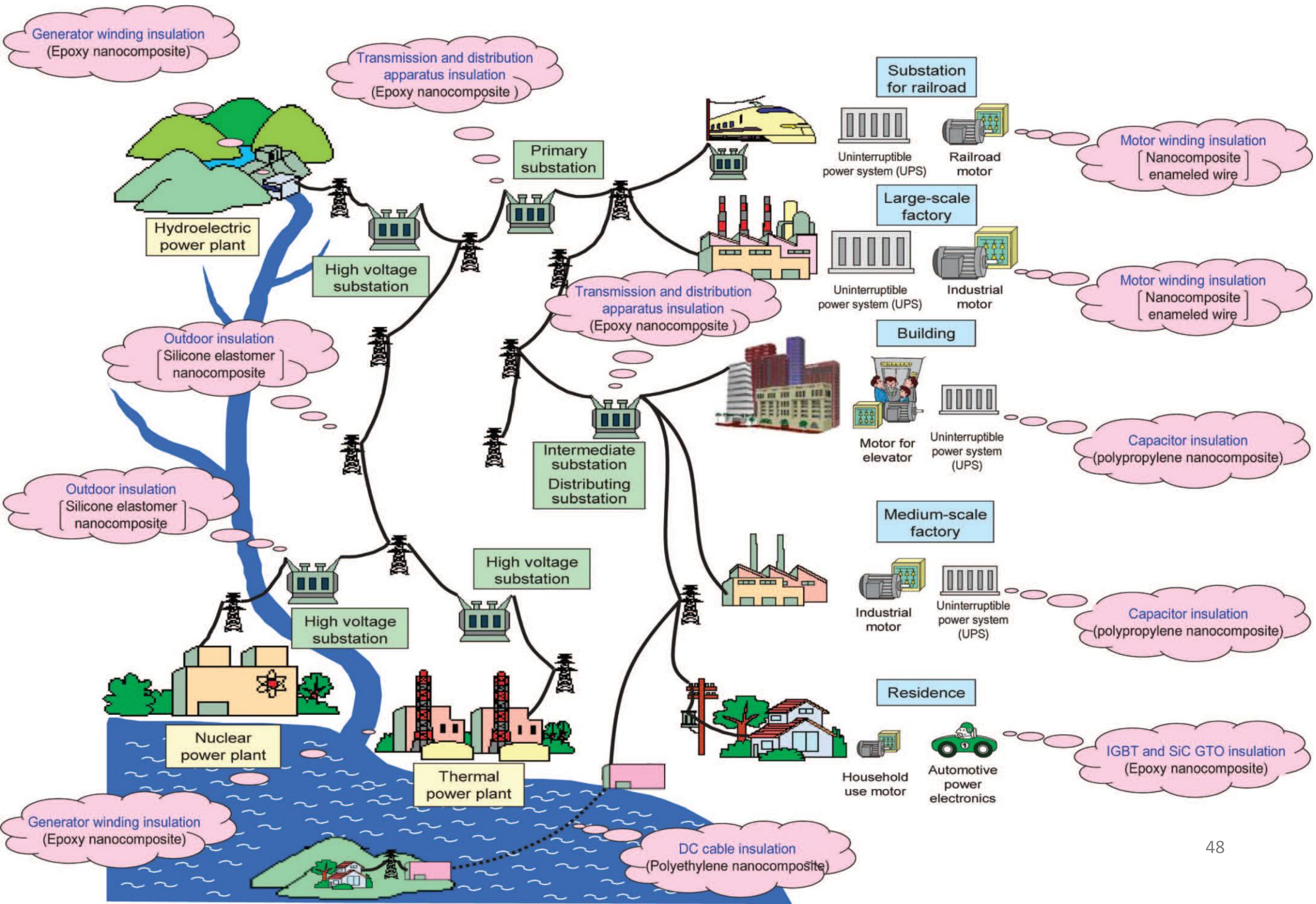


Applications of Polymer nanocomposites

- ❑ Automotive (gas tanks, bumpers, interior and exterior panels)
- ❑ Construction (building sections and structural panels)
- ❑ Aerospace (flame retardant panels and high performance components)
- ❑ Electrical and electronics (electrical components and printed circuit boards, electrical insulation)
- ❑ Food packaging (containers and wrapping films)



PLAUSIBLE APPLICATIONS OF NANOCOMPOSITES IN THE ELECTRIC POWER FIELD



Nanodielectrics - Polymer matrices

- Epoxy resins
- Polyethylene
- XLPE
- Polypropylene
- Ethylene vinyl acetate
- Polyester
- Polyimide
- Silicone elastomers

Nanodielectrics - Nanofillers

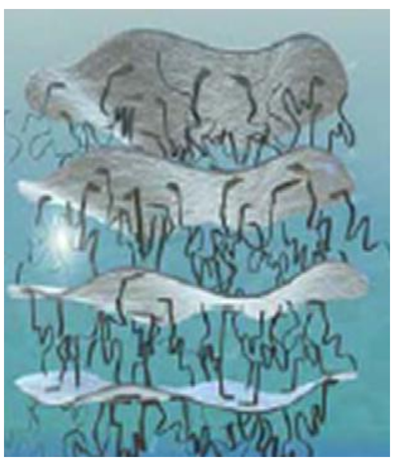
- Layered silicate (natural and synthetic clays, montmorillonite)
- Silica (SiO_2, fume fused, precipitated types)
- Titania (TiO_2)
- Silicon carbide (SiC)
- Alumina (Al_2O_3)
- Boehmite (AlOOH)
- Magnesia (MgO)
- Zinc oxide (ZnO)
- Zirconia (ZrO_2)
- Barium titanate ($BaTiO_3$),

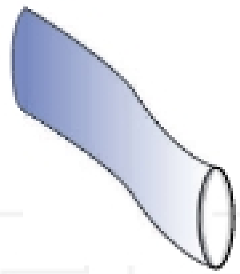
Nanofillers are often surface treated with silane coupling agents

TYPES OF NANOPARTICLES

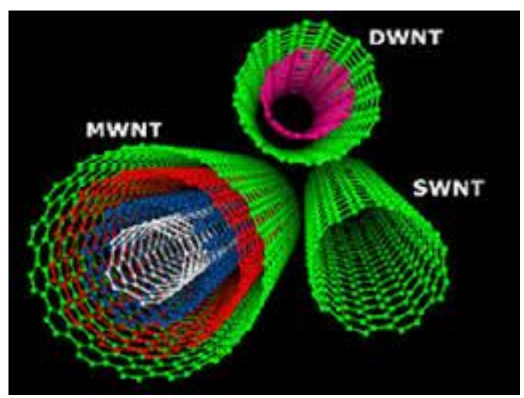
One dimensional	Two dimensional	Isodimensional

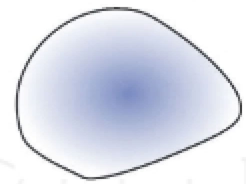
Nanoplate
Thickness < 100 nm



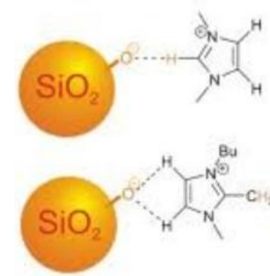


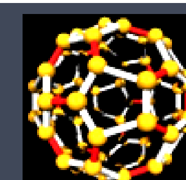
Nanofibre
Diameter < 100 nm





Nanoparticle
All dimensions < 100 nm





Buckyball C60

d=7-15 A

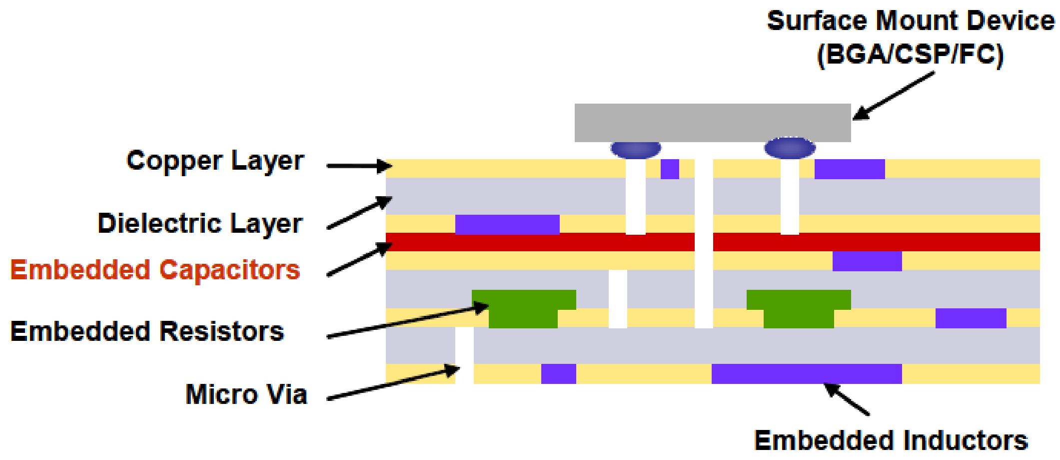
Why Epoxy?

- Very good insulator with High Breakdown Strength
- Easy processing
- Compatible with PCB manufacturing techniques
- Low Cost

Why Aluminum?

- High polarization
- Self passivated oxide layer
- Availability and low cost compared to Silver and Gold nanoparticles

EMBEDDED CAPACITORS



- Ceramic materials have high dielectric constant but low breakdown strength. They also need very high processing temperature (>600 °C) for sintering.

- Low adhesion strength and poor processibility make ceramic materials unsuitable for Printed Circuit Board (PCB) Applications.

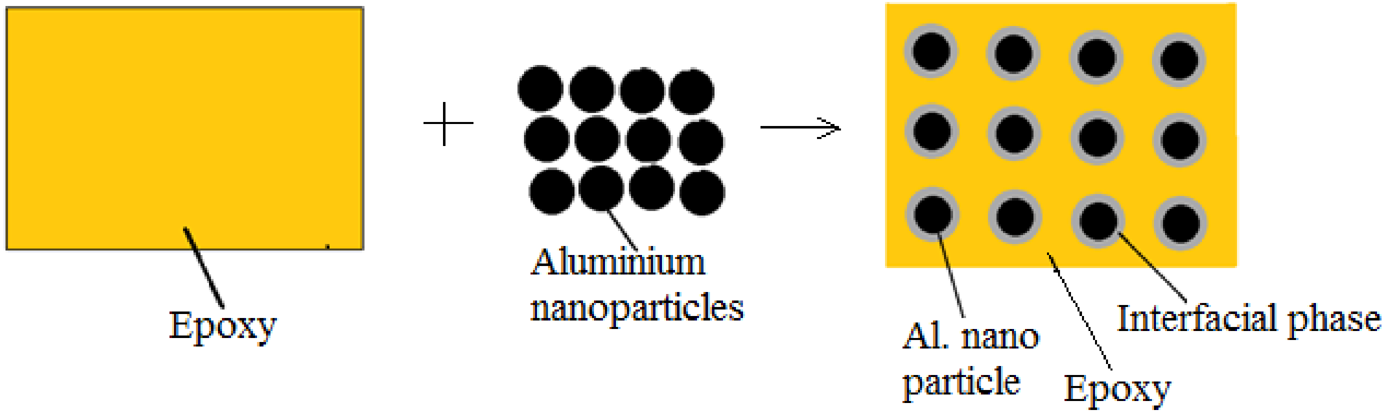
Epoxy-aluminum Nanocomposite

- Spherical aluminum particles
- Size less than 100 nm
- 40 nm, 70 nm (available)
- Particles passivated with Aluminum oxide

Modeling

Polymer Nanocomposite can be modeled as a three-phase material consisting of

i) Polymer matrix (phase 1)
ii) Interfacial phase of fixed thickness *l* (phase 2)
iii) Nanoparticle fillers (phase 3)



Modeling (contd…)

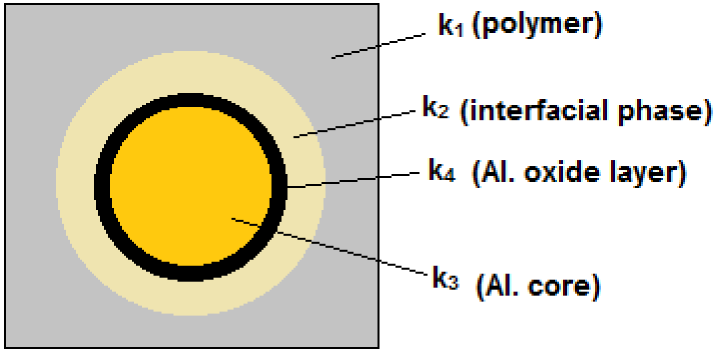
- There are large interfacial areas in a nanocomposite which lead to enhanced polarizability in polymer matrix near the interface.
- As a result, enhanced permittivity can be expected in the polymer matrix near the interfaces.
- The interfacial phase has fixed thickness, independent of nanoparticle size.
- Volume fraction of the interfacial phase is given by:

$$f_2 = \frac{(r+l).^3 - r^3}{r^3} f_3$$

Where f_3 is the volume fraction of nanoparticles, r is the nanoparticle radius and l is the interphase thickness.

- f_2 increases substantially when the nanoparticle size decreases.

Effective permittivity of the composite.



- The effective permittivity k^* can be expressed as :

$$k^* = k_1 + f_2(k_2 - k_1)a_2 + f_3(k_3 - k_1)a_3 \quad ....(1)$$

Where a_r is the electric field concentration factor for corresponding phase r and k_1, k_2, k_3 are the relative permittivity of phases 1,2,3 respectively and $k_2 = (k_1 + k_3 + k_4)/3$

- The average electric field in phase r due to the field E_0 applied at boundary $\langle E_r \rangle = a_r E_0$
- Electric field concentration factor

$$a_r = 1 - s[(k_r - k^*).^{-1} k^* + s].^{-1} \quad ....(2) \qquad for \;\; r = 2,3$$

s is a constant; For spherical particles: s=1/3

- a_1 can be determined from the normalization condition $\sum_{r=1}^{3} f_r a_r = 1$

Solution for k*

Solving equations (1) and (2),

$$4(k^*)^3 + [(2(k_2+k_3))-(4k_1+6X+6Y)](k^*)^2 + [k_2k_3-2(k_1k_2+k_1k_3)+ 3(k_3X+k_2Y)](k^*) - k_1k_2k_3 = 0$$

Where $X = f_2(k_2-k_1)$

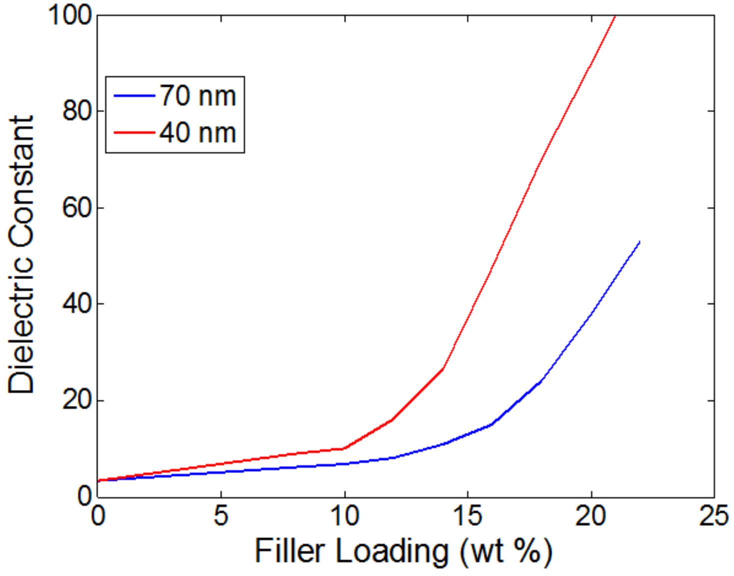
and $Y = f_3(k_3-k_1)$

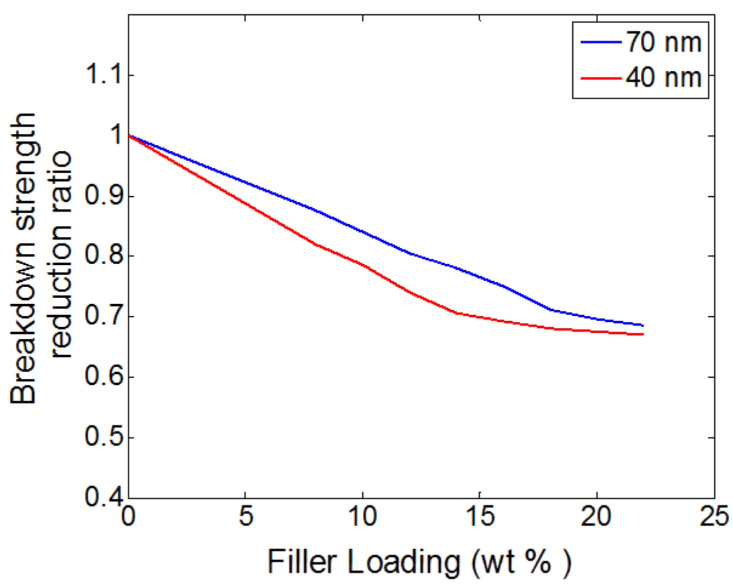
- With the addition of nanoparticles of larger permittivity, the average electric field in polymer matrix $\langle E_1 \rangle$ will be enhanced as:

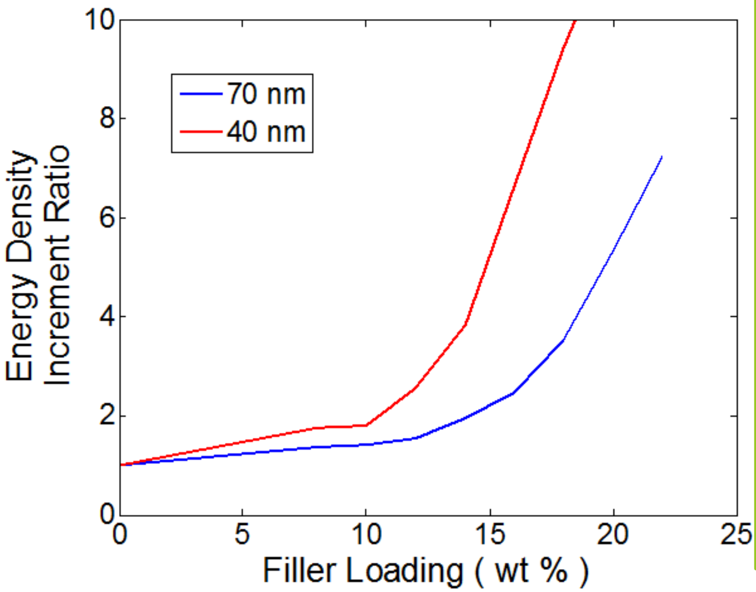
$$\langle E_1 \rangle = a_1 E_0$$

- Breakdown strength of the nanocomposite will be decreased accordingly.

