Applications of NanoDiamond in Thermally Conductive / Electrically Nonconductive Polymers

Gavin Farmer – Carbodeon / Business Development

15th Anniversary HVM 2017 & 4th Graphene New Materials Conference
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www.cir-strategy.com/events

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Carbodeon in Brief

- uDiamond® NanoDiamonds
  - >12 M€ investment in NanoDiamond production and application technologies
- Offering
  - ***For Engineering polymers***
    - **20-200% improvement in thermal conductivity**
    - **Tailored glass transition temperature**
    - **Significant improvements in compound mechanical properties**
  - *For Wear and corrosion resistant metal coatings*
    - >200% improvement in electroless nickel coating wear resistance, without impairing friction or corrosion properties
  - *For Industrial polymer coatings*
    - Fluoropolymer coatings with doubled wear resistance, improved corrosion resistance and tailored friction properties.
    - Transparent coatings with improved wear and corrosion resistance, without impairment of optical properties
- USP's
  - High performance with very low NanodDiamond loadings, easy to use and implement to current production processes, cost efficient
  - Industrially applied
- IP
  - Both product line and key applications are IP protected

- HQ in Finland, Helsinki Region
- Established 2006
- 10 employees
- Sales on 4 continents

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Carbodeon in Brief

Artwork: Nancy Farmer / www.nancyfarmer.gallery

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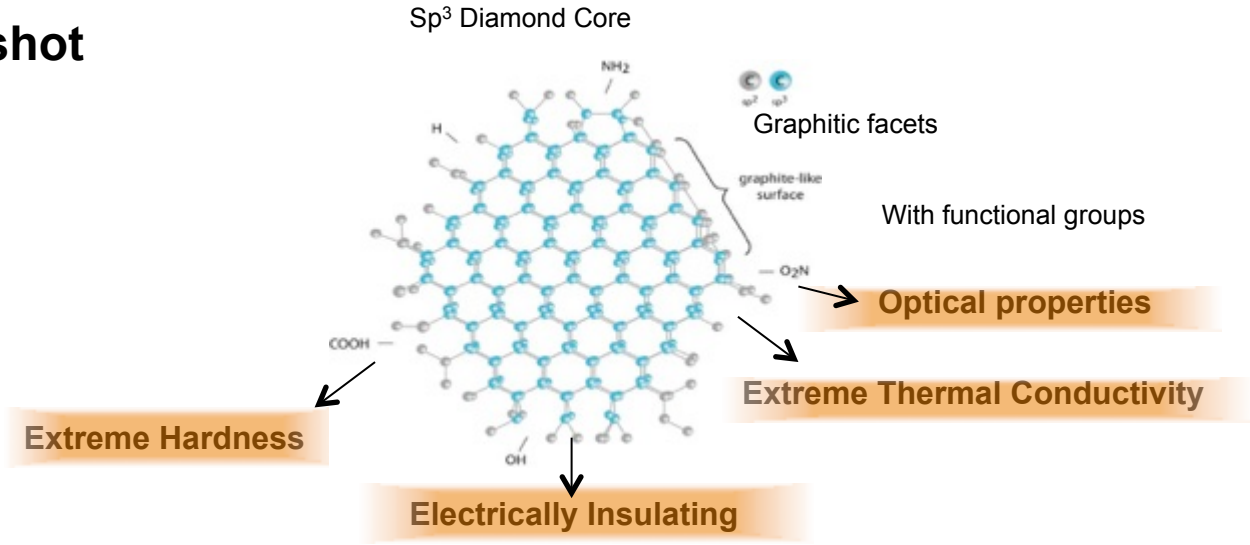
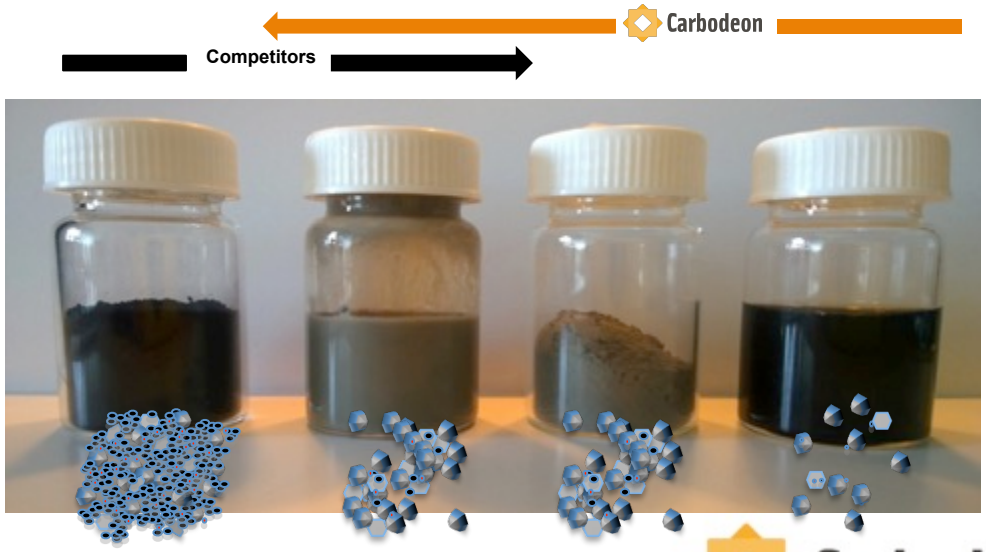
Nanodiamond Material

