

Potential of thermally conductive polymers based on carbon allotropes in the development of new heat management components on board a car

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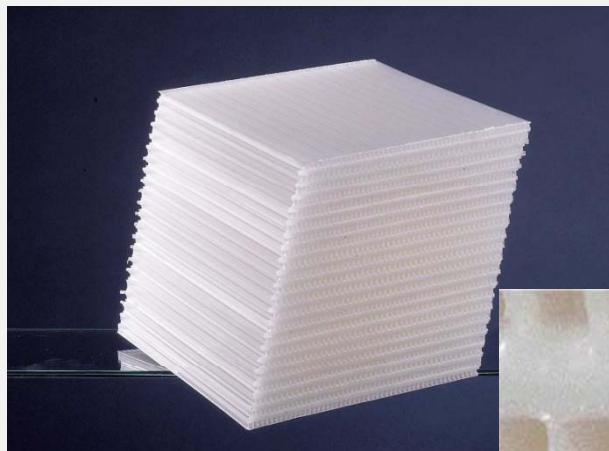
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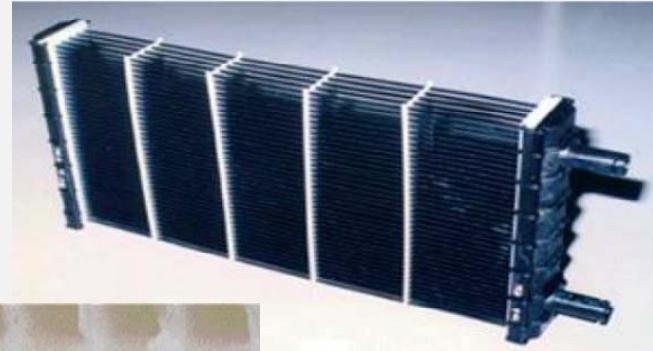
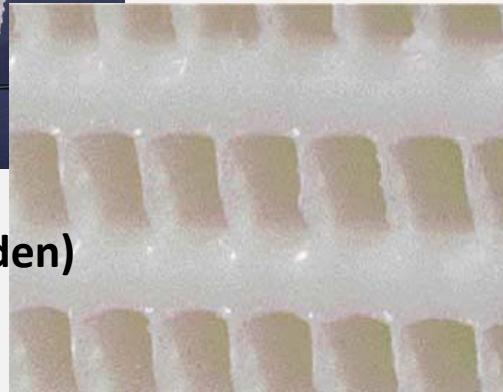
Centro Ricerche FIAT, Orbassano, Italy



Polymer heat exchangers state of the art



PP extruded plates
(AB Segerfröjd- Sweden)



Nylon car radiator
(Dupont)



Calorplast exchanger
(G. Fisher)



Immersion coils

Limited Thermal Conductivity of Polymers



Material	k at 25° C [W/m·K]
LDPE	0.30
HDPE	0.44
PP	0.21
PS	0.14
PMMA	0.21
PA6	0.25
PPS	0.30
PVC	0.19
PTFE	0.27
Epoxy	0.19

Heat mainly transported by **Phonons**: quantized modes of vibration occurring in a rigid crystal lattice

$$k = \frac{C_p \cdot v \cdot l}{3}$$

C_p = specific heat capacity per unit volume
 v = average phonon velocity
 l = phonon mean free path



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Conventional Fillers for Thermally Conductive Composites

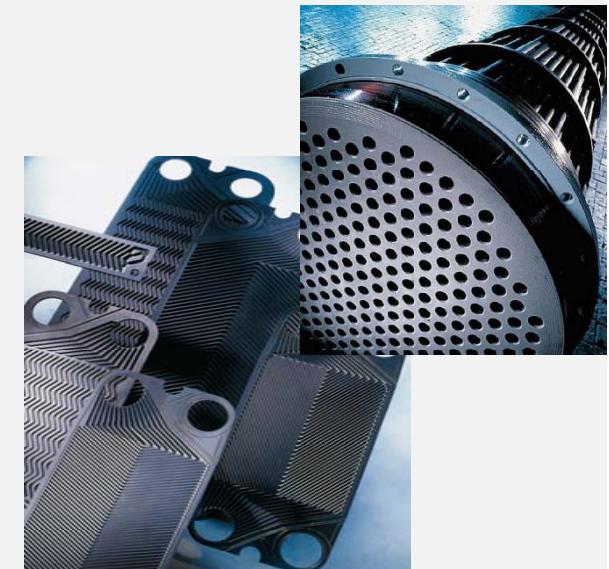


Material	Thermal Conductivity at 25° C [W/m·K]
Graphite	100~400 (on plane)
Carbon black	6~174
PAN-based Carbon Fibre	8~70 (along the axis)
Pitch-based Carbon Fibre	530~1100 (along the axis)
Copper	483
Silver	450
Boron Nitride	250~300
Aluminum oxide	20~29