Theoretical Modeling - Results







- Permittivity increases rapidly when a particular volume fraction (transition point or percolation point) is reached.
- Breakdown strength decreases rapidly with the increase of nano filler loading.
- Beyond the transition, energy density rises rapidly.
- Transition point will be shifted towards lower volume fractions as the size of nanoparticles are reduced.

Inference

- The inclusion of aluminum nanoparticles increases the effective permittivity of the composite.

- Interfacial interaction increases the effective dielectric constant but decreases the breakdown strength, and thus gain in electric energy density could be limited, since electric energy density $U = \frac{1}{2} \varepsilon_0 \varepsilon_r E^2$

- For composites with lower size nano fillers, higher values of energy density are obtained at lower filler concentrations.

- This model can be used to evaluate the dielectric constant, breakdown strength and energy density of polymer nanocomposites with different fillers at different filler concentrations.

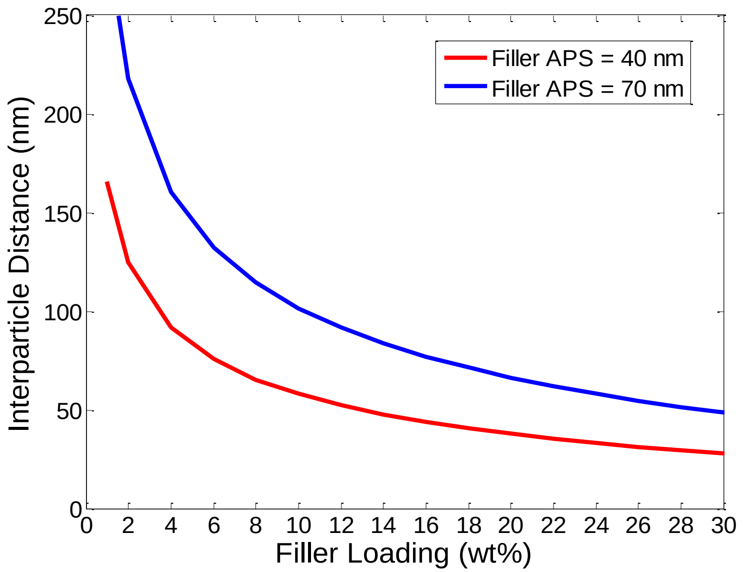
Interparticle distance

- Inter particle distance plays an important role in determining the dielectric properties of a nanocomposite.

- Equation for inter particle distance [Ref. Tanaka et. al]:

$$D = \left\langle \left\{ \frac{\pi}{6}\left(\frac{\rho_n}{\rho_m}\right)\frac{100}{wt\%}\left[1-\frac{wt\%}{100}\left(1-\frac{\rho_m}{\rho_n}\right)\right]\right\}^{\frac{1}{3}} -1 \right\rangle d$$

Where
ρ_m = specific gravity of matrix
ρ_n = specific gravity of filler
d = diameter of nanoparticle



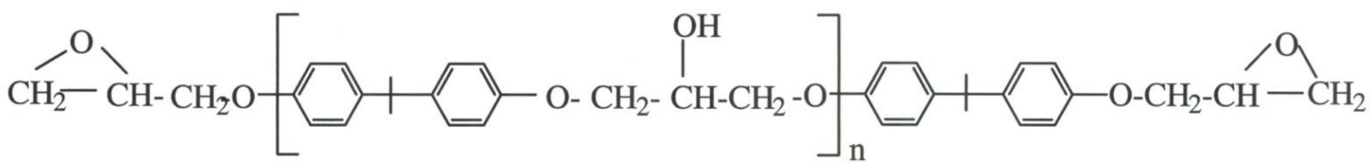
- The filler concentrations are selected such that the interparticle distance between them becomes almost in the same range as that of the particle diameter itself.

- Hence for the present study, filler concentrations of 8,10,12,14,16,18 and 20 wt% of nano aluminum were chosen.

MATERIALS USED

- Bisphenol-A epoxy resin (CY1300, density 1.16 g/cm^3) along with a Triethylene Tetramine (TETA) hardener (HY956, density 1.02 g/cm^3) of Huntsman make.

Bisphenol-A



TETA

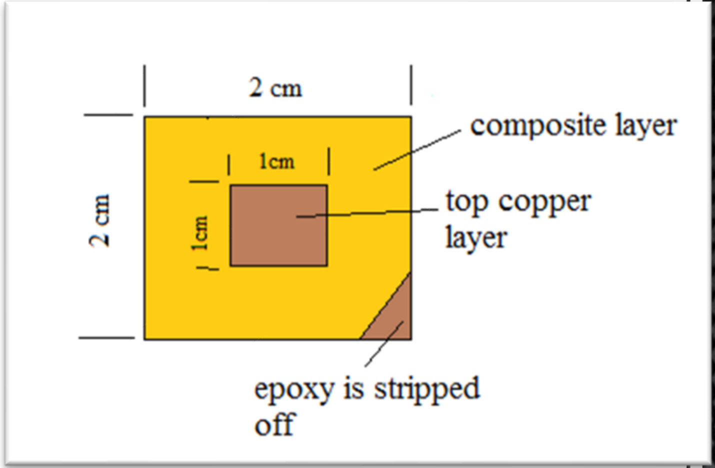
$NH_2—C_2H_4—NH—C_2H_4—NH—C_2H_4—NH_2$

- The nanofiller material used was spherical aluminum nanoparticles of average particle size (APS) (i) 70 nm and (ii) 40 nm and purity 99.9%, passivated with thin layer (2-3 nm) of aluminum oxide. Supplied by Hongwu Nanometer Technologies, Hongkong.

Fabrication of capacitors

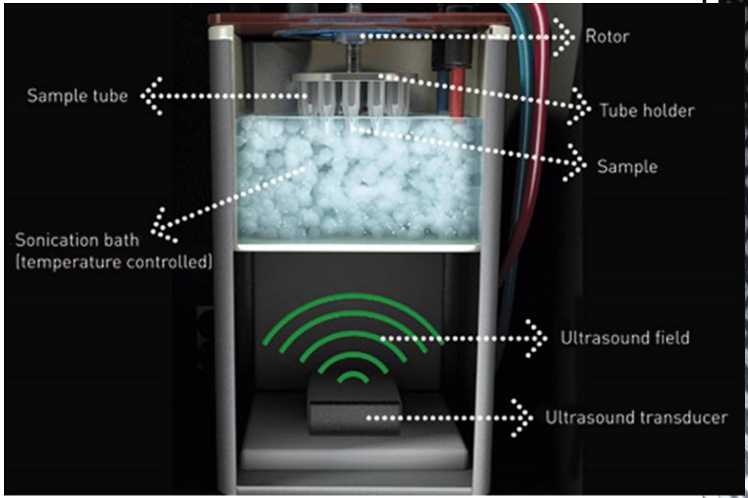
(for permittivity and dissipation factor measurements)

Samples were prepared in the glove box in Polymer Processing Lab (at CeNSE, IISc Bangalore).

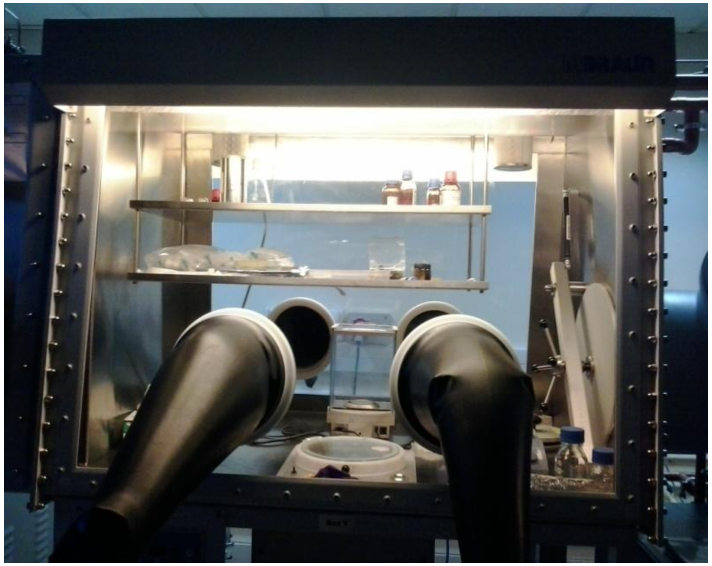


Process Flow

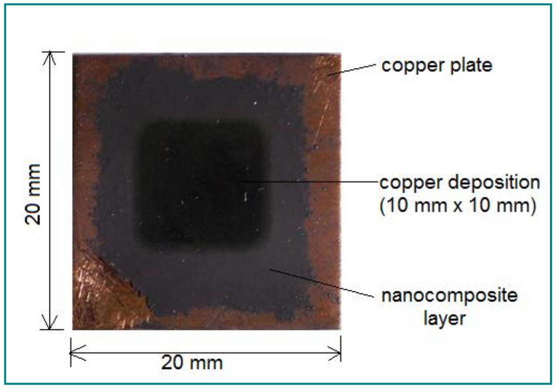
1. Epoxy was heated at 40^0C for degasification.
2. Required qty of Nanoparticles were weighed using a precision digital balance (with readability 0.1 mg) and added to epoxy.
3. Magnetic stirring for 1 hour and then Ultrasonication for 1 hr at a frequency of 33 kHz in a water bath.
4. Hardener was added in the ratio 1 : 4 and magnetic stirring for 2 minutes
5. Spin coating on a copper substrate at 1000rpm for 50 seconds.
6. Curing of the samples at 60^0C for 4 hrs.
7. Top layer copper deposition by thermal evaporation.



Glove box



Photograph of Glove box
(in which samples were prepared).



Photograph of capacitors fabricated.

- Capacitors were fabricated with pure epoxy as well as epoxy- aluminum nanocomposites with filler concentrations of 8,10,12,14,16,18 and 20wt%.

Relative Permittivity (Dielectric Constant) & Tanδ (Dissipation Factor)

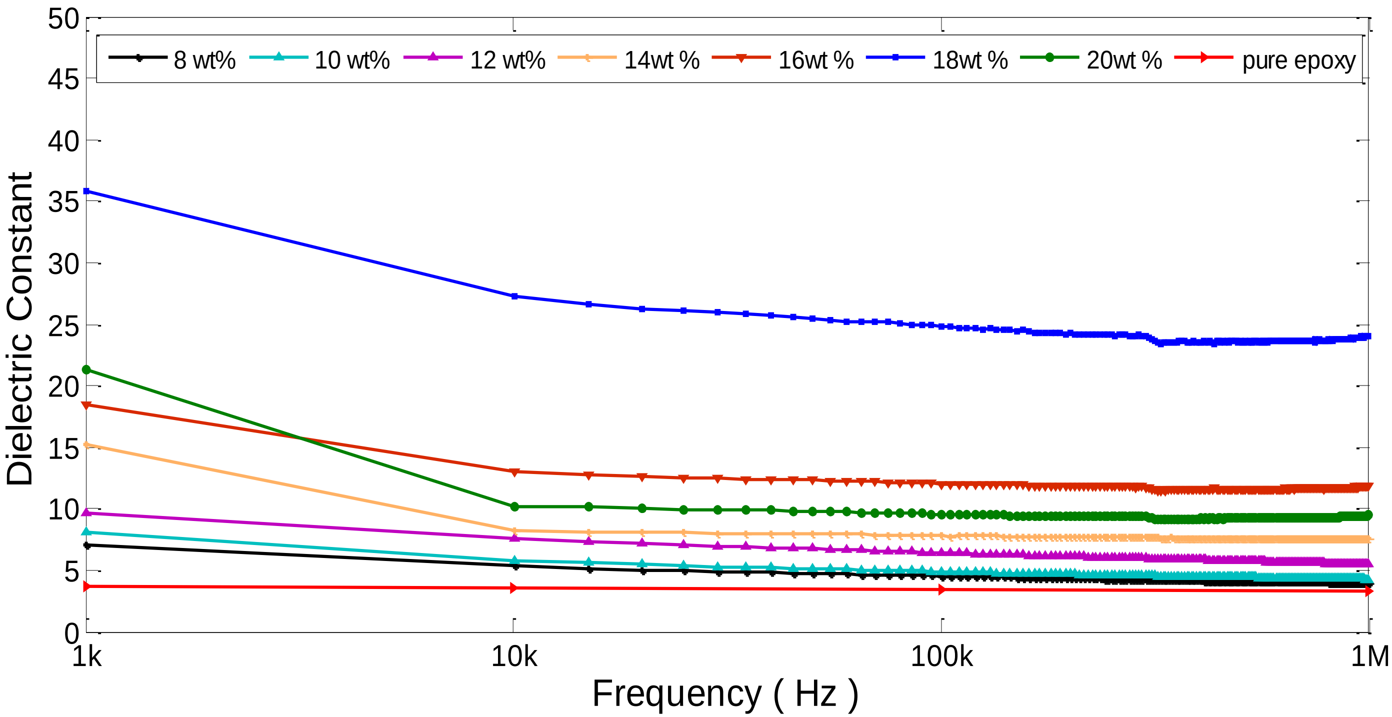
Instruments used:

- Impedance Analyzer (Agilent 4294A) : C-V, C-f, tanδ-f
- Surface Profiler (DEKTAK Stylus Profiler) : For thickness measurement

$$C = \varepsilon_0 \varepsilon_r A/d$$

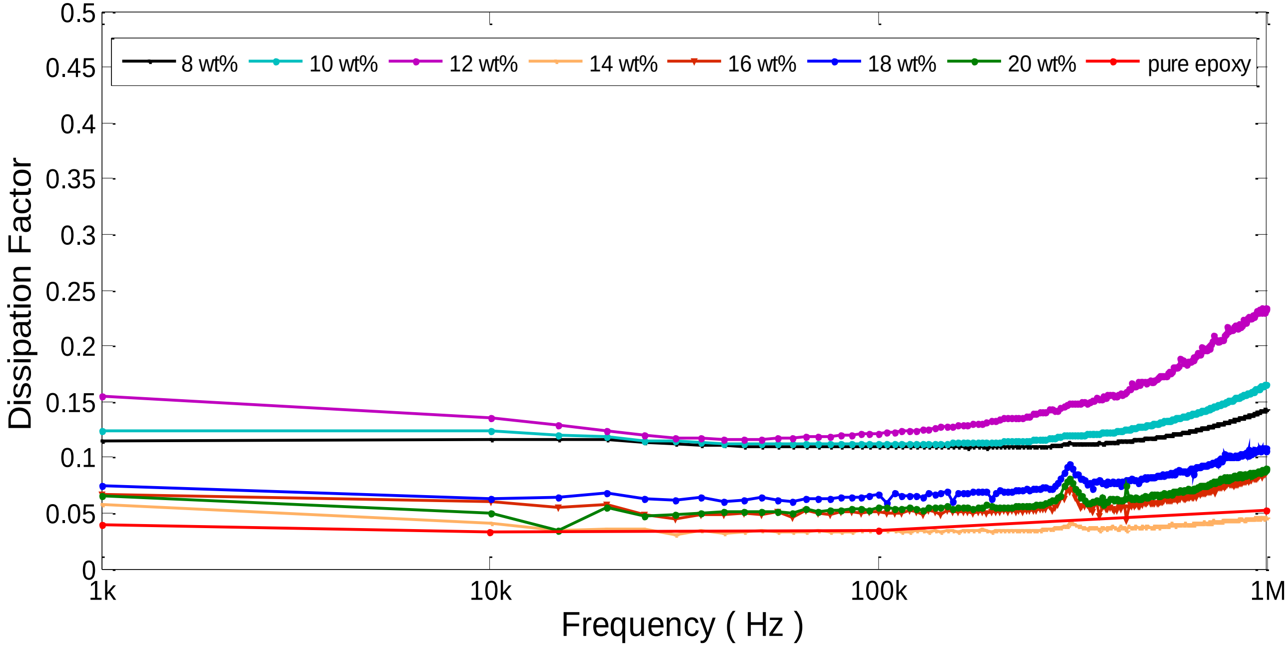
Where C=capacitance, ε_0 = permittivity of free space, ε_r = relative permittivity (dielectric constant) of the nanocomposite, A = area of top copper layer, and d = thickness of composite layer.

Dielectric constant of epoxy-aluminum nanocomposite as a function of frequency (Composites with filler APS 70 nm)



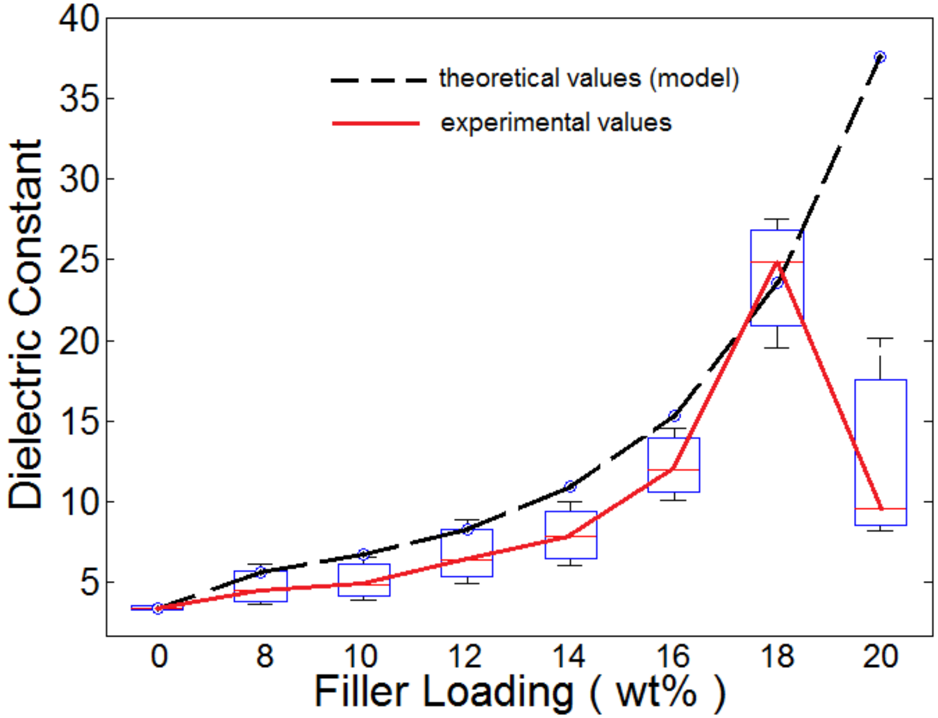
- Dielectric constant is maximum for samples with filler concentration of 18 wt% .