Nanodiamonds - Snapshot

- Detonation produced 4-6 nm particles
- Base technology invented 1963 – not “getting there”
- Carbodeon disruptive technologies realizing the industrial potential
- Able to manufacture and utilize the primary particles
- “Less is More”





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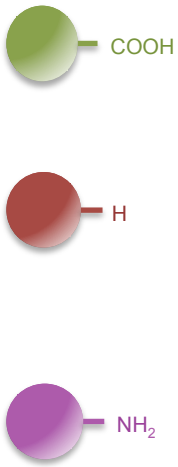
Application Dependent Surface Chemistry and Morphology

Powder grades	Surface	Zeta potential	Solid content**
Molto	Multi-functionalized	Slightly negative	100 wt.%
Vox P	Carboxylated	Highly negative	100 wt.%
Hydrogen P	Hydrogen terminated	Highly positive	100 wt.%
Amine P	Amine-fucntionalized	Highly positive	100 wt.%



Dispersion grades	Surface	Zeta potential	Solid content
Vox D, in water	Carboxylated	Highly negative	5 wt.%
Vox D, in NMP	Carboxylated	Highly negative	2 wt.%
Vox D, in DMA	Carboxylated	Highly negative	2 wt.%
Hydrogen D, in water	Hydrogen terminated	Highly positive	2.5 wt.%
Hydrogen D, in ethyl glycol	Hydrogen terminated	Highly positive	4 wt.%
Hydrogen D, in GBL	Hydrogen terminated	Highly positive	3 wt.%
Hydrogen D, in NMP	Hydrogen terminated	Highly positive	3 wt.%
Hydrogen D, in NEP	Hydrogen terminated	Highly positive	2 wt.%
Hydrogen D, in DMA	Hydrogen terminated	Highly positive	3 wt.%
Amine D, in water	Amine-functionalized	Highly positive	0.5 wt.%
Amine D, in NMP	Amine-functionalized	Highly positive	3.0 wt.%
Amine D, in ethyl glycol	Amine-functionalized	Highly positive	3.0 wt.%
Amine D, in GBL	Amine-functionalized	Highly positive	3.0 wt.%
Amine D, in DMA	Amine-functionalized	Highly positive	2.0 wt.%

Specialty Additive Grades	Surface	Zeta potential	Solid content
Plating Additive	Proprietary, in water	Highly positive	2 wt.%
Fluoropolymer coating additive	Proprietary, in GBL	Highly positive	0.5 wt.%

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Intellectual Property

Carbodeon invested heavily in the **IP protection of its developments** over the entire supply chain