High filler loadings
(>30 vol.%)
necessary



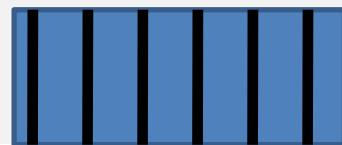
- Processability
- Mech. properties
- Cost



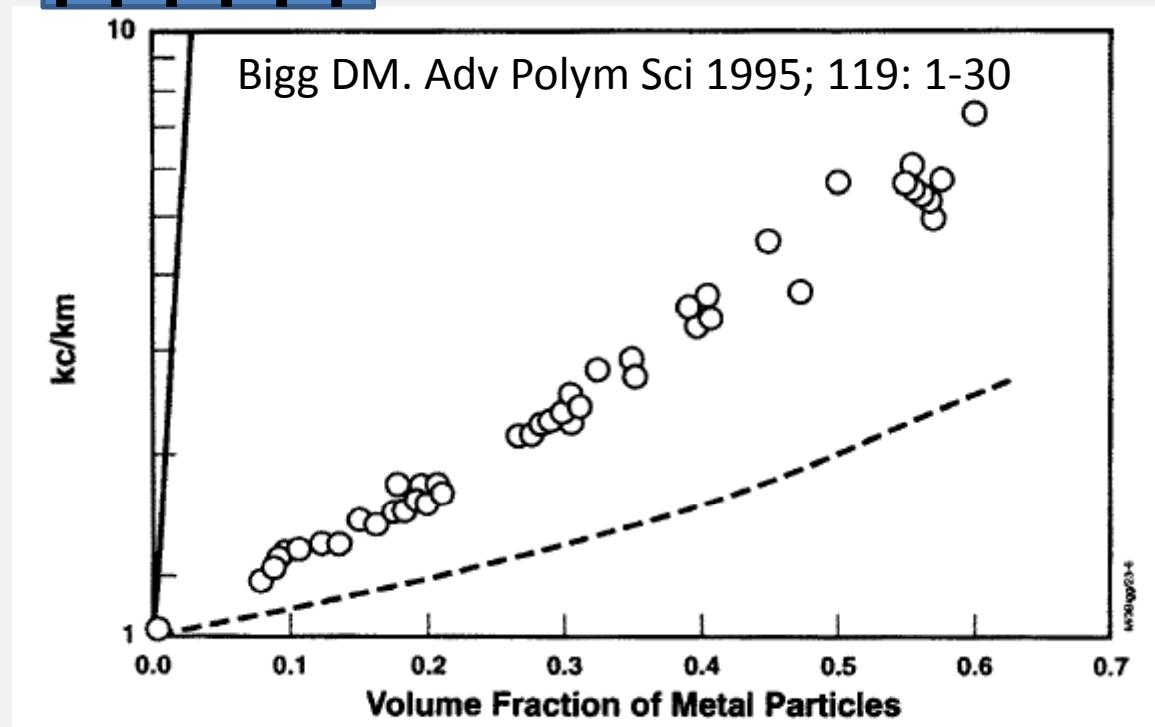
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Thermal conductivity modelling (rule of mixture)

Heat Flow



$$k_c = k_p \cdot \Phi_p + k_m \cdot \Phi_m$$

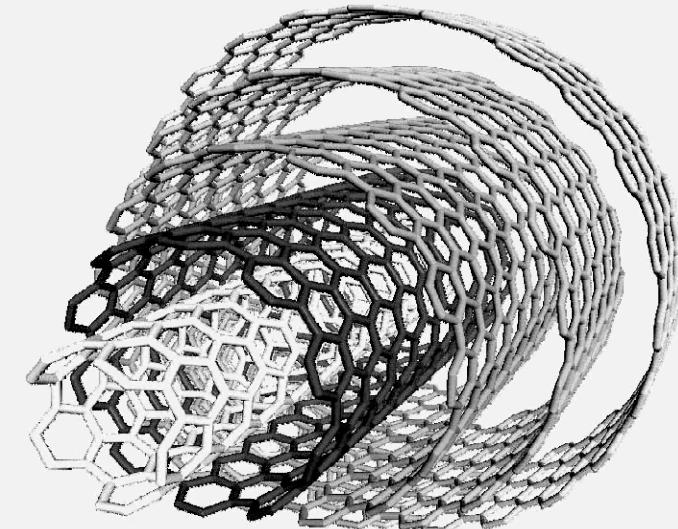
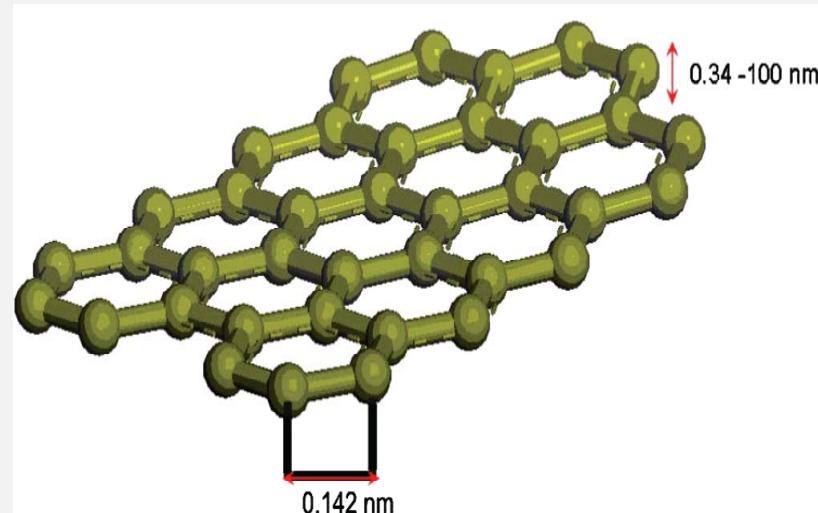