Dissipation factor as a function of frequency (70 nm)



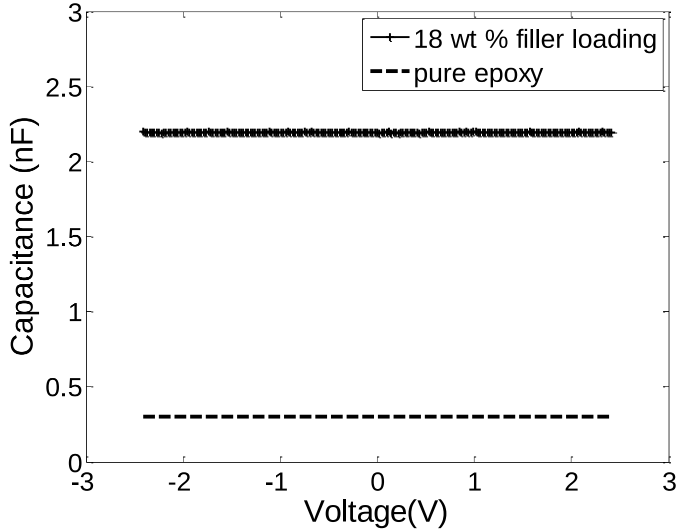
- The dissipation factor increases slightly with increase in frequency because, as the frequency is raised, the interfacial dipoles have less time to orient themselves in the direction of the alternating field.
- Dissipation factor of the nanocomposites is slightly higher than that of pure epoxy.
- Very low dissipation factor is desired for radio frequency applications to avoid signal losses, but higher values can be tolerated for energy storage applications.

Dielectric constant of epoxy-aluminum nanocomposites (70nm) as a function of filler loading (at 100kHz).

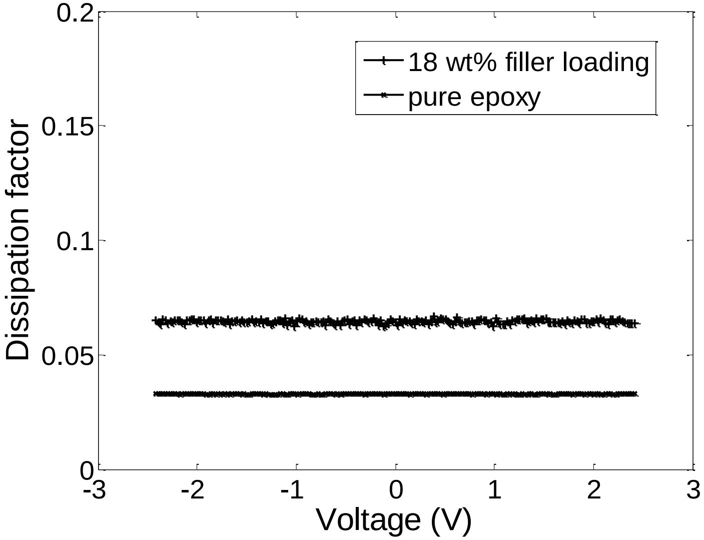


- The dielectric constant of epoxy-aluminum nanocomposite is increased to 25 at a filler loading of 18 wt% ; which is 7 times as that of the pure epoxy matrix, which is 3.43 (at 100kHz).

C-V plot and tanδ-V plot



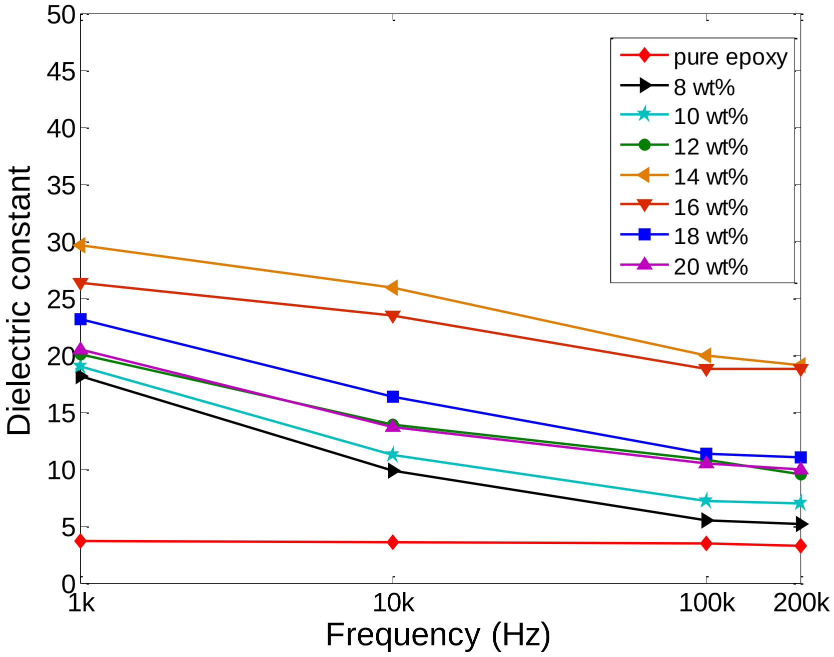
C-V Plots of capacitors with (a) pure epoxy and (b) epoxy-aluminum nanocomposite at 100kHz [area 1cm^2 and thickness 10μm] .

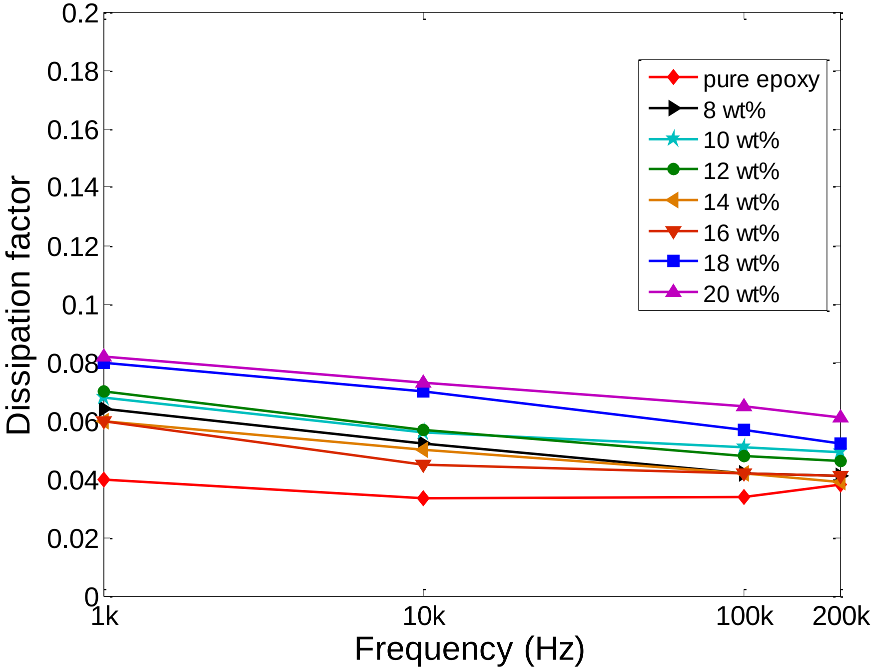


Tan δ (Dissipation factor) as a function of Voltage (at 100kHz)

- C-V Plots show that permittivity and tanδ of epoxy-aluminum nanocomposites are independent of polarity and magnitude of the Voltage applied.

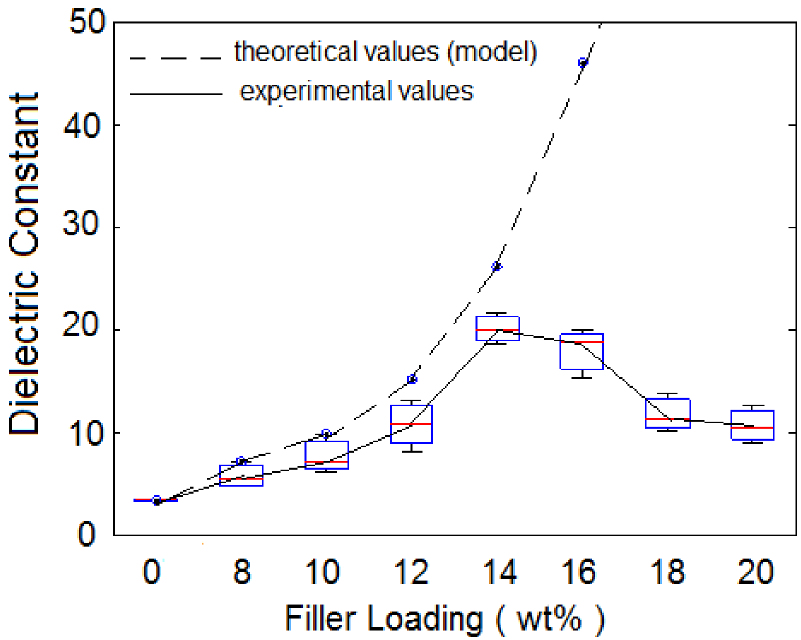
Dielectric constant and Dissipation factor of 40nm composites





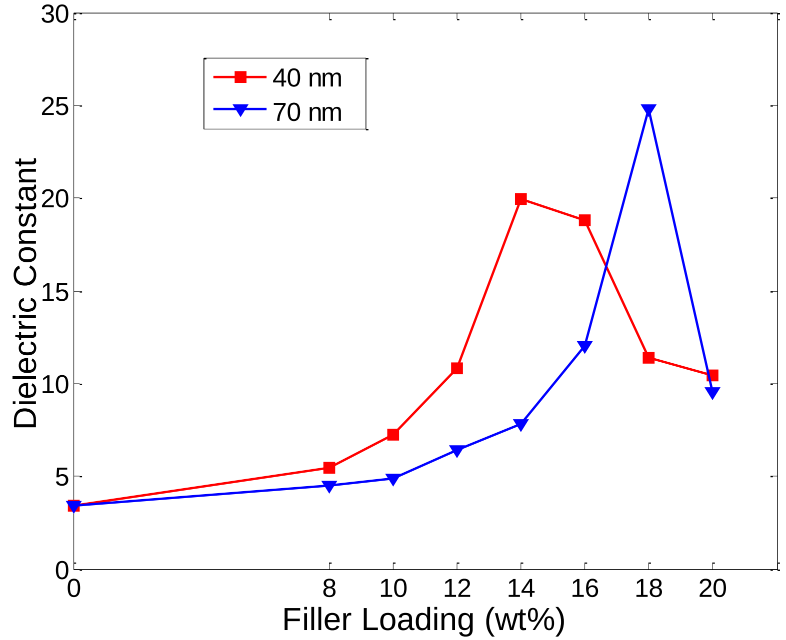
- Dielectric constant of the nanocomposites is stable in terms of frequencies when test frequency is greater than 100 kHz.
- Dielectric constant attains high values at lower frequencies because interfacial polarization is more predominant at lower frequencies.

Dielectric constant of 40nm composites as a function of filler loading (at 100kHz).



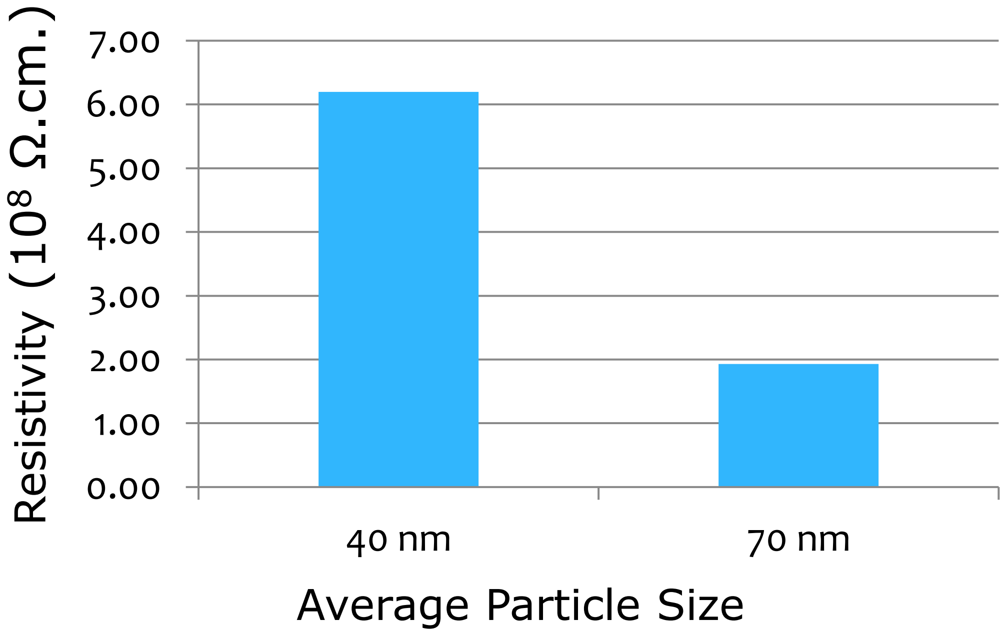
- The dielectric constant of epoxy-aluminum nanocomposite is increased to 20 at a filler loading of 14 wt% ; which is 6 times as that of the pure epoxy matrix.
- After 14 wt %, dielectric constant decreases, again this is attributed to agglomeration of the particles.
- Experimental values match well with theoretical values at lower filler concentrations.

Comparison between Dielectric constants of nanocomposite with filler APS (i) 70 nm and (ii) 40 nm (at 100 kHz)



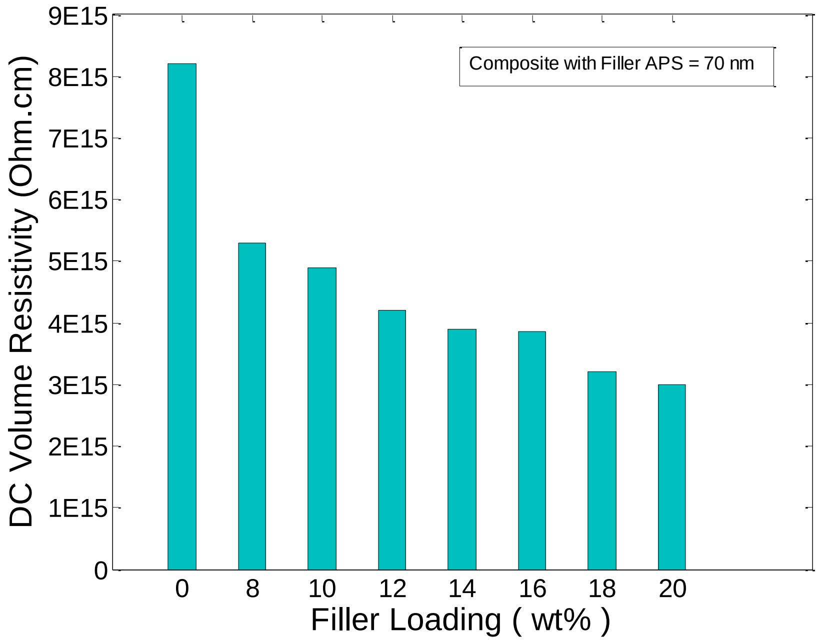
- Maximum value of Dielectric constant obtained is 25 (7 times as that of pure epoxy) at 18 wt% of 70 nm composites.
- For 40 nm composites maximum value of 20 obtained at a lower filler loading of 14 wt%.
- High dielectric constant along with low dissipation factor makes the composite suitable for Embedded Capacitor applications.

Resistivity of nanopowder

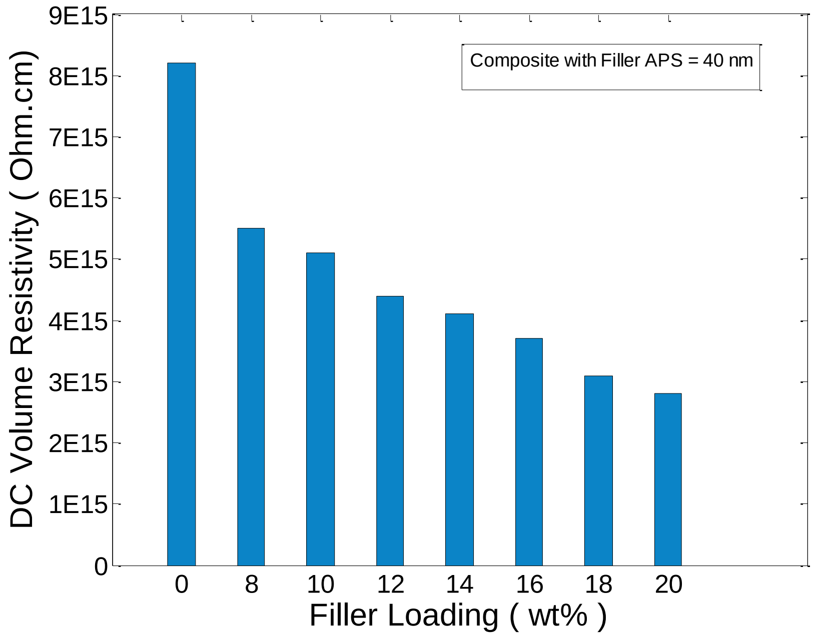


- Nanopowder is pelletized in a Hydraulic pellet press at 125 tons load.
- V-I measurement (at 50 V) of pellets using Keithley source meter-2400
- High resistivity values confirm the presence of oxide layer around the nanoparticles.

Resistivity of nanocomposite samples



70 nm samples

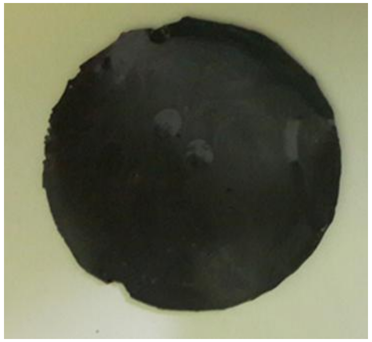


40 nm samples

HV Breakdown Studies

Sample preparation for breakdown studies

- Epoxy was heated at 40^0C for degasification.
- Appropriate quantity of Nanoparticles were weighed and added to epoxy
- Mechanical mixing and then Ultrasonication for 1 hr.
- Hardener was added in the ratio 1:4 and mechanical stirring for 2 minutes
- The mix obtained is poured in to a mould and the mould is then kept in an oven at a temperature of 60^oC for 4 hours to cure the samples of 1 mm thickness and 75 mm diameter (6 samples each per 8, 10, 12, 14, 16,18,20 wt% for fillers 40 APS and 70 APS).