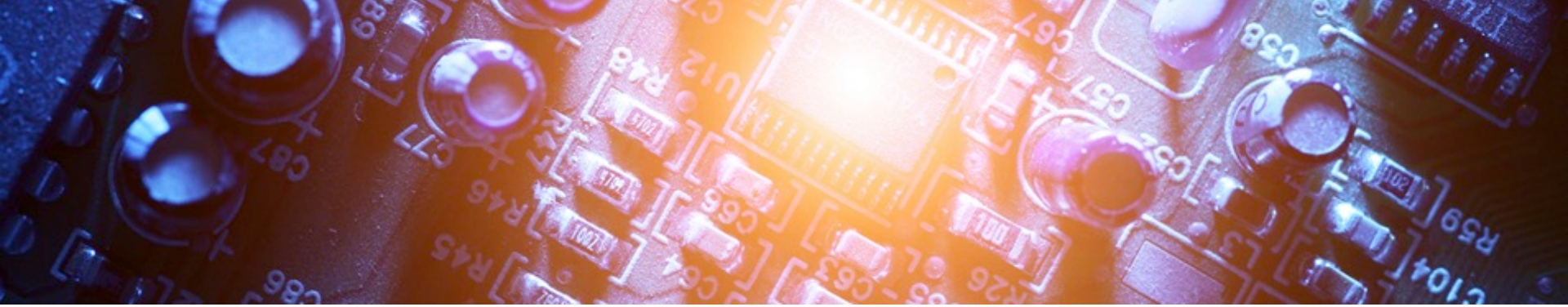
- The uDiamond® trademark is worldwide* registered
- The IPR are based upon a combination of 3 pillars: 1) Product 2) Production 3) Application

	Patent	Finland	PCT	EPO	USA	Japan	Korea	China	Russia	India
Products & production	Blend Purification method			P	P	P		P		
	Carboxylated SDND	G		P	P	P	P	P	P	
	Hydrogenated SDND	G		P	P	P	P	P	P	
	Amine SDND	G		P		P		P		
Applications	Thermoplastic ND containing thermal compounds	G		G	G	P	P	P		P
	Polymer ND containing thermal compounds	P			P	P				
	Mechanically enhanced Fluoro-polymer Coatings, 1st application	G		P	G	P	P	P		
	Metal coating, with SDND's	P	X		P					
	Mechanically enhanced Fluoro-polymer Coatings, 2nd application	P								

P = Pending / **P** = Pending (positive Official Action(Notice of Allowance

G = Granted

* Worldwide: Finland, EPO, USA, Norway, India, Canada, Russia, Japan, China, South Korea



Nanodiamond Additives Within Polymer Materials for Thermal Management

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Nanodiamond – Advanced Thermal Additive for Polymers

	Diamond	H-BN	Al_2O_3	SiO_2	AlN	ZnO
Thermal Properties						
Thermal conductivity, (W/m K)	**2000**	300+	30	1.4	260	54
Theoretical Density, g/cm^3	3.1-3.2	3.9	3.98	2.2	3.26	5.64
Electrical Properties						
Dielectric constant	3.4	3.9	9.7	3.8	8.8	9.8
Electrical Resistivity, Ω•cm	10^{13}	10^{15}	10^{14}	10^{14}	10^{14}	10^{7}
Surface properties, for coupling effect						
Chemical Functionalization	**Yes**	No	No	No	No	No

- Optimized control of interaction between the filler, resin and other fillers (when present)
  - Reduced thermal resistance
  - High wettability
- Isotropic filler, with size fitting between the polymer chains

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Nanodiamond Thermal Management Milestones

- **Silicone based thermal interface materials**
  - Nanodiamond+aluminium oxide filled silicone interface material in mass production for use in OEM consumer electronics devices **since 2012** . Carbodeon supplies nanodiamond and nanodiamond filler mixes mainly to formulators.

- **Thermally conductive thermoplastic materials**
  - In house developments on PA and PP since 2012 – Nanodiamond + boron nitride, Nanodiamond + graphite filler combinations
  - Production on the way - validated **since 2016** – consumer electronics devices – Carbodeon supplies nanodiamonds and nanodiamond filler mixes at various levels in the supply chain
  - Patent granted on nanodiamond thermoplastic compounds **2015 WO 2014049212**

- **Epoxy materials**
  - Customer validations **2017** in both coatings and thermal management applications for electronics – Carbodeon supplies nanodiamonds and nanodiamond filler mixes at various levels in the supply chain.