$$k_c = \frac{1}{\left(\frac{\Phi_m}{k_m} + \frac{\Phi_p}{k_p} \right)}$$

Heat Flow



www.thermonano.org



Multi Wall Carbon Nanotubes

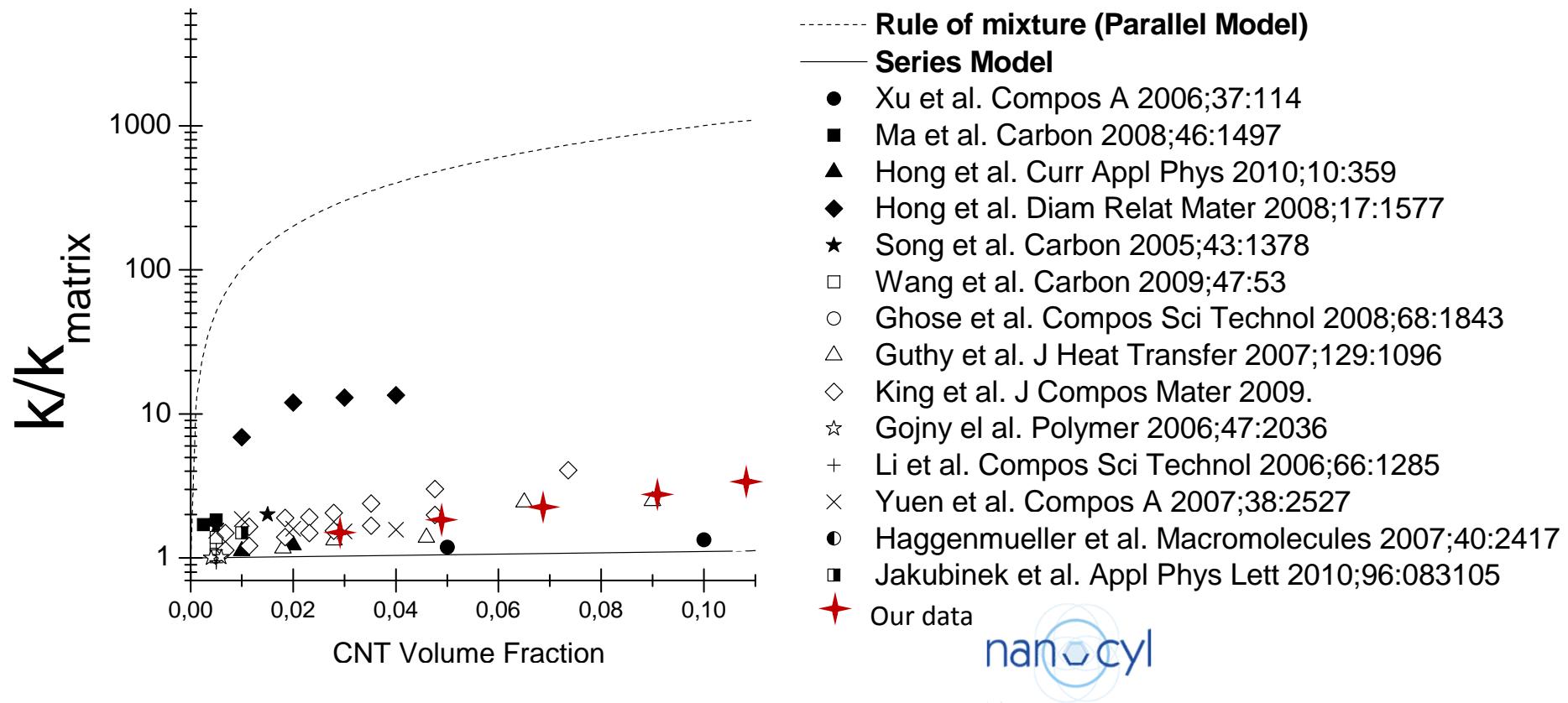
Material	Thermal Conductivity at 25° C [W/m·K]
Carbon Nanotubes	2000~6000
Diamond	2000
Graphene	800-5000

Very Much Dependent on:

- defects/graphitisation
- functionalisation
- chirality
- size
- walls number (for CNTs)