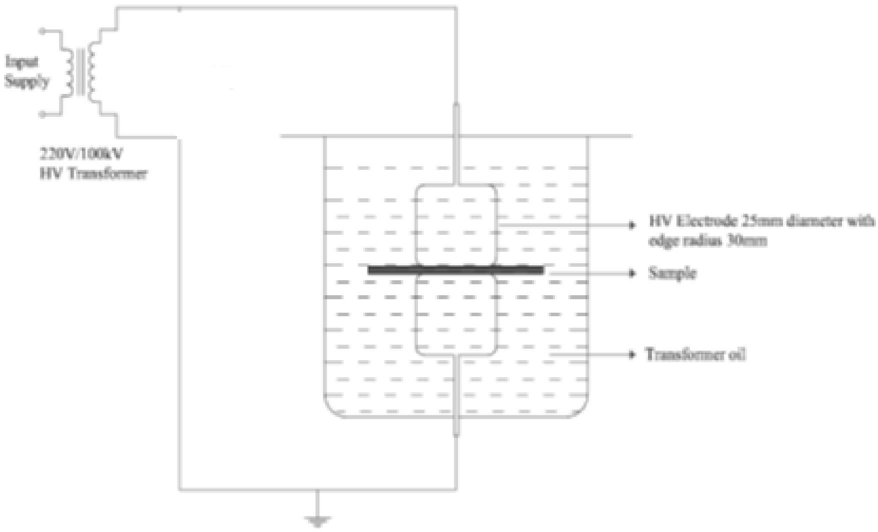
Photograph of a sample

High Voltage Test Set-up
(according to ASTM D 149 standards)

High Voltage Test Set-up

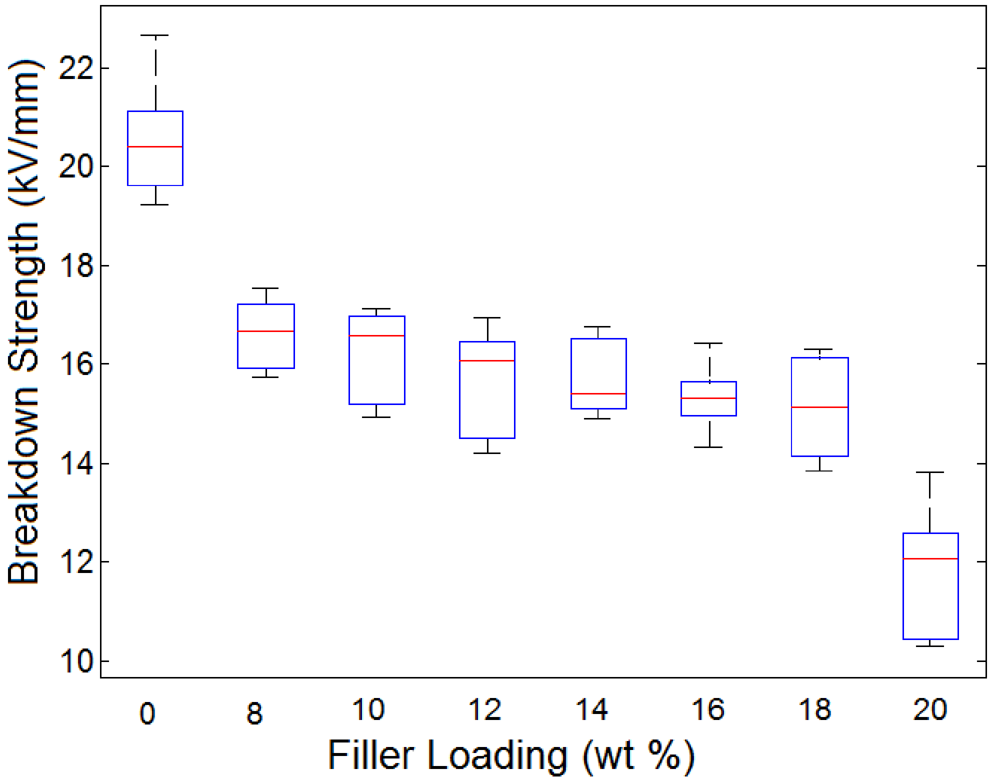
High Voltage Test Set-up

High Voltage Test Set-up



- The electrodes were made of brass, 25mm in diameter with an edge radius of 3.2 mm.
- The entire electrode setup was immersed in a vessel containing transformer oil to avoid surface flashover.
- The experiment was performed by applying an ac voltage (50 Hz) to the high voltage electrode at the rate of 0.5 kV/s till the sample broke down.

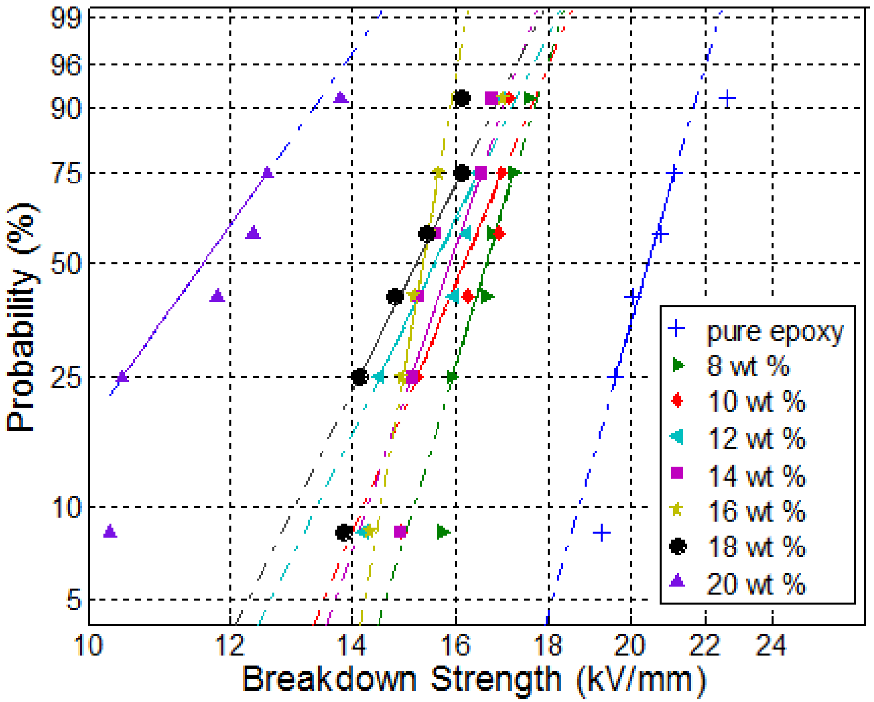
Breakdown Strength (70 nm composite)



- AC breakdown strength E=V/d
- V=breakdown voltage
- d=thickness of the sample in the region close to the puncture point.

- Compared with pure epoxy resin, there is reduction in breakdown strength for all filler concentrations of epoxy nanocomposites.

Weibull plot (70 nm composites)

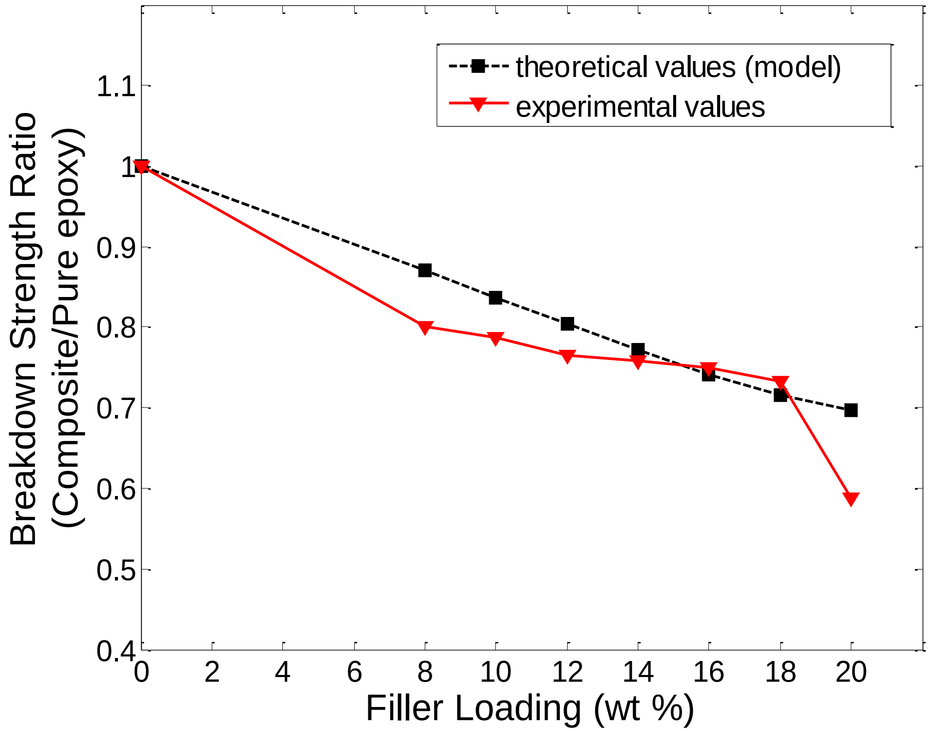


Weibull parameters

Composition	Scale Parameter (α)	Shape Parameter (β)
Pure epoxy	21.13	17.79
8 wt %	16.93	29.63
10 wt %	16.62	24.57
12 wt %	16.16	19.95
14 wt %	16.03	23.17
16 wt %	15.83	18.09
18 wt %	15.49	19.99
20 wt %	12.44	10.78

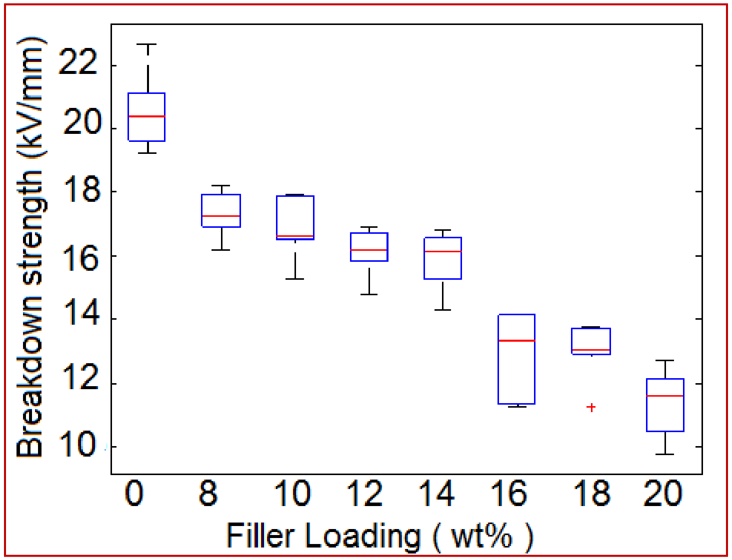
- Scale parameter α represents the breakdown strength at the cumulative failure probability of 63.2% and is called the Weibull breakdown strength.
- Shape parameter β represents the inverse of data scatter.

Breakdown Strength Ratio (70 nm composites)

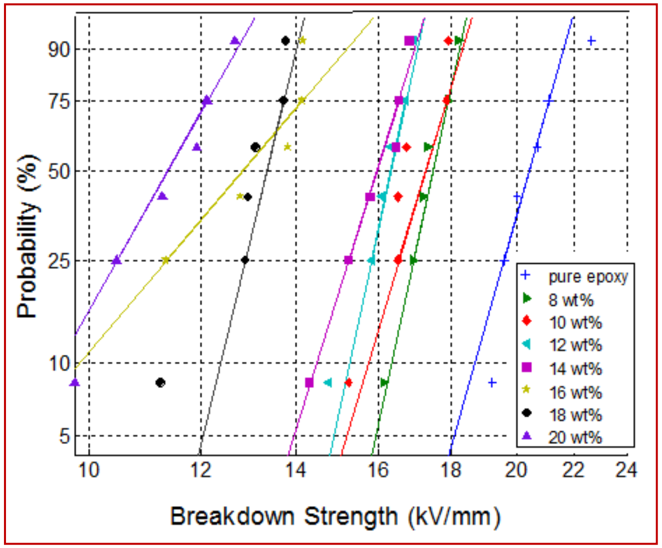


- Breakdown strength reduces as the filler concentration increases.
- Theoretical model approximates experimental values of breakdown strength.

Breakdown strength (40 nm composites)



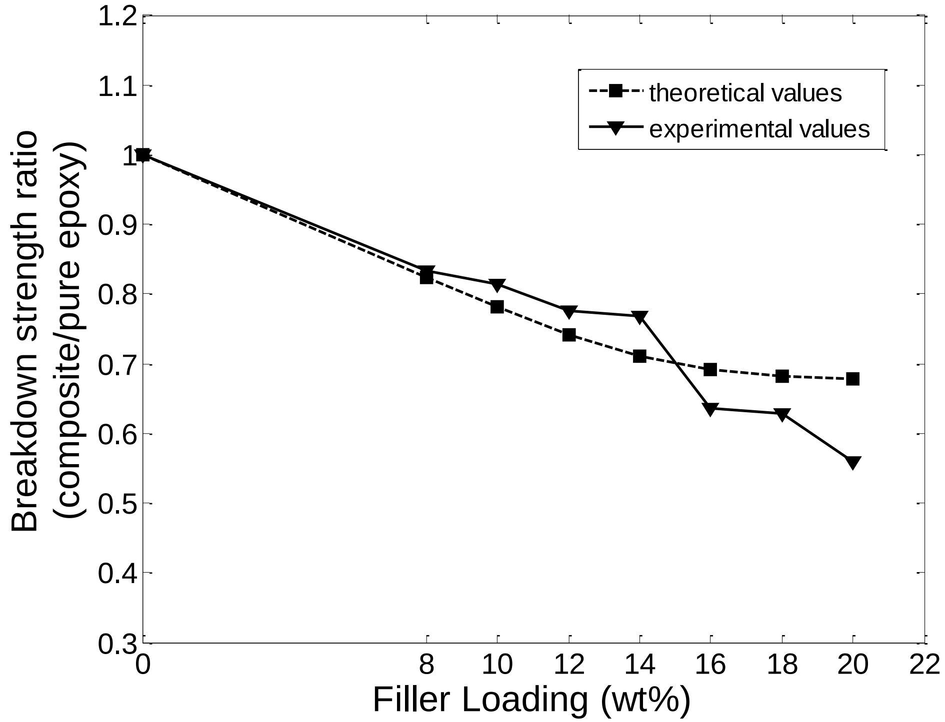
Weibull plot



Composition	Scale Parameter (α)	Shape Parameter (β)
Pure epoxy	21.13	17.79
8 wt %	17.60	30.42
10 wt %	17.22	21.92
12 wt %	16.41	30.40
14 wt %	16.24	24.40
16 wt %	13.46	13.40
18 wt %	13.29	22.38
20 wt %	11.81	14.01

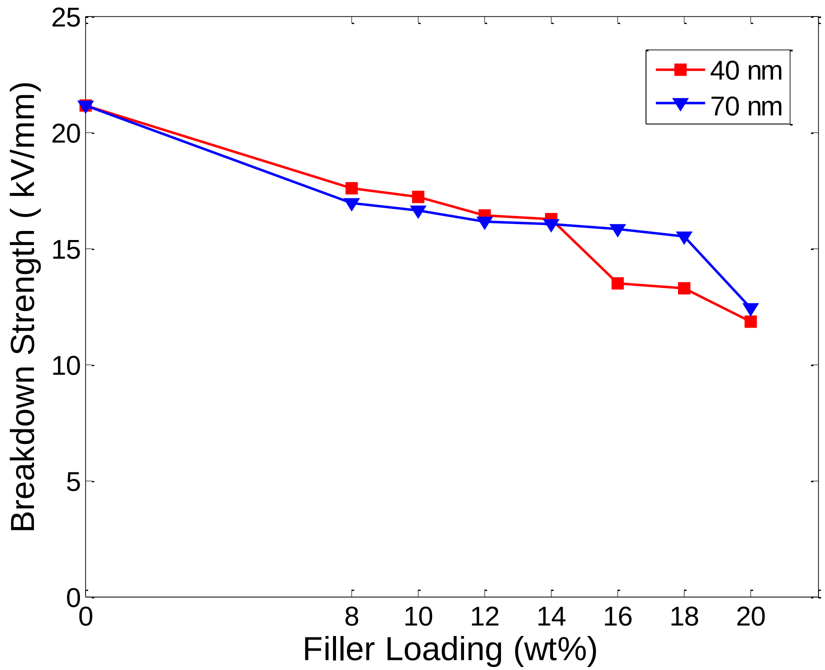
Weibull parameters

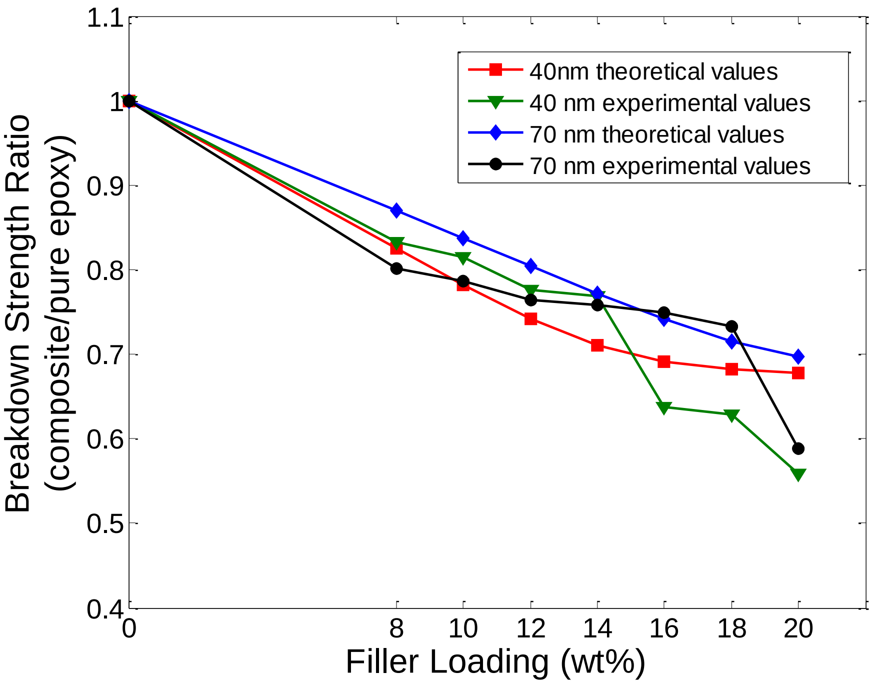
Breakdown Strength Ratio (40 nm composites)



- For all filler concentrations, there is reduction in breakdown strength.
- Experimental values of breakdown strength are near to theoretical values.