- **Nanodiamond containing thermal compounds**
  - Patent granted **2017**, new invention encompassing both thermoplastic and thermoset materials **US 9598558**

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Case Example: Nylon-66 Thermal Compounds

- **Materials:**
  - PA-66: Zytel 135F
  - Boron Nitride: ESK Boronid® thermal filler, 15 µm
  - Nanodiamond: Carbodeon mono-functionalized ND's
- **Processing:**
  - Compounding: Xplore15 micro-compounder
  - Injection molding: Thermo-Haake Minijet, 25*25*3 mm mold
- **Thermal analyses:**
  - Laser flash method (ISO 18755; LFA 447, Netzsch GmbH)

VTT

ESK

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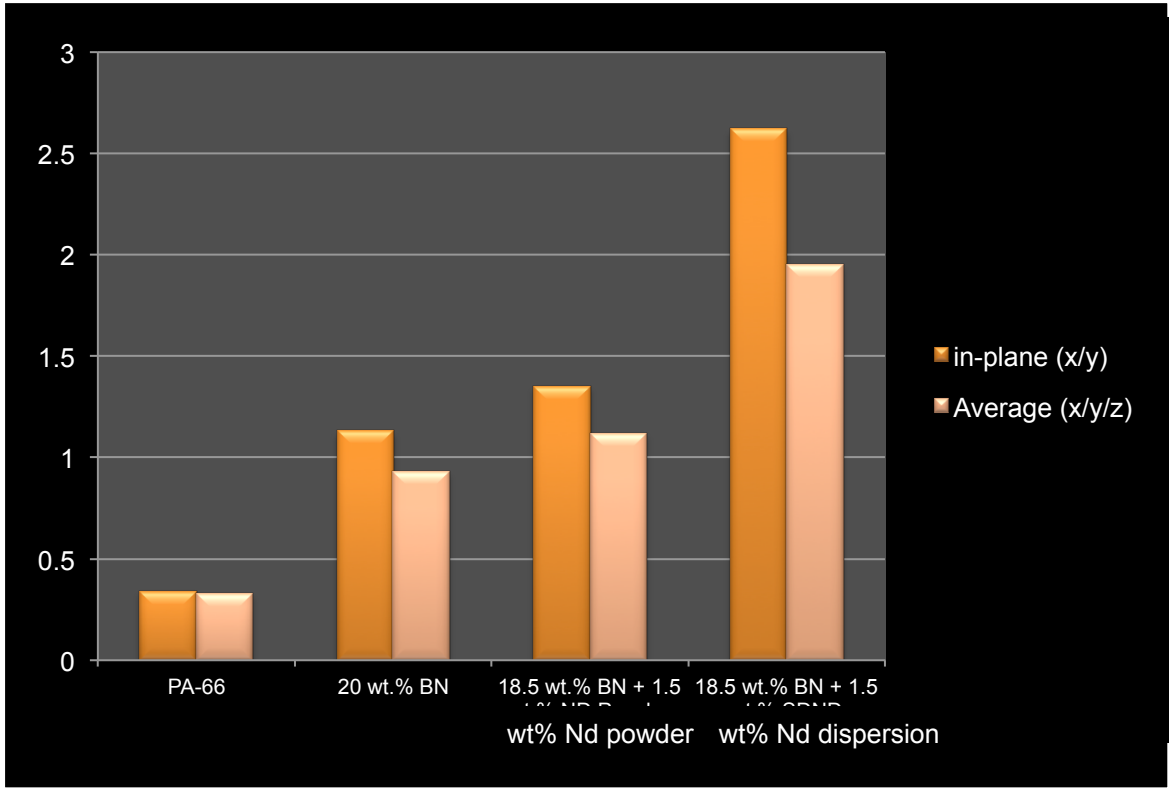
PA-66 Thermal Compound, 20 wt.% Overall Filler Loading