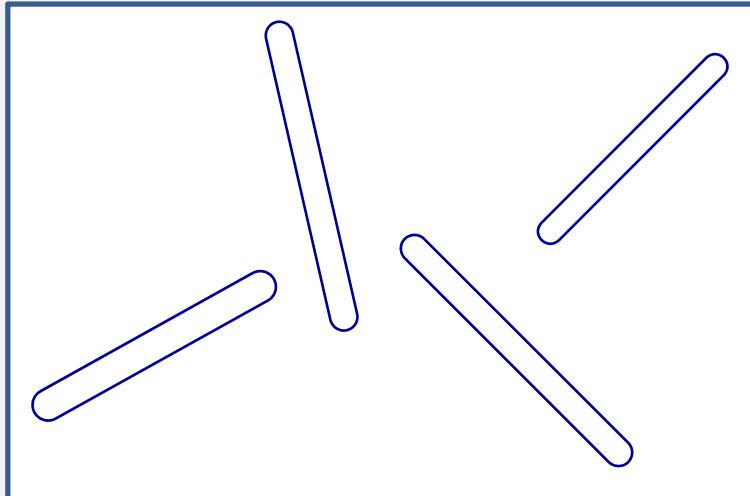
CNT nanocomposites

State of the art



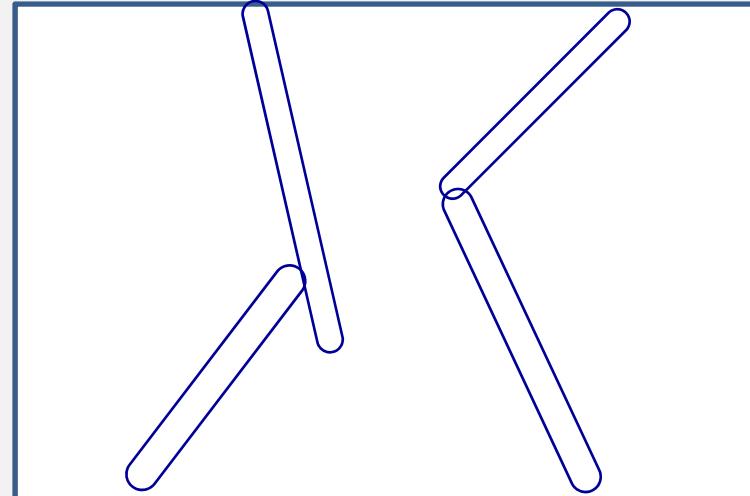
Z. Han, A. Fina. Thermal Conductivity of Carbon Nanotubes and their Polymer Nanocomposites: A Review. Progress in Polymer Science 2011, 36, 914–944