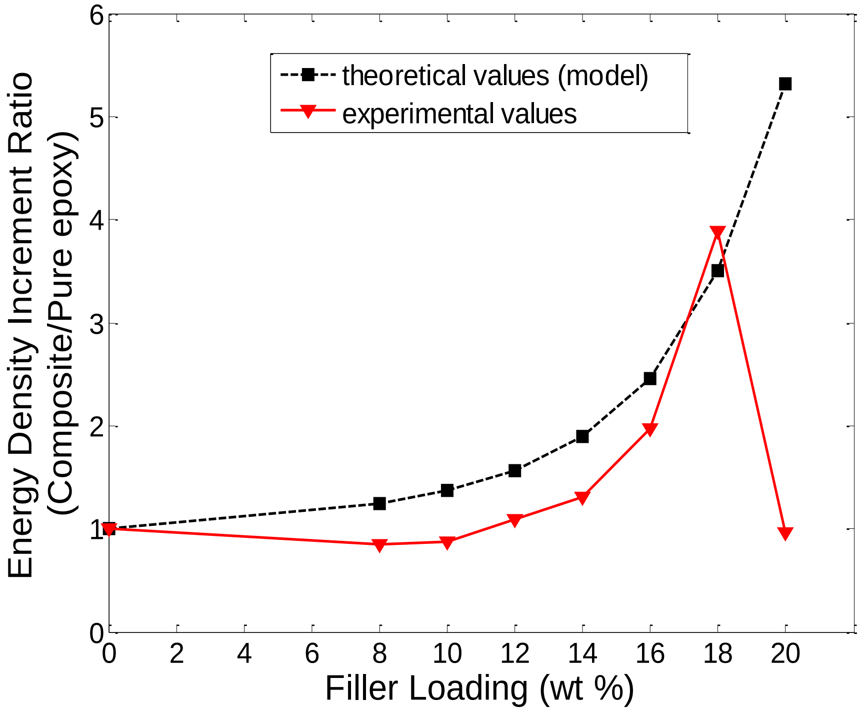
Comparison of Breakdown strength
(between 70 nm and 40 nm composites)





- Reduction in Breakdown Strength is more in 40 nm composites when filler loading is increased above 14 wt%.

Energy density increment ratio (70 nm composites)



Energy Density

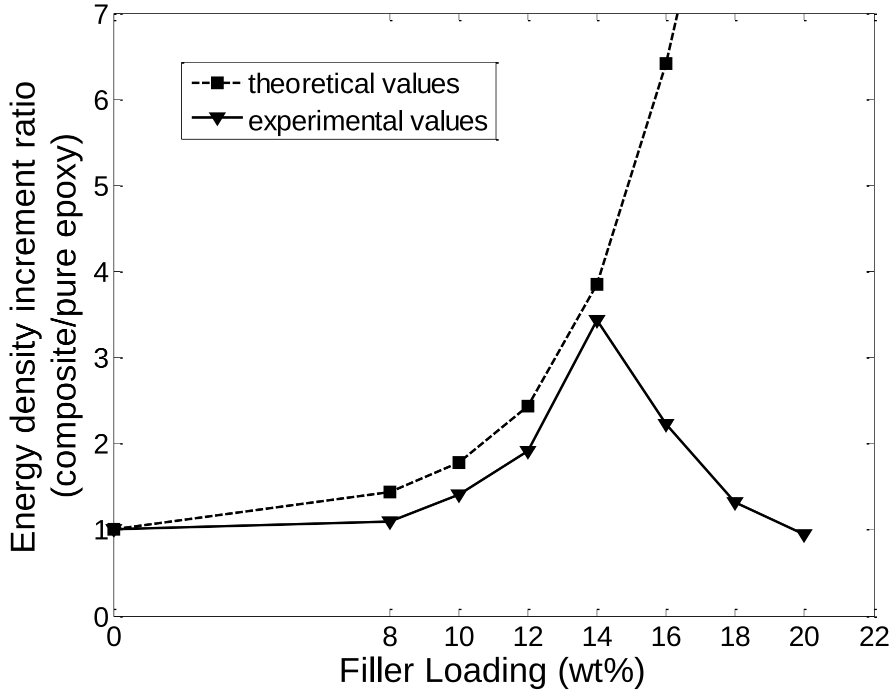
$$E = \frac{1}{2} k\, Eb^2$$

where k is the permittivity and E_b is the breakdown strength of the composite.

- Energy density of the composite increases with filler concentration and reaches maximum value at 18 wt % filler loading and then decreases.

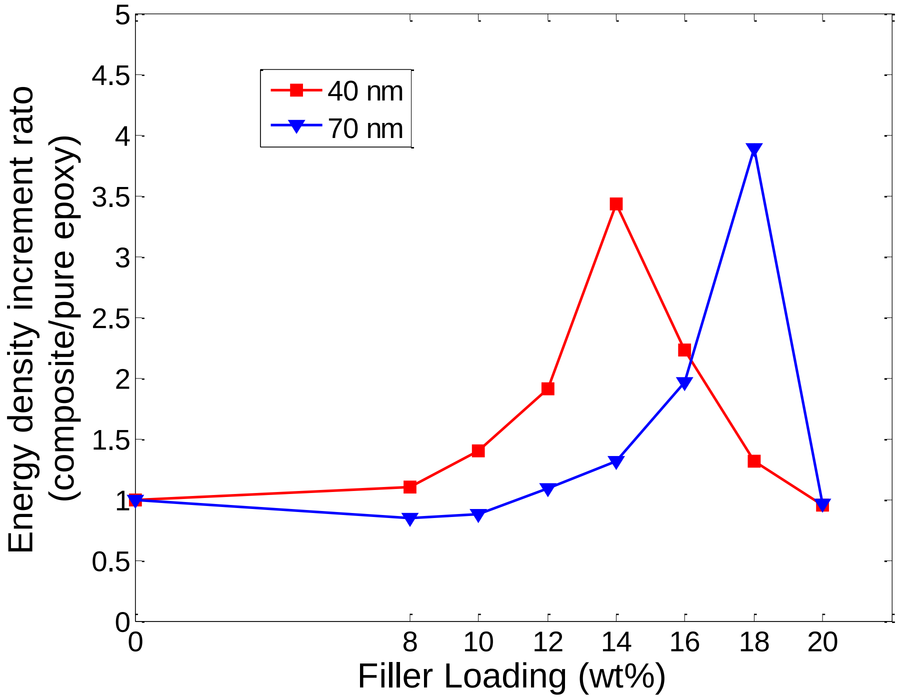
- Energy density of epoxy-aluminum nanocomposite is increased by factor 4 at filler loading of 18 wt% as compared with that of pure epoxy.

Energy density increment ratio (40 nm composites)



- Maximum energy density obtained for 40 nm composites is 3.5 times as that of pure epoxy; at 14 wt % filler loading.
- Experimental values match well with theoretical values.

Energy Density – Comparison between 70 nm and 40 nm composites



- Maximum Energy density obtained for 40 nm composites is slightly less than that of 70 nm composites, but obtained at a lower filler concentration.
- As the energy density is enhanced by factor 4, four times energy storage is possible in capacitors of same size.

MATERIAL CHARACTERIZATION

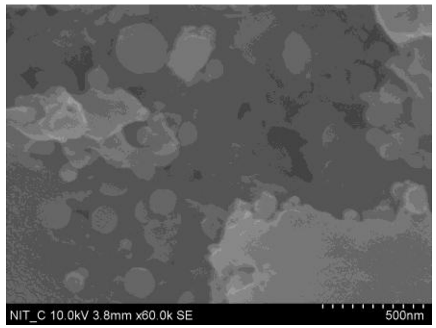
- **SEM** (Scanning Electron Microscope) **:** Dispersion of particles
- **EDS** (Energy Dispersive X-Ray Spectroscopy) **:** Nanoparticle composition
- **XRD** (X-ray Diffraction) **:** Confirmation of metallic phase
- **TGA** (Thermogravimetric Analysis) **:** Thermal stability
- **DSC** (Differential Scanning Calorimetry) **:** Glass transition temperature

Scanning electron microscope (SEM)

- Scanning electron microscope (SEM) analysis involves detection of secondary and backscattered electrons from a sample exposed with a focused primary electron beam and leads to a surface image with a great depth of field.
- SEM has an energy dispersive X-ray spectrometer (EDX or EDS) attachment which can detect the X-rays emitted from the sample and provide information about the chemical composition of a specimen.
- The SEM was used to study the dispersion uniformity of the filler particles.
- For non-conductive dielectric samples, a thin layer of gold was sputter coated on the sample surface in order to obtain good images.
- HITACHI SU 6600 Field Emission Scanning Electron Microscope (FESEM) was used.

SEM Images of 70 nm composites

8%



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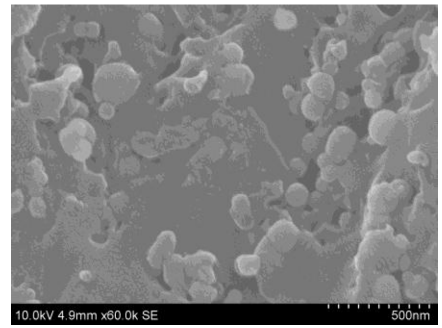

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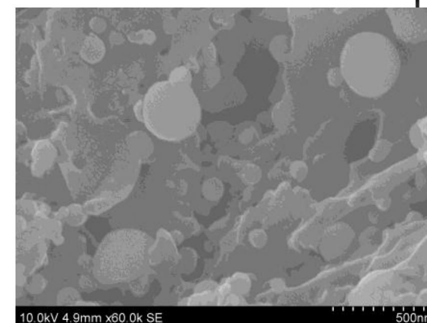

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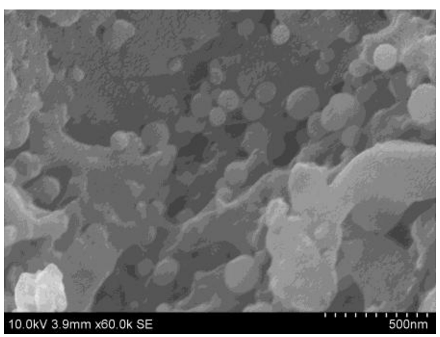

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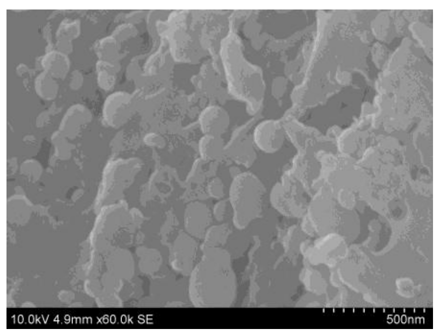

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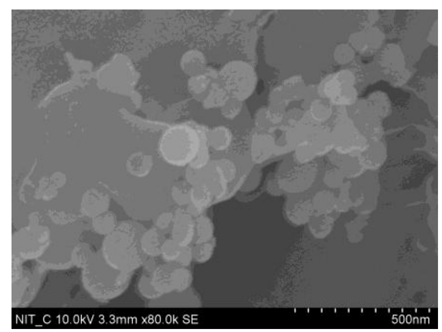

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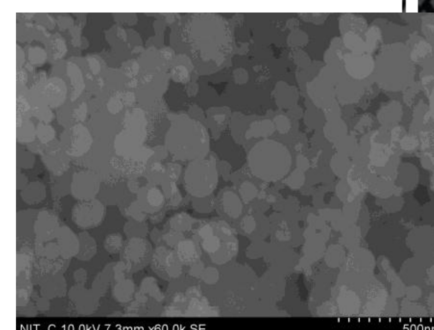
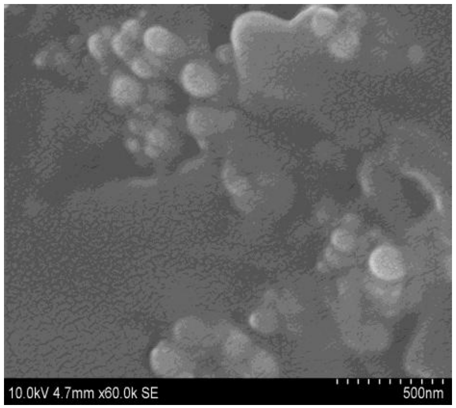


70 nm Al.particles

SEM Images of 40nm composites



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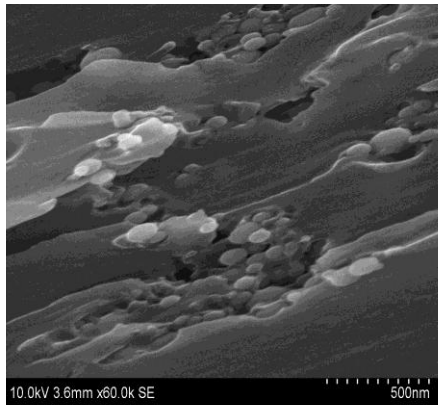

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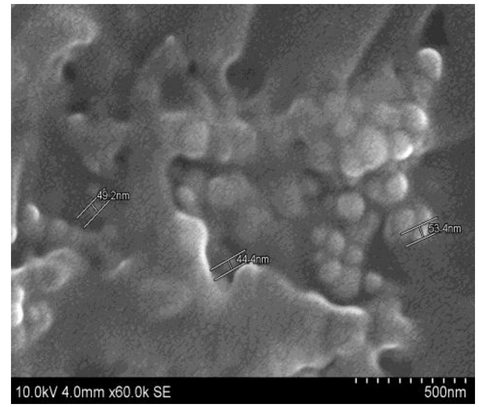

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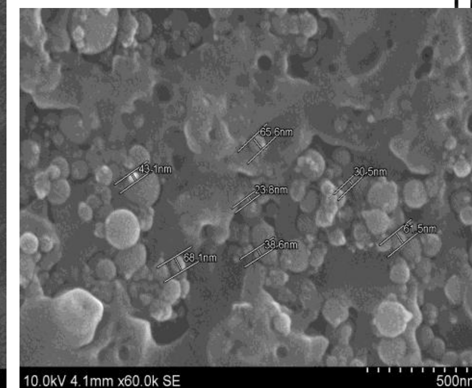

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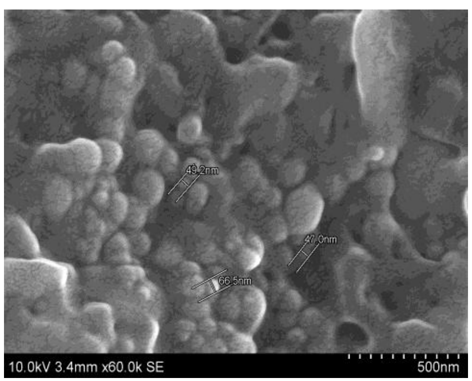

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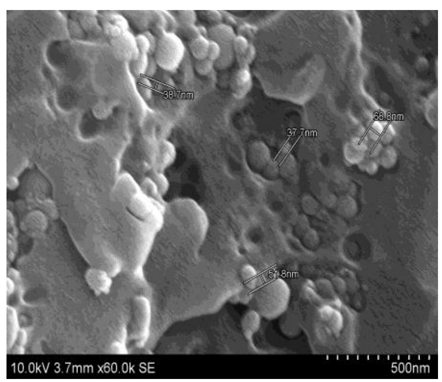

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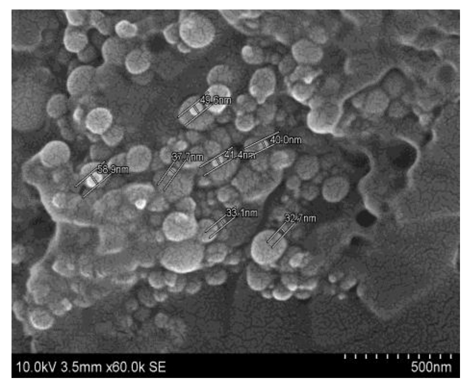

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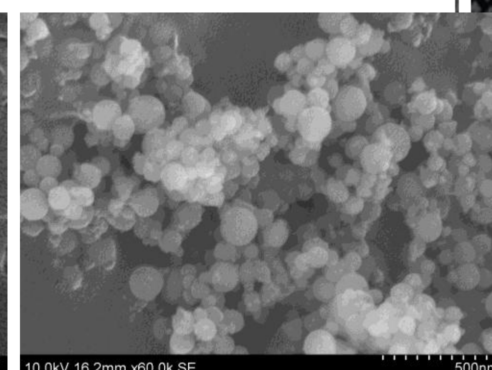
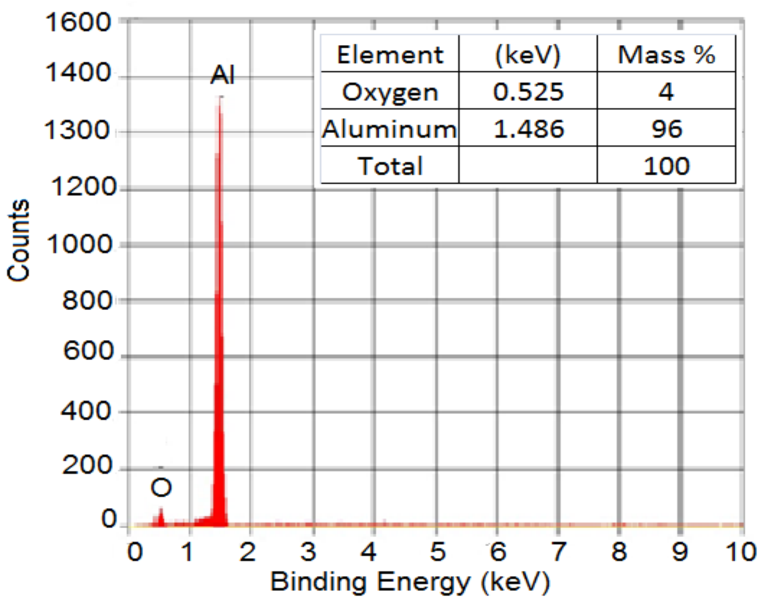


40 nm Al.particles

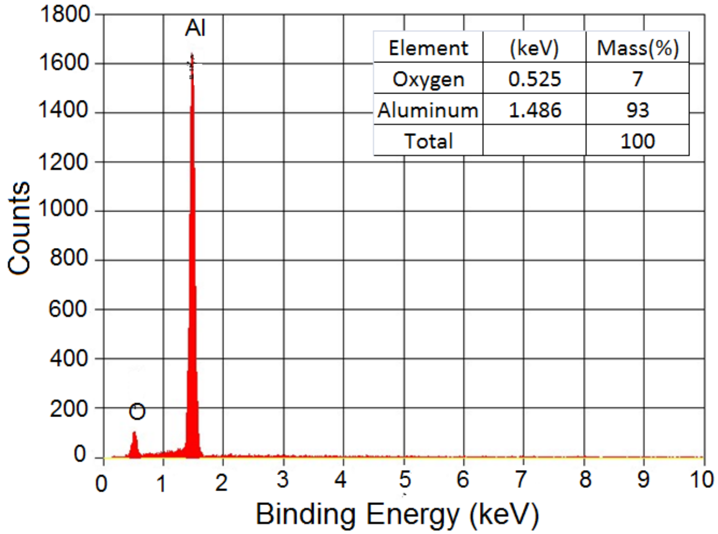
EDS of 70 nm Aluminum nanopowder



Element	Mass %
Aluminum	96
Oxygen	4

- Peaks correspond to aluminum and oxygen were obtained with percentage mass of 96% and 4% respectively, which confirms the presence of thin oxide layer around aluminum nanoparticles.