- References:
  - Neat PA-66
  - Compound with 20 wt.% BN loading
- ND-containing compounds:
  18.5 wt.% BN + 1.5 wt.% ND
- Performance (W/m · K)
  - Powder grade: > **22%** improvement in average thermal conductivity
  - Dispersion grade:
    - **132%** improvement within in-plane thermal conductivity
    - **105%** improvement within average thermal conductivity



- **Highlights the importance of the preparation method**

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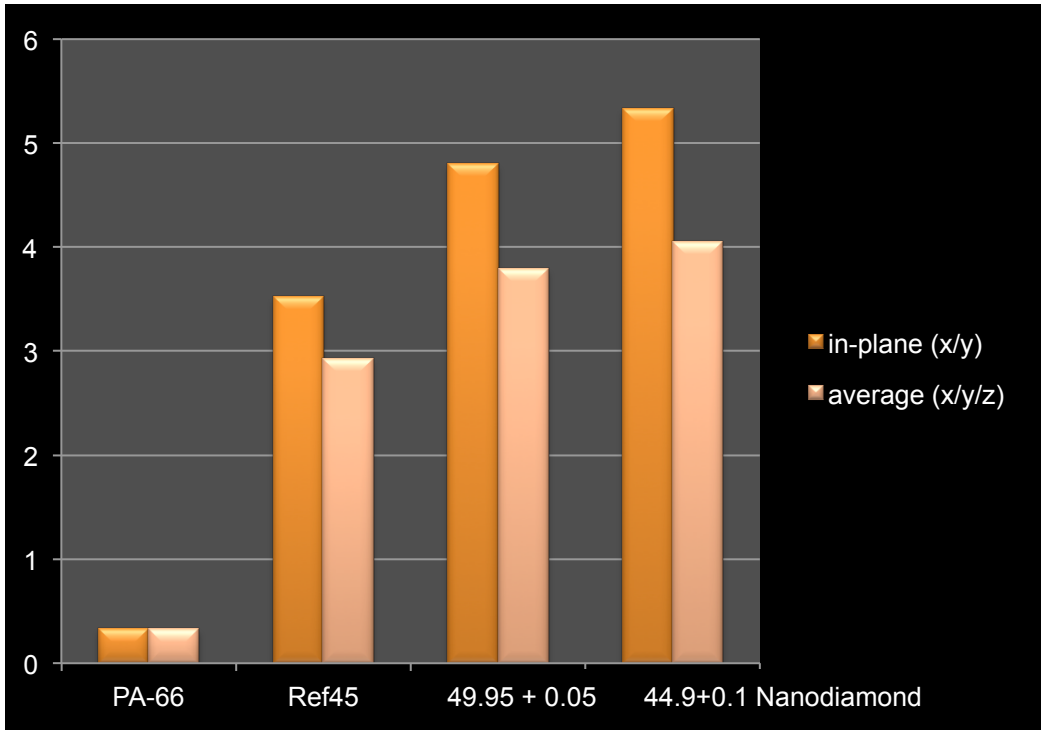
PA-66 Thermal Compound, 45 wt.% Overall Loading

- References:
  - neat PA-66
  - compound with 45 wt.% BN loading
- Processing:
  - Carbodeon proprietary
- Performance (W/m · K):
  - 0.05 wt.%
    - **36.3%** improvement within in-plane thermal conductivity
    - **29.4%** improvement within average thermal conductivity
  - 0.1 wt.%
    - **51.4%** improvement within in-plane thermal conductivity
    - **38.2%** improvement within average thermal conductivity