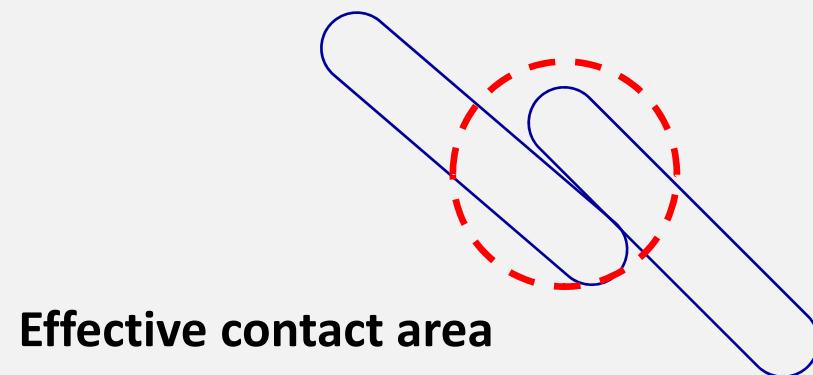


Interfacial resistance

Contact area between CNTs is limited by the tube geometry

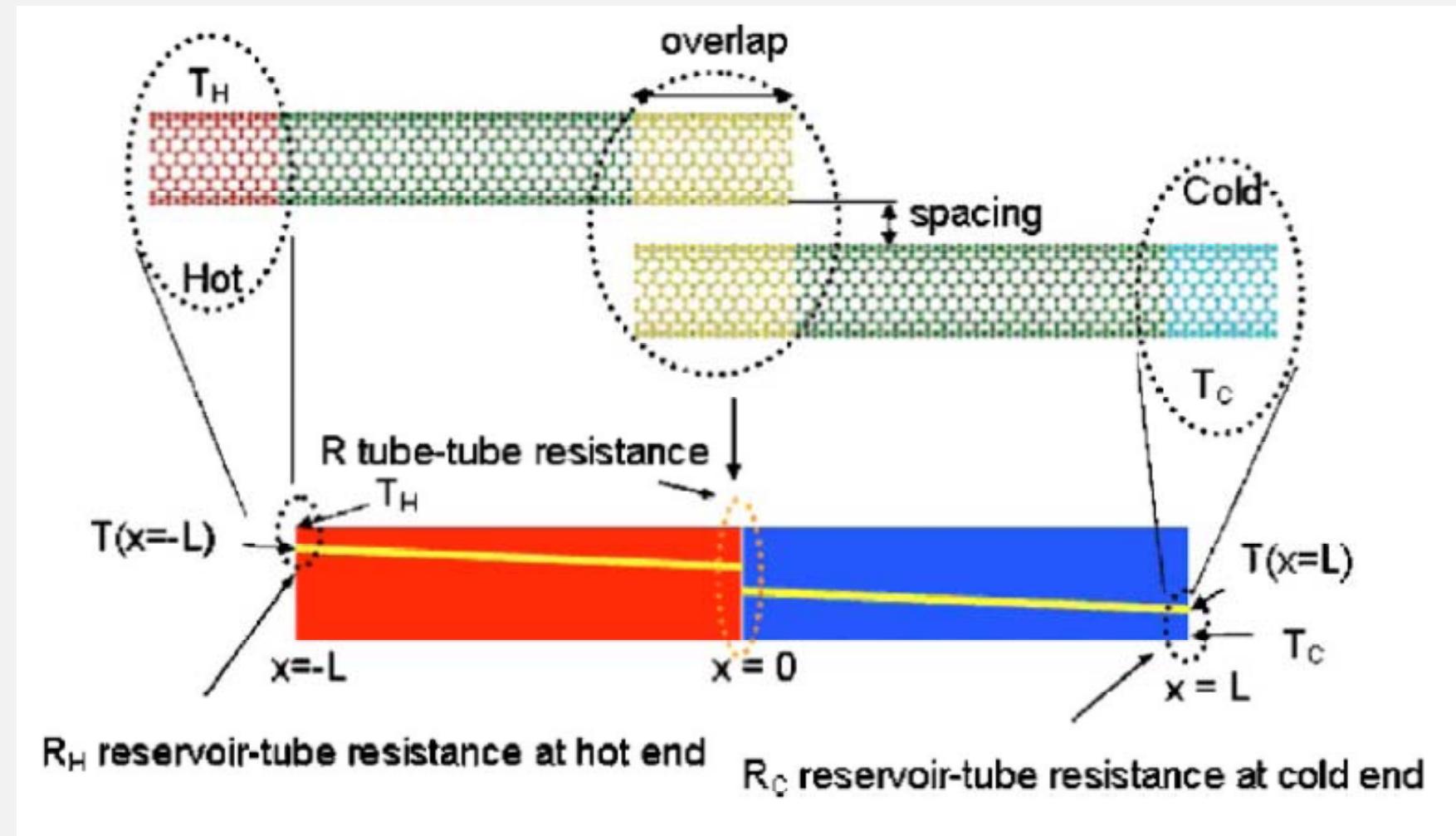


Contact resistance



Effective contact area

Contact Resistance



Zhong H, Lukes JR. Phys Rev B 2006;74, 125403/1–10.

Graphene vs CNT nanocomposites

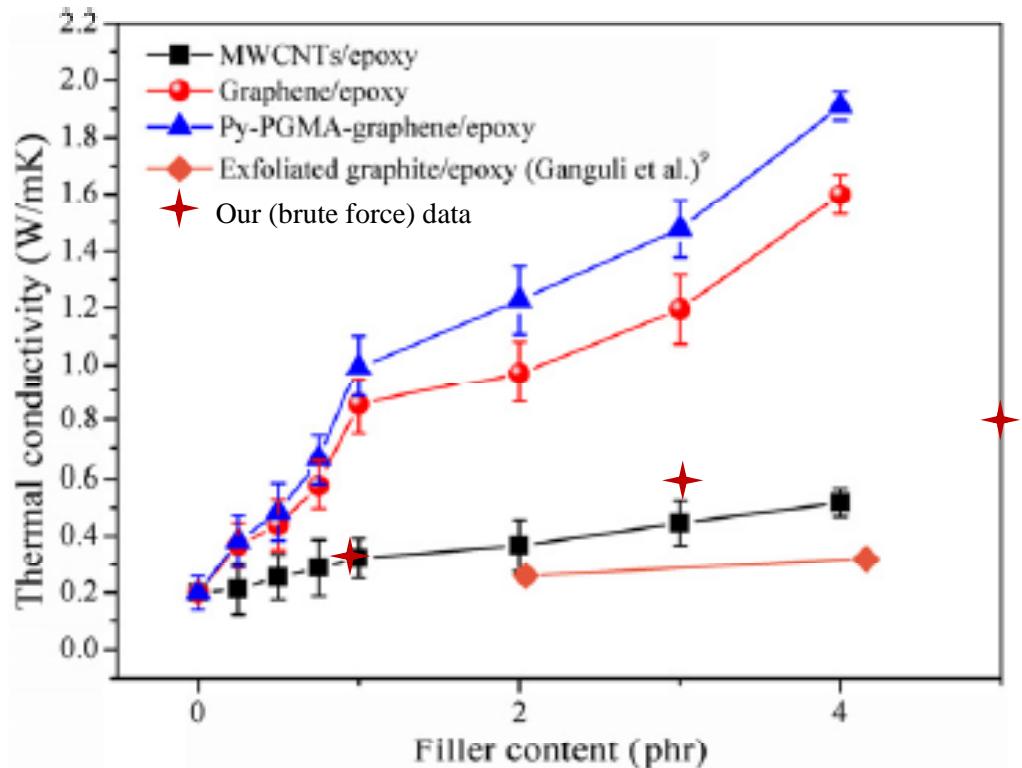
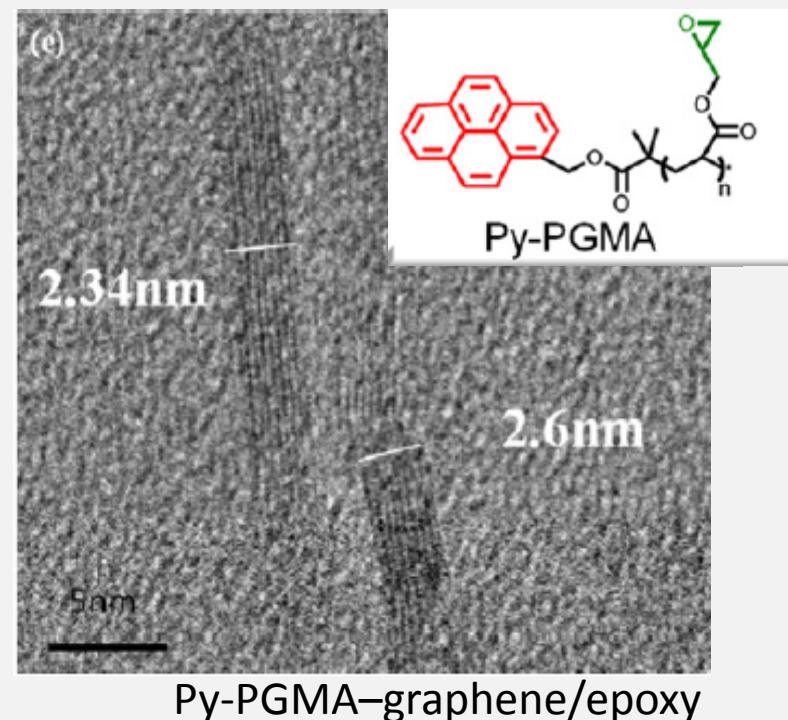