EDS of 40 nm Aluminum nanopowder



Element	Mass %
Aluminum	93
Oxygen	7

- Peaks correspond to aluminum and oxygen were obtained with percentage mass of 93% and 7% respectively, which confirms the presence of thin oxide layer around aluminum nanoparticles.
- Percentage mass of oxygen is more compared to 70 nm powder due to large surface area of smaller particles.

X-ray diffractometer

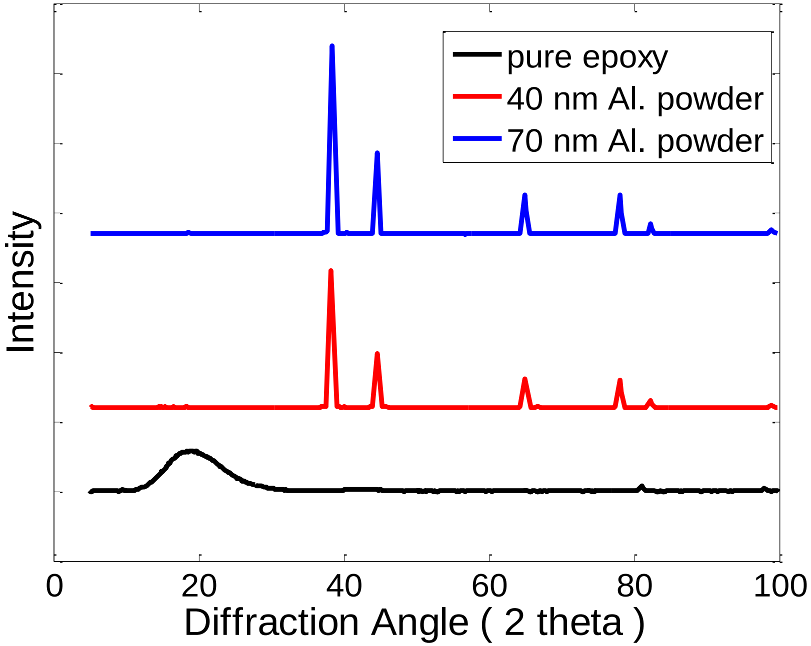
- X-ray diffraction (XRD) is powerful and nondestructive technique used for crystallographic characterization of solid materials, based on the basic principles that the angle of reflection of X-rays from a sample is related to the crystal structure and composition of the material.

- XRD can provide structural information of materials, and also the composition of crystallographic phases present in a sample.

- XRD was used to investigate the crystal structure of filler particles and to identify the material from the characteristic peaks.

XRD Plot

- The XRD patterns were recorded in the 2θ range 5-100 using an X-ray power diffractometer (Bruker AXS D8 Advance).
- XRD is used to confirm the metallic phase. Typical peaks of metallic Al phase are observed.
- The XRD spectrum of the nanoparticles showed well defined strong peaks at 2θ = 39.1, 45.3, 65.7, 78.8, 82.9, 99.6 corresponding to the (111), (200), (220), (311), (222), (400) respectively of the cubic Al phase.
- Epoxy shows the characteristic peak at 2θ = 17.8.



Thermogravimetric Analysis (TGA)

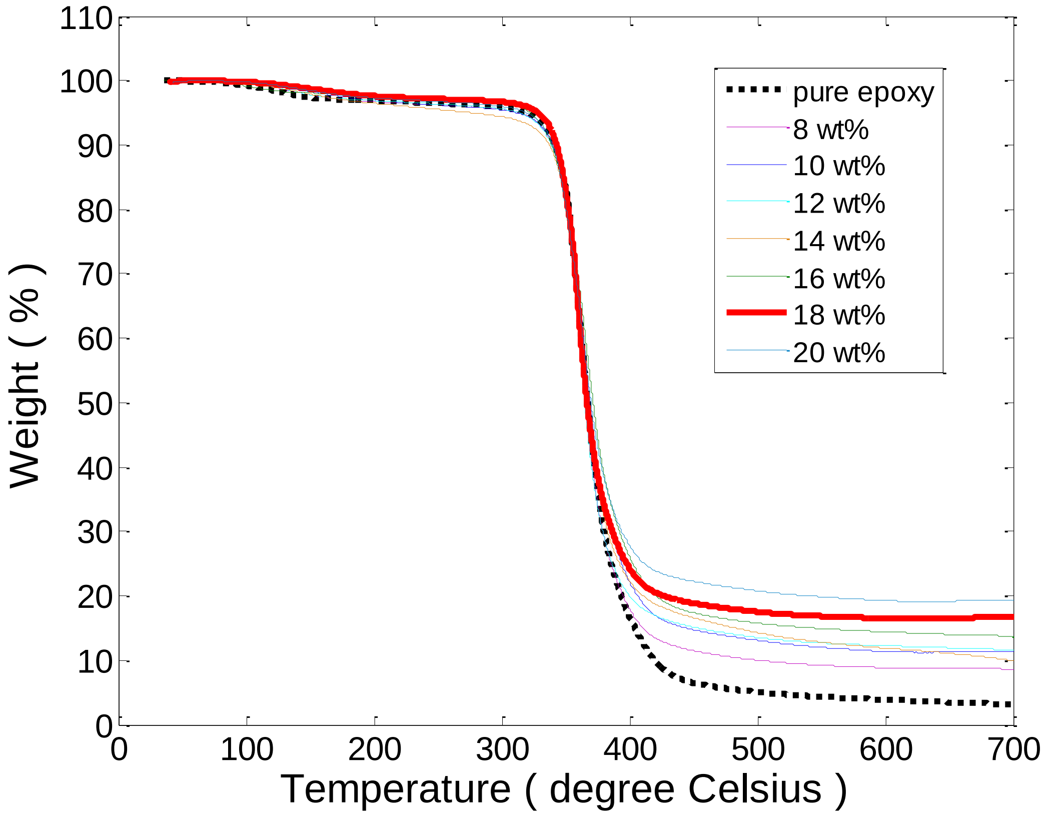
- A Thermogravimetric analyzer (Perkin Elmer Diamond) was used to characterize the material mass change as a function of temperature in a controlled atmosphere.

- TGA can be used to characterize any material that exhibits a weight change due to decomposition, oxidation, or dehydration.

- In TGA measurement, the weight of sample, temperature, and time were recorded.

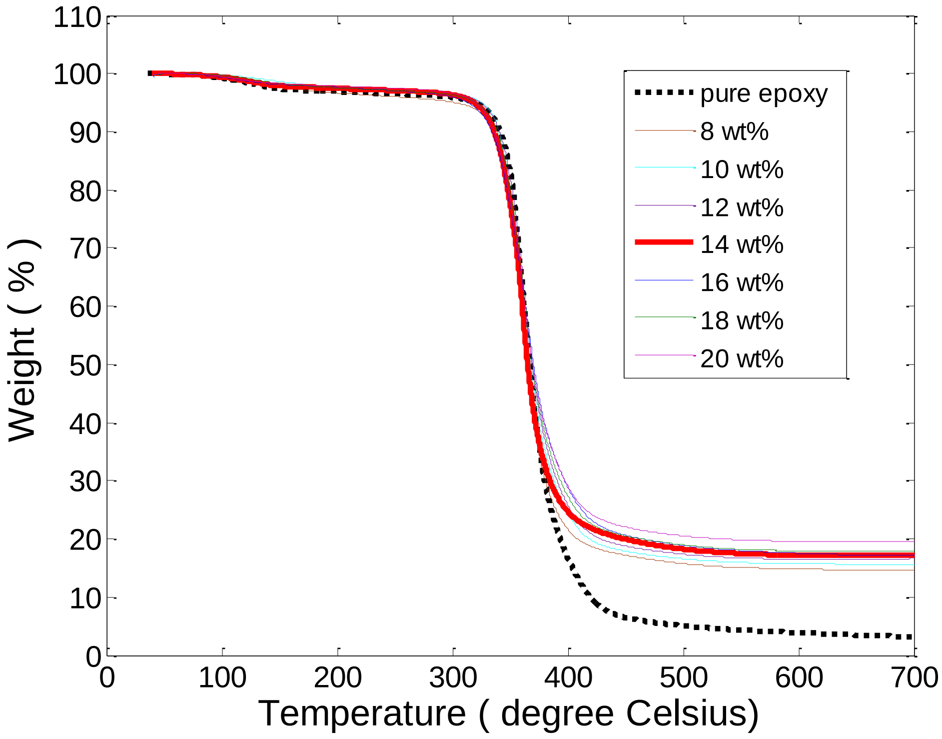
- TGA was used to investigate thermal stability (weight loss) of the nanocomposite samples.

Thermogravimetric Analysis (TGA) (70 nm samples)



- The decomposition region of pure epoxy as well as the composites is centered between 350 and 420 ^{o}C.

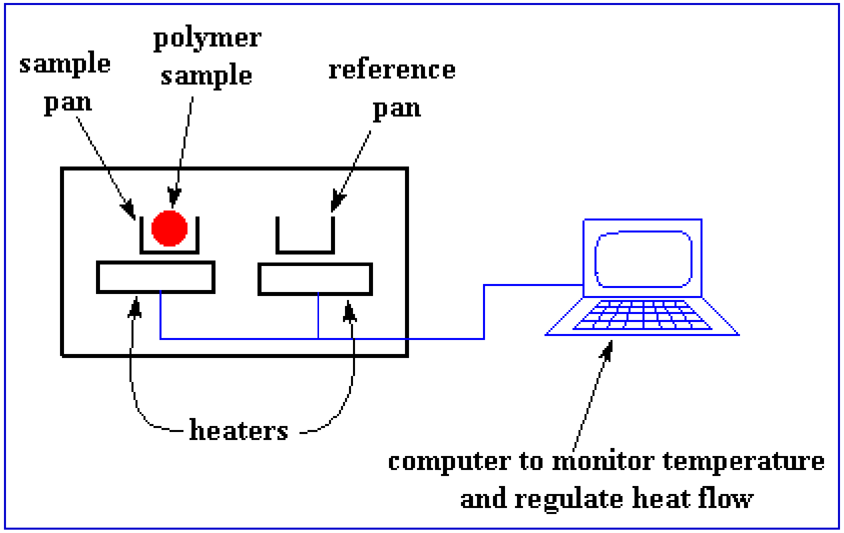
Thermogravimetric Analysis (TGA) (40 nm samples)



- It is observed that, the addition of aluminum nanoparticles do not have any influence on the thermal stability of the base material.

Differential Scanning Calorimetry (DSC)

- DSC is a technique used to study the *thermal transitions* of a polymer.
- There are two pans. In the sample pan, the polymer sample is kept and the reference pan is kept empty.
- It will take more heat to keep the temperature of the sample pan increasing at the same rate as the reference pan.
- The computer will plot the difference in heat output of the two heaters against temperature, that is the heat absorbed by the polymer against temperature.



Glass Transition Temperature (Tg)

- The Glass Transition Temperature (Tg) is one of the most important properties of any epoxy and is the temperature region where the polymer transitions from a hard, glassy material to a soft, rubbery material.

- Tg is not a discrete thermodynamic transition, but a temperature range over which the mobility of the polymer chains increase significantly.

- Polymers have a higher heat capacity above the glass transition temperature than they do below it.

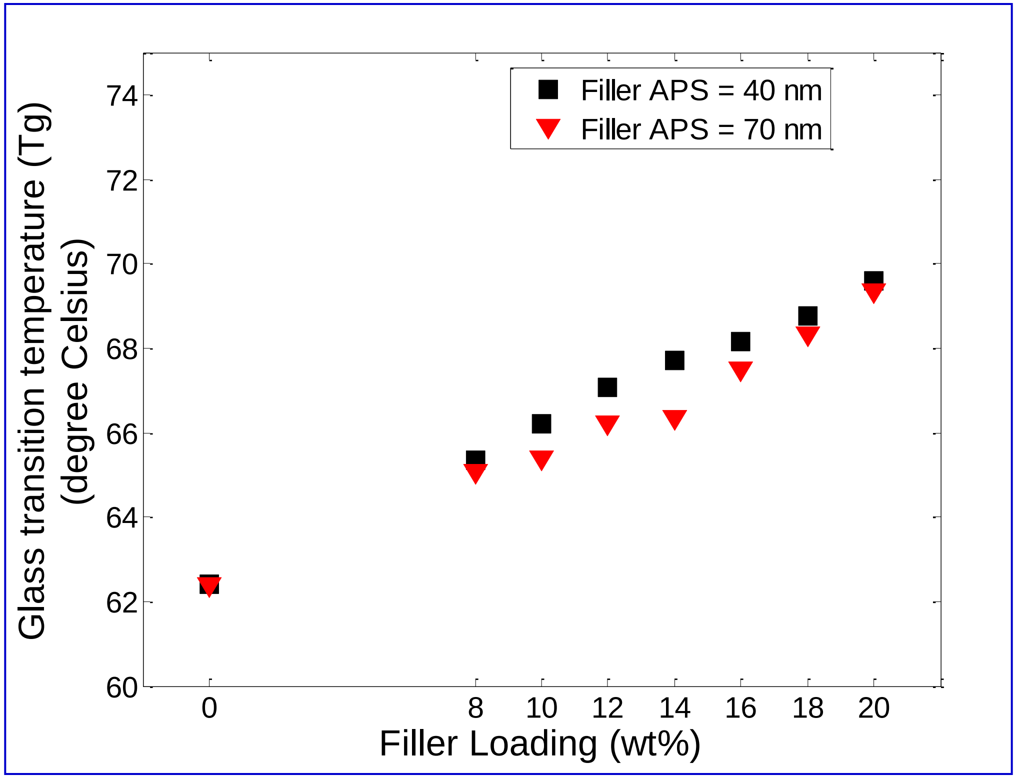
- Because of this change in heat flow that occurs at the glass transition we can use DSC to measure a polymer's glass transition temperature.

- Tg is defined as the midpoint of the temperature range, bounded by the tangents to the two flat regions of the heat flow curve.

Tg of Epoxy-Aluminum Nanocomposites

- the temperature region where the polymer transitions from a hard, glassy material to a soft, rubbery material.

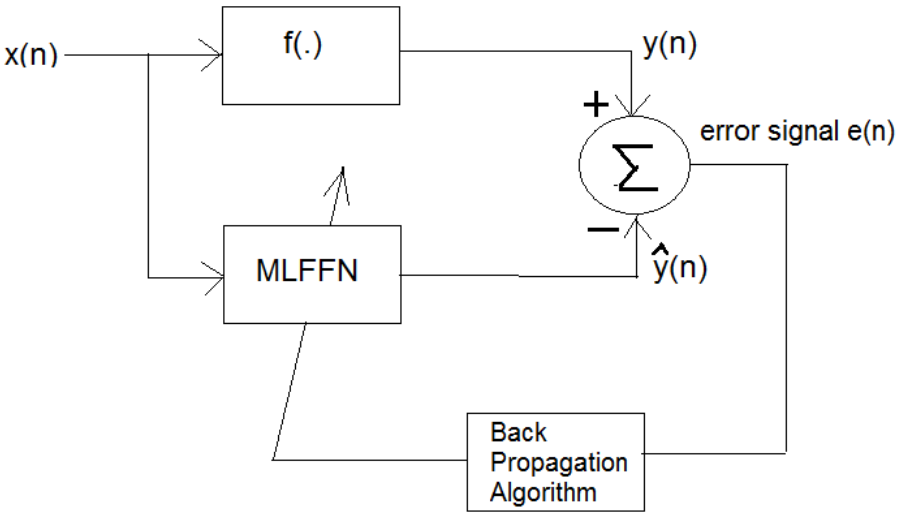
The glass-transition behavior of epoxy aluminum nanocomposites have been investigated with DSC Analysis using a Mettler make DSC equipment.



- Sample (15 mg) is heated at a ramp rate of 10°C/min, from the ambient temperature to 150°C, to obtain the heat-flow diagram from which the glass transition temperature of the composite will be obtained.

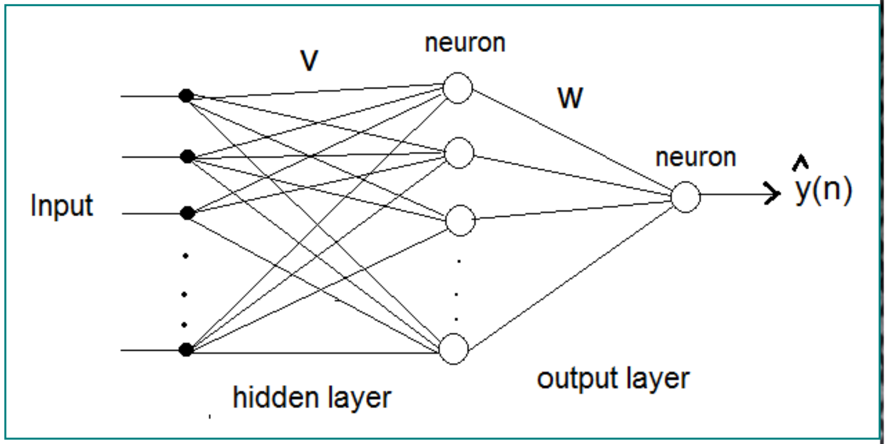
Artificial Neural Network model

- Since it is difficult to do experiments for all the filler concentrations and particle sizes, an Artificial Neural Network model is developed which can predict the dielectric constant and breakdown strength of the nanocomposite with any size nano fillers at different filler concentrations.
- Neural network is a very good approach for system modeling when only the inputs and corresponding outputs are known.



Block diagram of system modeling using Neural network

MLFFN



Artificial Neural Network model

- A Multi layer Feed forward Neural Network is used to model the nanocomposite system to predict the dielectric constant and breakdown strength at different filler concentrations of different size fillers added.