- **Works at very low nanodiamond concentrations**

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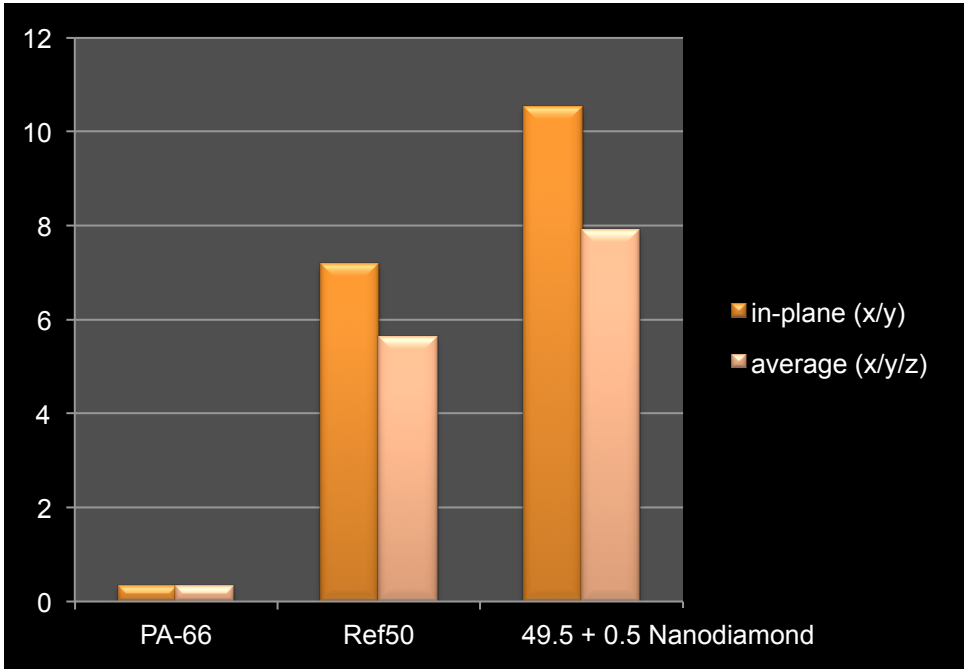
PA-66 Electrically Conducting Thermal Compound, 50 wt.% Overall Loading

- References:
  - neat PA-66
  - compound with 50 wt.% graphite loading
    - Graphite filler material, TIMCAL TIMREX® KS5-75TT Primary Synthetic Graphite
- Performance:
  - 0.5 wt.%
    - **46.3%** improvement within in-plane thermal conductivity
    - **40.7%** improvement within average thermal conductivity
- **Works with a wide variety of filler materials**



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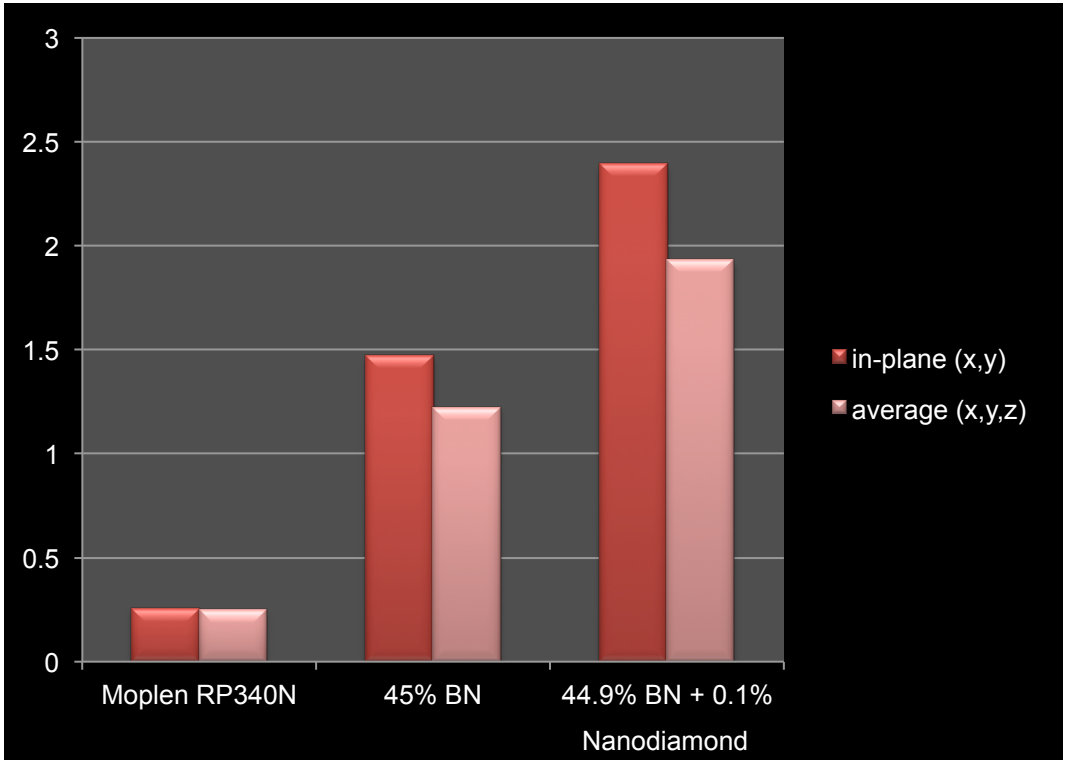
PP Electrically Insulating Thermal Compound