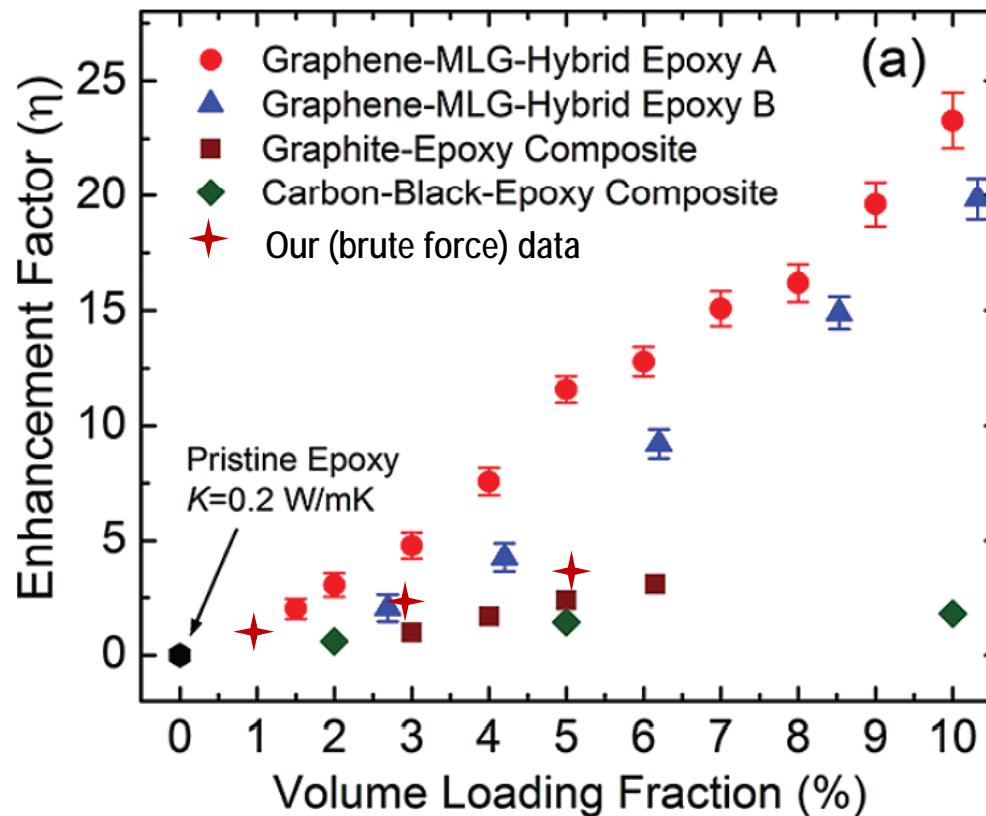
Fig. 10 – Thermal conductivity with various filler contents of MWCNTs/epoxy, graphene/epoxy, and Py-PGMA-graphene.