- Inputs to the system are :

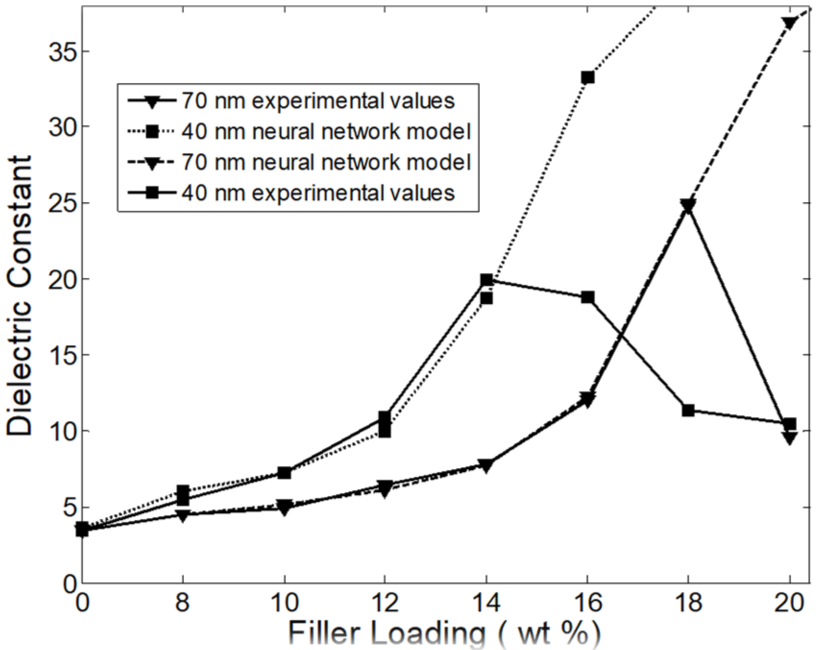
  (i) Permittivity of polymer matrix
  (ii)Permittivity of filler
  (iii)Size of filler particles
  (iv)Concentration of filler

- For training the Neural Network model, experimental results obtained for 70 nm nanocomposites are used.

- The well known Back Propagation Algorithm can be used to train the network.

Artificial Neural Network model

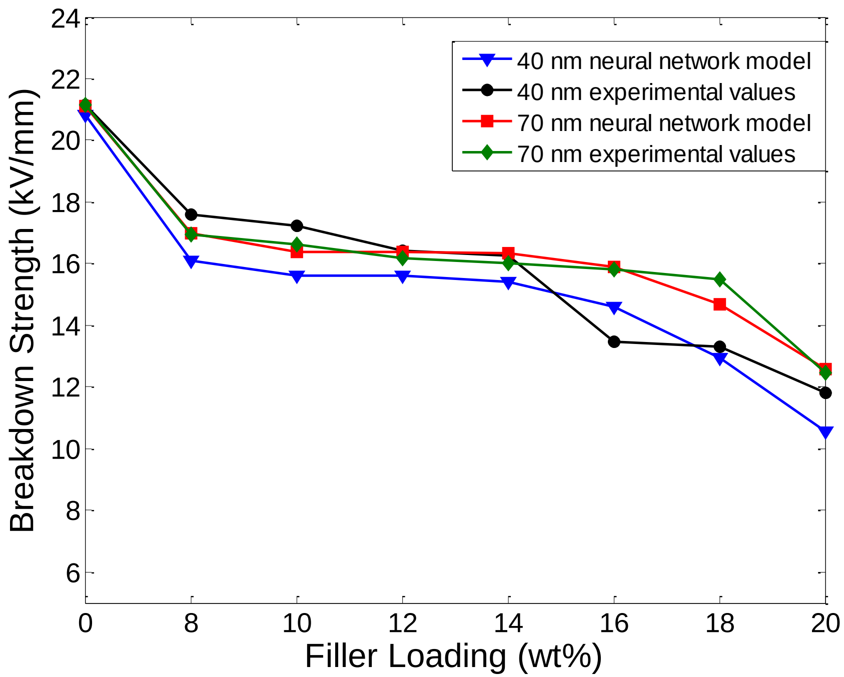
Dielectric Constant

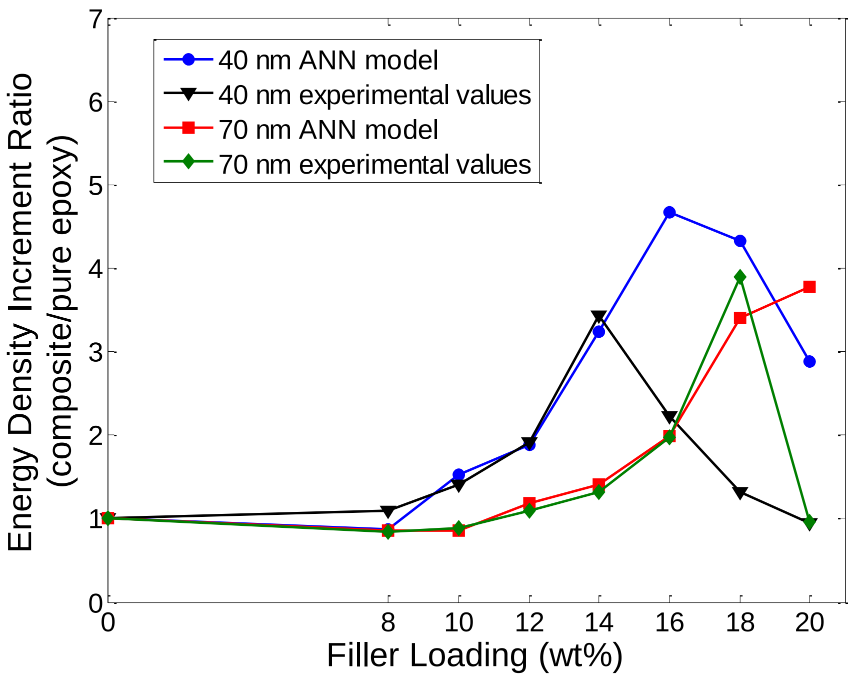


- The predicted values of 40 nm composites match very well with experimental values at lower filler loadings.
- The model can be used for predicting the dielectric constant of the nanocomposites with any filler size at different concentrations.

Artificial Neural Network model

Breakdown strength & Energy Density

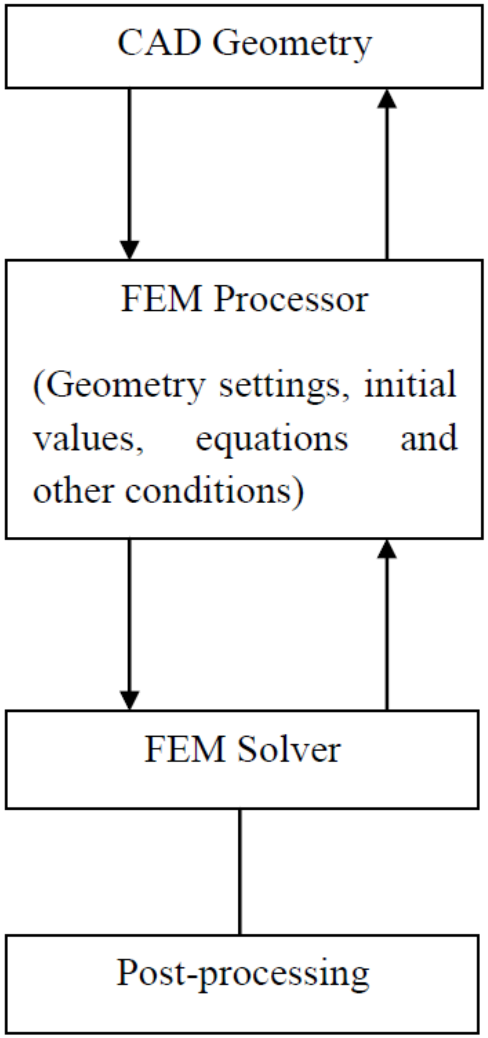


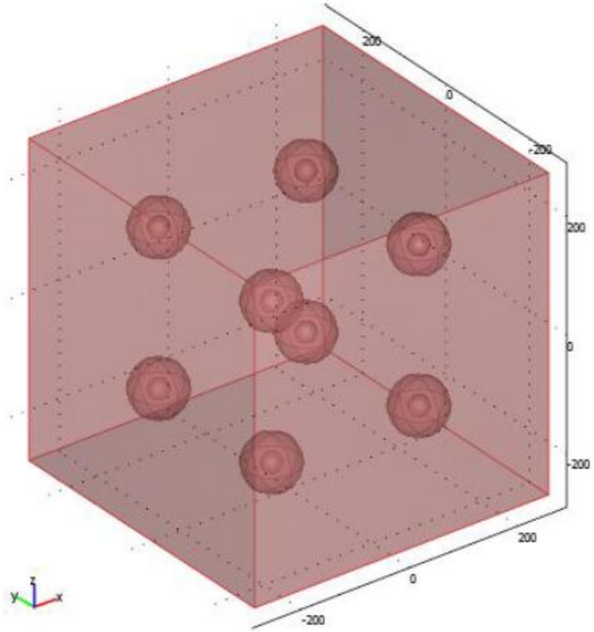


- The ANN model approximates experimental values at lower filler concentrations and the model can be used for predicting the Energy density of the composites at different filler concentrations with any filler size.

COMSOL MULTIPHYSICS

- COMSOL MULTIPHYSICS is a software based on FEM (Finite Element Method)
- Geometry is divided into finite number of small elements.

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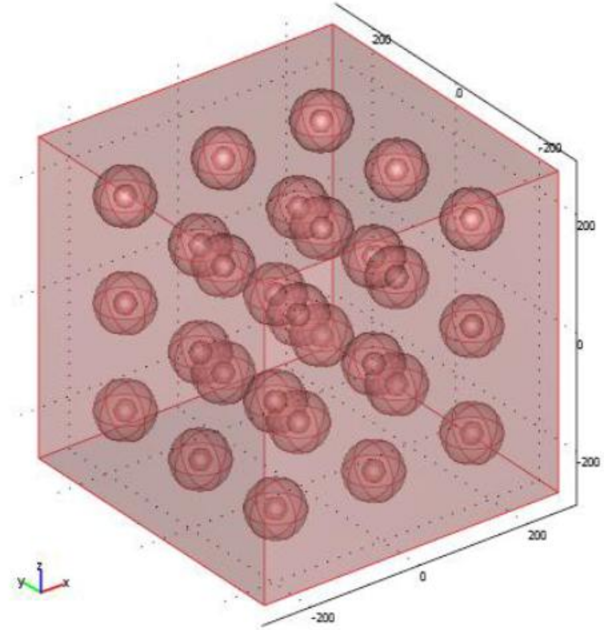
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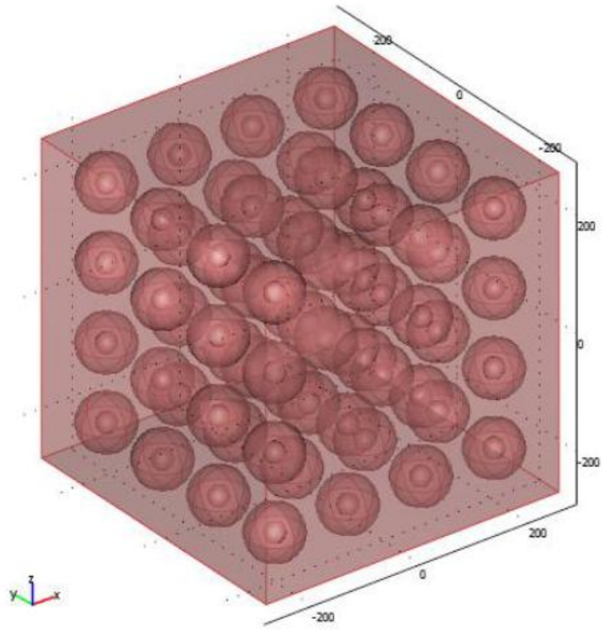
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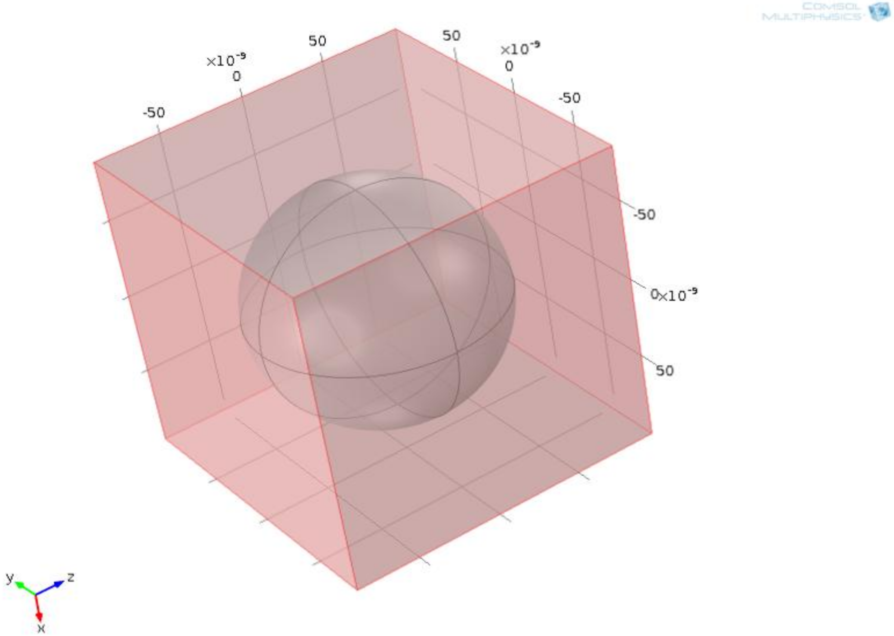
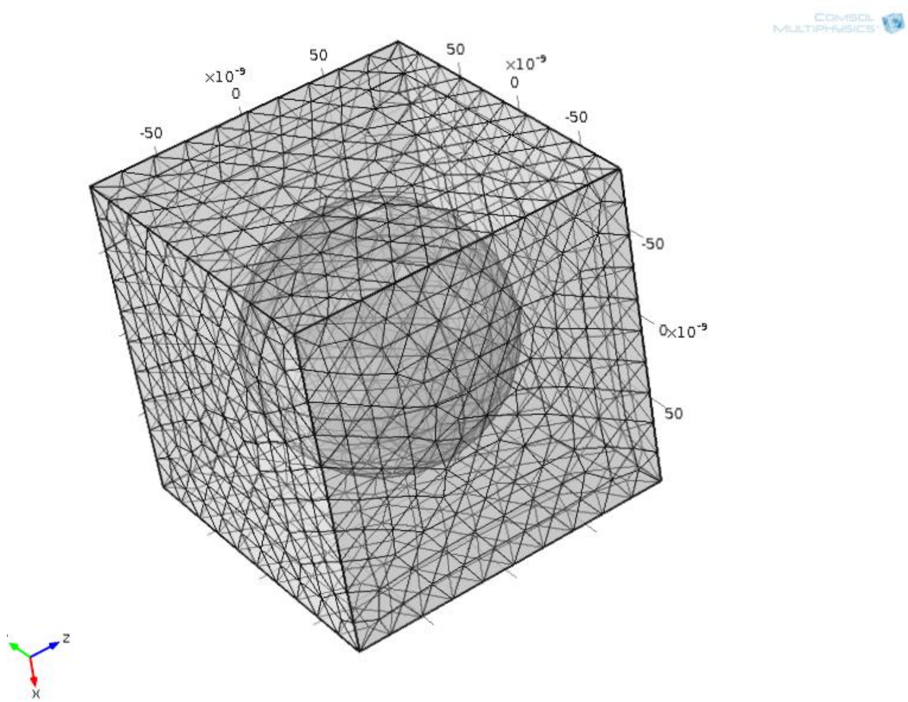
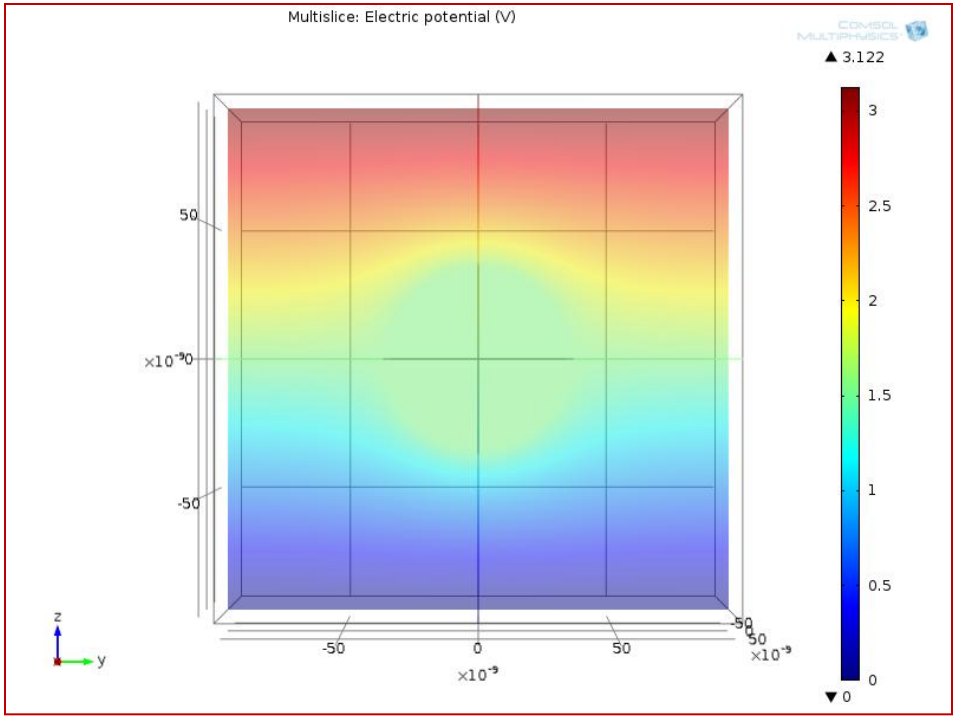
Unit cell after meshing