- 45 wt.% overall filler loading
- References:
  - neat PP; Moplen RP340N
  - compound with 45 wt.% BN loading
    - ESK Boronid® thermal filler, 15 µm
- Performance:
  - 0.1 wt.%
    - **63%** improvement within in-plane thermal conductivity
    - **58%** improvement within average thermal conductivity
- **Works with a wide variety of thermoplastic polymers**



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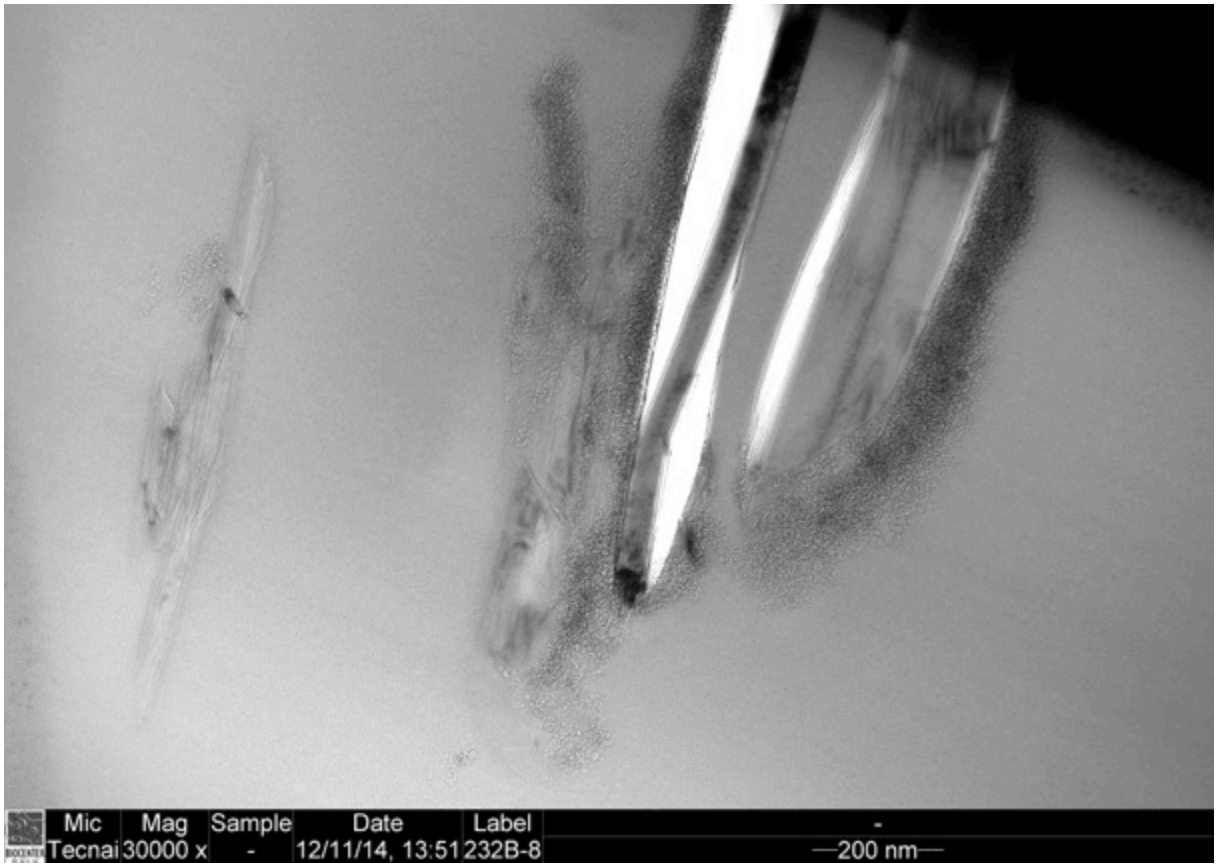
Verifying the Coupling Concept