Thermally reduced graphite oxide (organofunctionalised or not), dispersed in epoxy by solvent process

Limited literature available on thermal conductivity of graphene nanocomposites



Graphene vs CNT nanocomposites



Mixture of graphene and multilayer graphene (MLG) with 1-10 graphene layers

Added to epoxy in suspension

Why graphene has more potential than CNT or graphite?

- Reduction of particle/polymer interfacial resistance
- Possible reduction in particle/particle contact resistance
- Lower entanglements compared to CNT (i.e. better dispersion/lower defectivity)

Khan M. F. Shahil and Alexander A. Balandin,
Nano Lett. 2012, 12, 861–867

Materials costs are as issue!

Cost per ton for graphene nanoplatelets (GnP) is likely to significantly undercut carbon nanotubes. Main producers are all planning large production increases to allow them to offer materials for under \$40/kg.

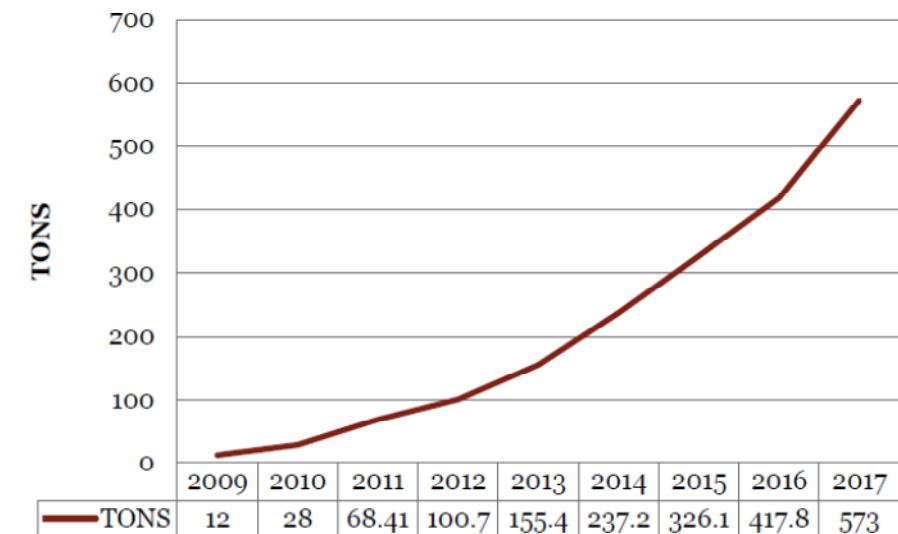
Table 5: Cost comparison of graphene

Material	Cost
SWCNT	~100 \$ / g
MWCNT	~ 300\$/Kg
Milled VGCF	80 – 100 \$ / lb.
Fibril VGCF	40 – 50 \$ / lb.
xGnP	~ 10 – 20 \$ / lb.

Graphite is 5-10 €/kg

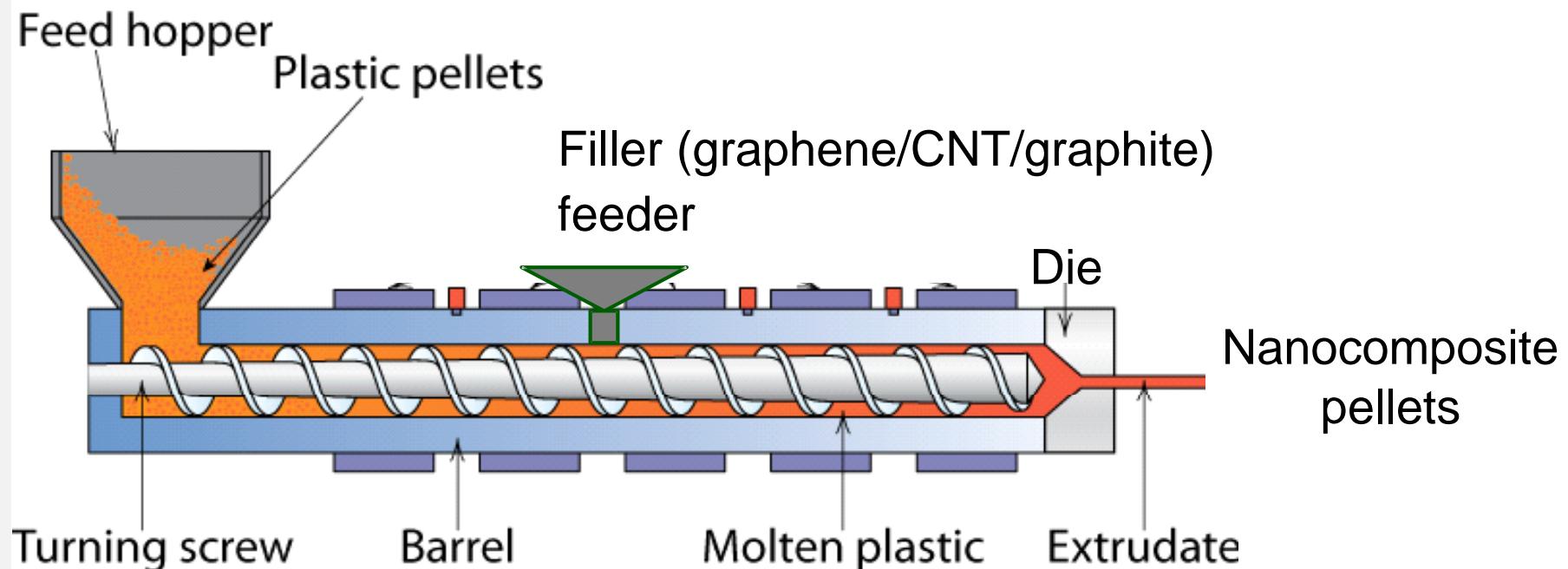
Single layer graphene or multilayer graphene much more expensive and not available on the market yet