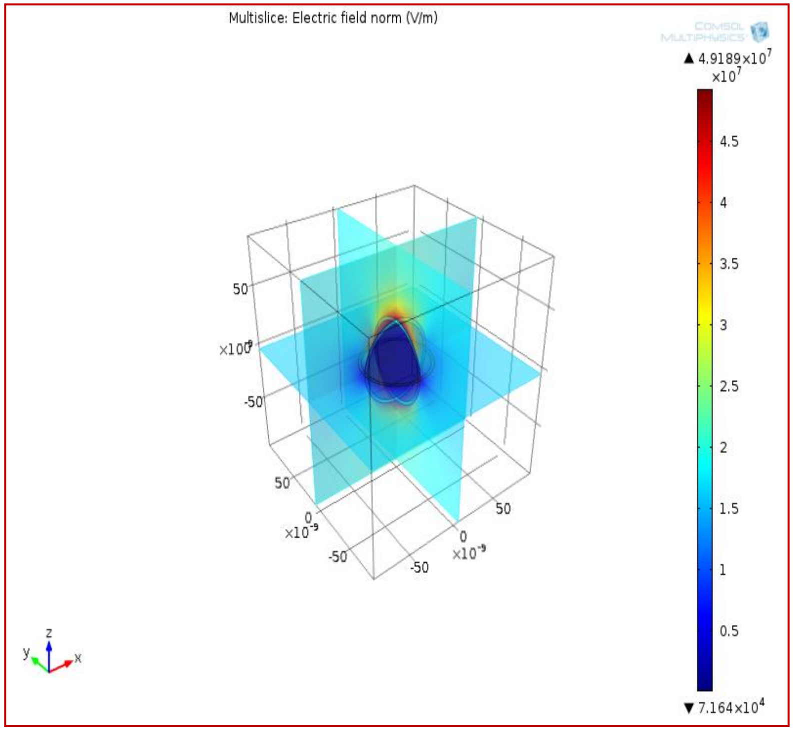




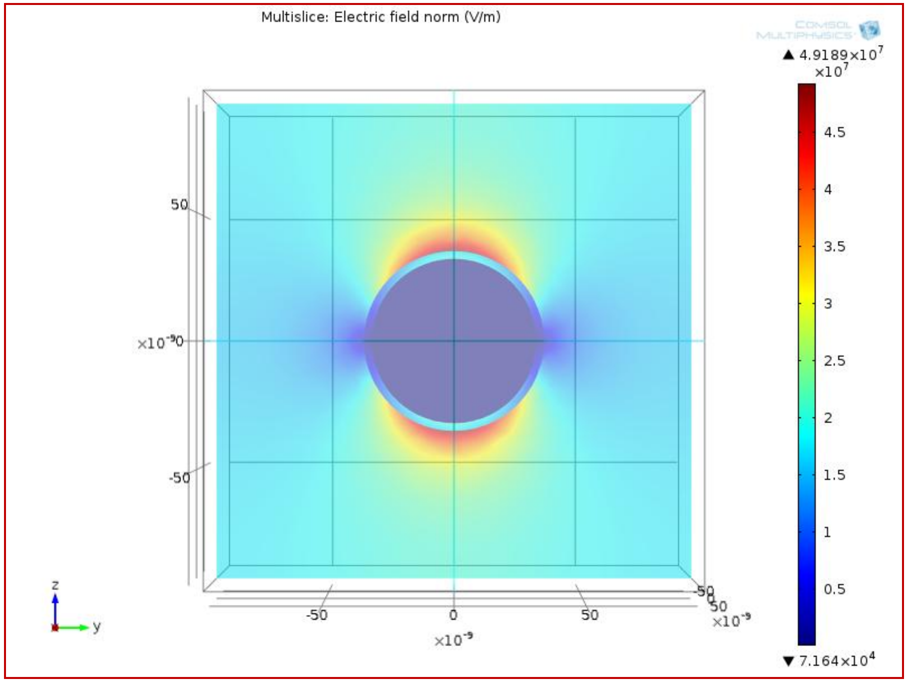
ELECTRIC FIELD DISTRIBUTION IN COMPOSITE (unit cell)

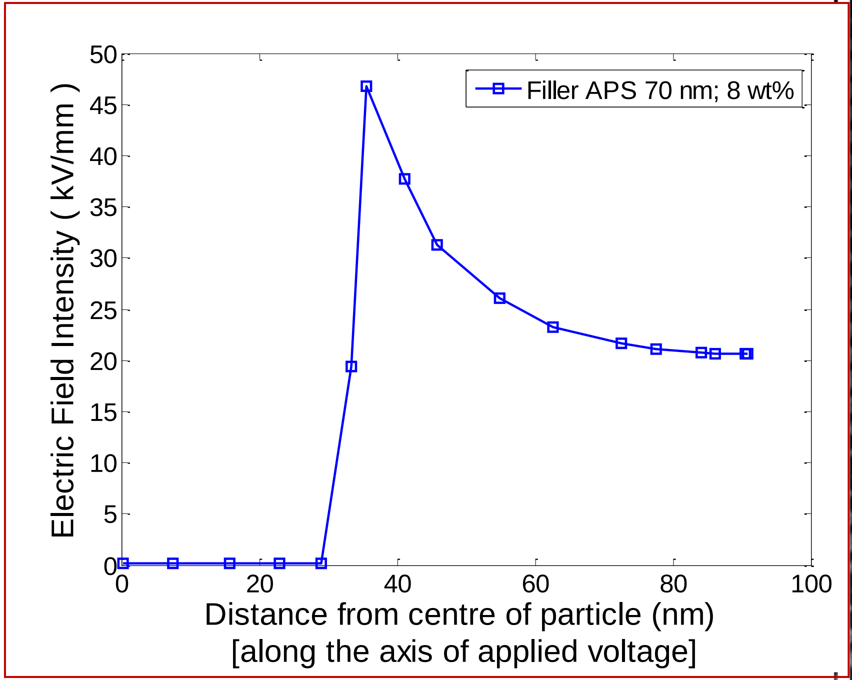
Applied 3.122 V (eqvt voltage of experimental BDV) to unit cell 184.42e-9 m [70nm composites at 8 wt%]





ELECTRIC FIELD DISTRIBUTION IN COMPOSITE (unit cell)





- Maximum Electric Field appears at the interface along the axis of applied voltage.

Applications

- Epoxy-aluminum nanocomposites can be used for embedded capacitor applications since they possess high dielectric constant and low dissipation factor and also they are compatible with PCB manufacturing process.

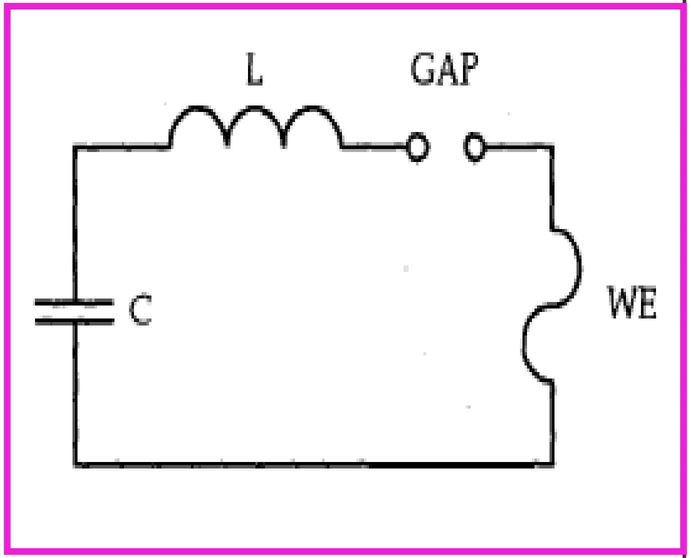
- Epoxy-aluminum nanocomposites can be used for energy storage applications. High energy density capacitors are used in pulsed power circuits where very large amounts of energy are to be delivered in a very short time.

- Future Energy storage device: Capacitors and batteries can be used together in hybrid energy storage systems.

Production of Nanoparticles

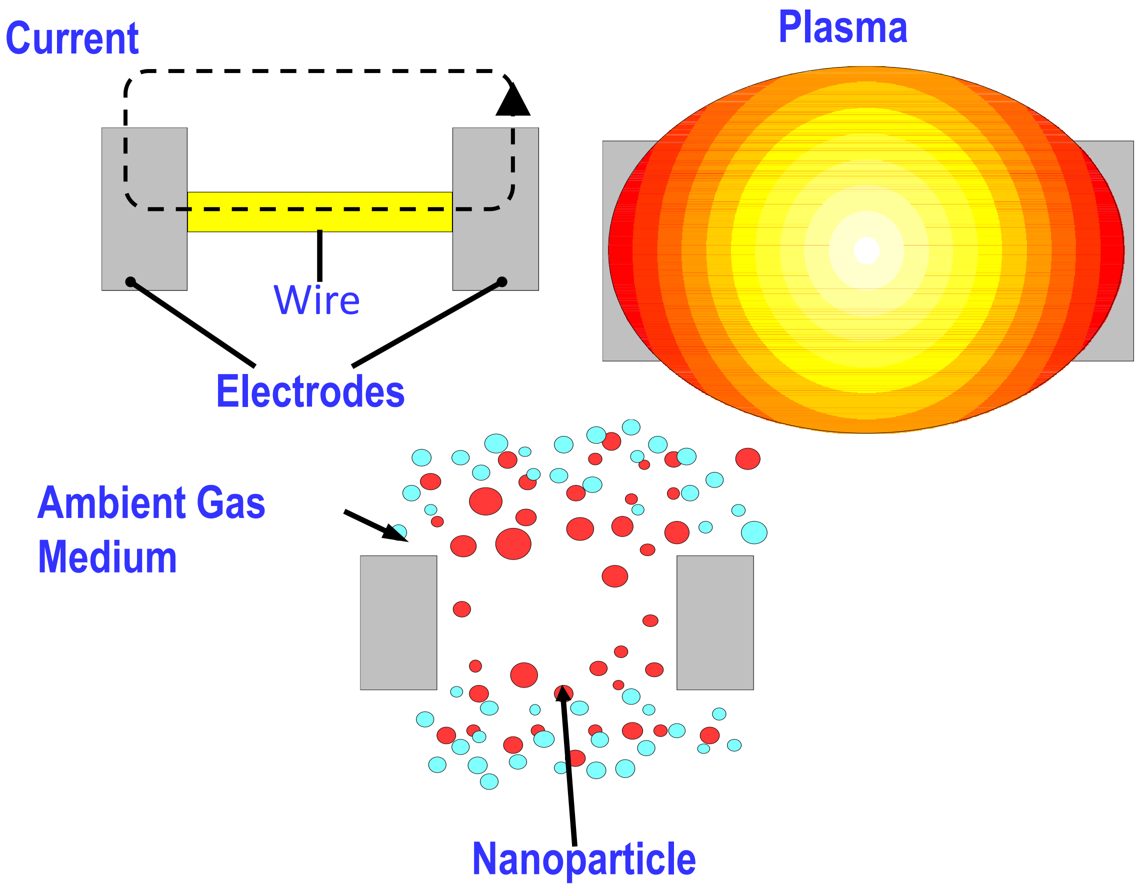
Wire Electric Explosion

- Wire electric explosion (WEE) is a top-down method
- A thin metallic wire is the bulk material
- Wire is made the most resistive part of the circuit
- When passing a high density current through the wire, heating occurs and wire explodes
- The products of the wire explosion are finest particles of metal.

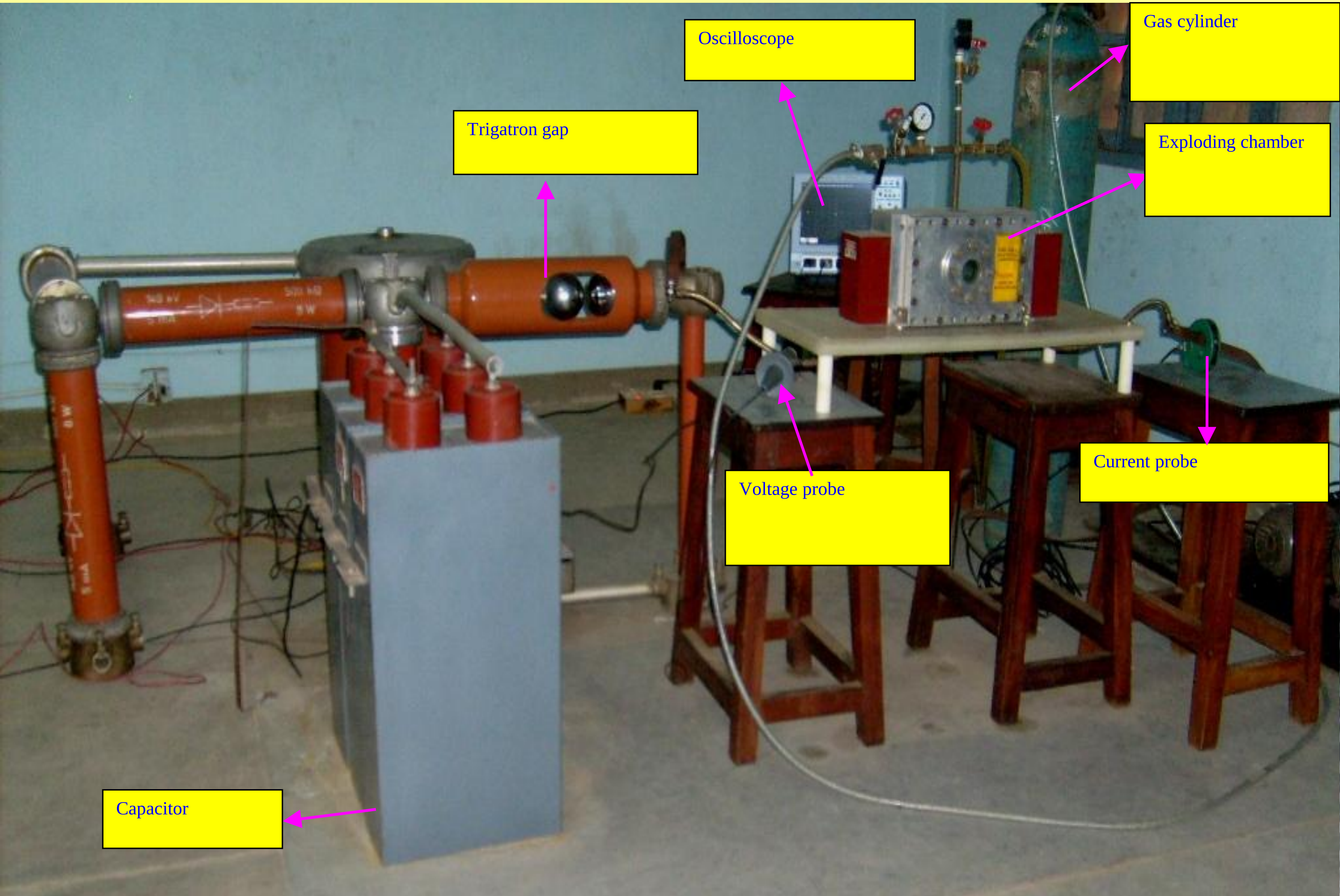


Wire explosion (one method to produce metal nanoparticles)

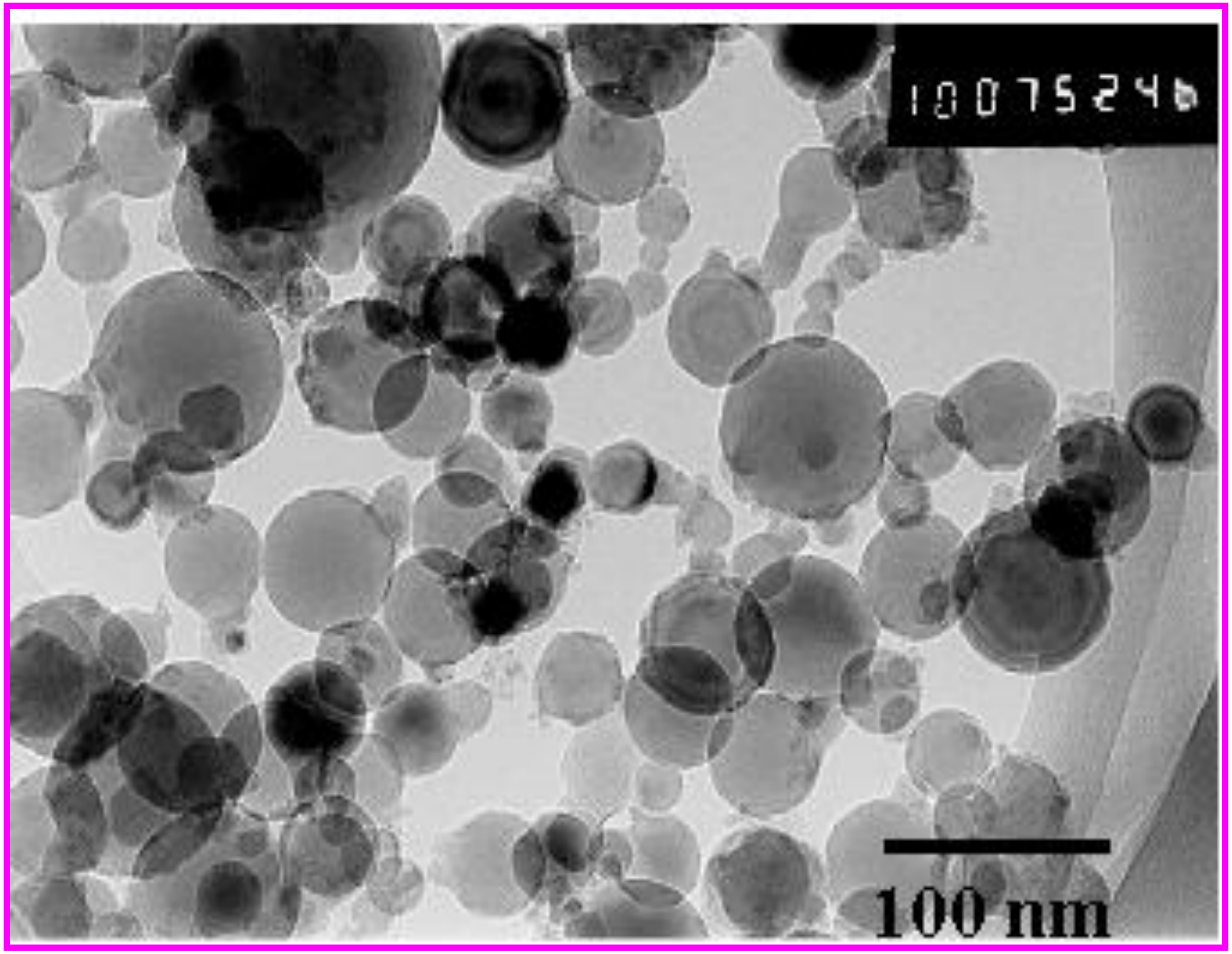
Wire electric explosion (WEE) is a phenomenon of explosive destruction of a metallic wire when passing a high density current through the wire.



Experimental Set-up



Transmission Electron Microscope Image



Electron microscope picture of nanoaluminium particles

H V Lab at EEE Department, MACE Kothamangalam

Nanotechnology Centres

- IISc Bangalore – Centre for Nanoscience and Engineering
- IITs
- NITs
- NIT Calicut – School of Nanoscience and Technology
- Amritha Coimbatore
- Cochin University
- M.G. University – Kottayam

INUP – Indian Nanoelectronic Users Programme:
IISc, IIT Bombay

Thank you