FIB-STEM on a ready PA-66/BN/ND compound



- Diamonds retain their adhesion to h-BN during compounding and injection molding

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Ongoing Activities With NanoDiamond Combined Fillers

- Thermoplastics
  - Main application area is in electronics and LED applications.
- Thermosets
  - Main application has been in thermal interface materials to date, but materials such as coatings of wires for electrical coils/ machinery could be a viable application.
- In house filler mixes
  - So far, about 90% of the developments involve nanodiamond supply only, with in-house filler mixing (in sample form) accounting for around 10%, but there is growing interest in this.
  - Ready preparations of nanodiamond and boron nitride, aluminium oxide or other materials will be easier to disperse into customer polymers.
- Supply Chain
  - Attacking mainly at component/ system level, formulators include both Carbodeon preferred partners and customer's existing suppliers

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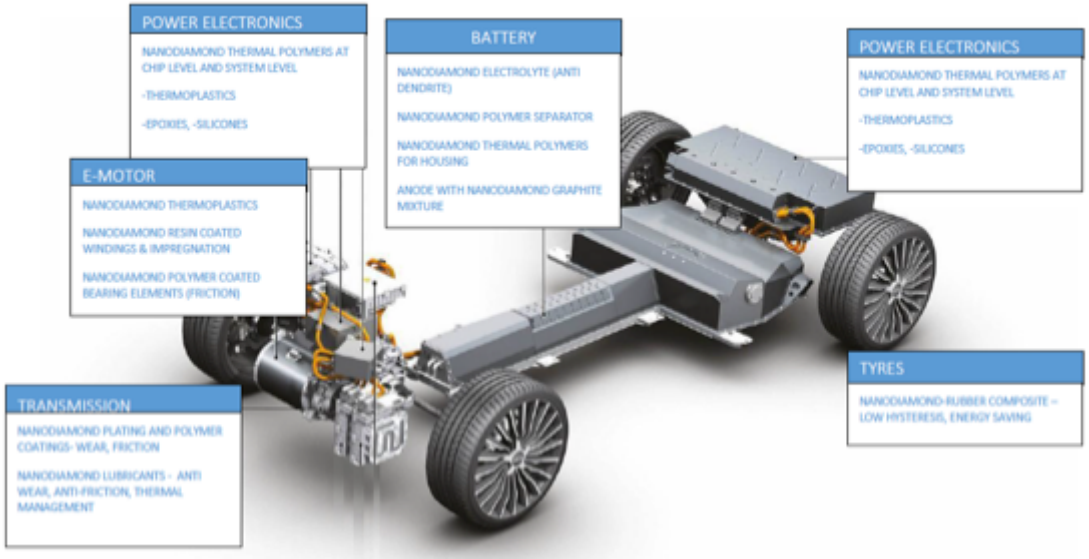
Industry Targets

- Consumer Electronics
- High Powered LED
- E-Mobility (New Focus)
  - Power electronics at device and assembly level - vehicles and charging systems
  - Coatings and insulating pieces for electrical machine coils
  - Nanodiamond electrolytes to control dendrite growth in Lithium batteries
  - Low friction/ wear resistant materials and coatings in driveline



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Nanodiamond USP within Polymer Thermal Management

- Technical performance
  - NanoDiamonds exhibit very high thermal conductivity and are electrically insulating
  - NanoDiamond surface functionalization allows efficient coupling to applied polymers and other thermal filler materials
  - Nanodiamond dispersions allow the improvements with very low nanodiamond concentrations
- Processing
  - Nanodiamonds can be applied within existing production processes & supply chains
- Cost
  - By using low concentrations, impact on material cost starts from approximately €1 per kg of the compounds. Most applications are in the range €2-10
- Commercial stage
  - NanoDiamonds are already applied in industrial solutions

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Superhard nanomaterials – where toughness really counts

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