Figure 1: Graphene production in tons, 2009-2017



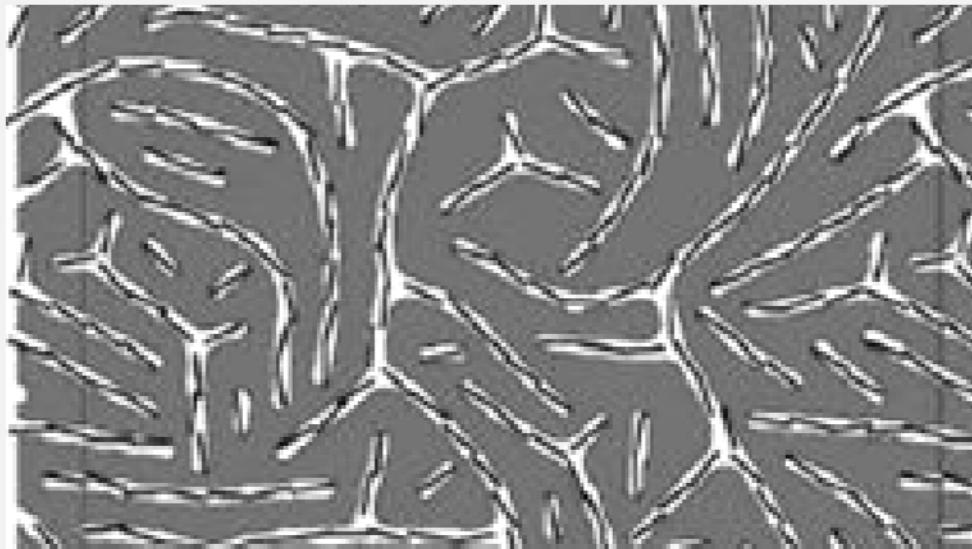
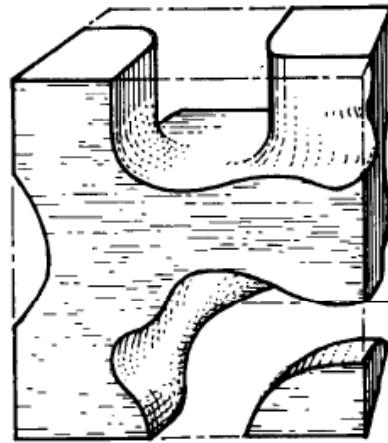
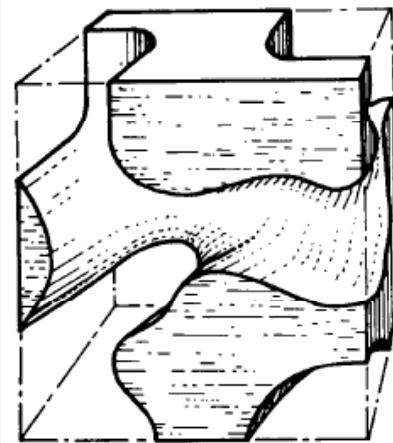
Source: "The World Market for Graphene to 2017", Future Markets, Inc. 2011

Direct melt blending processes in thermoplastic polymers are highly preferable (our brute force method)



How to improve this “cheap” method?

Improving extent/number of contacts by particles confinement in blends

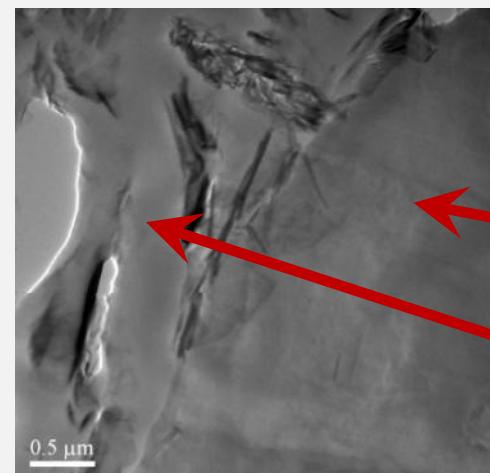
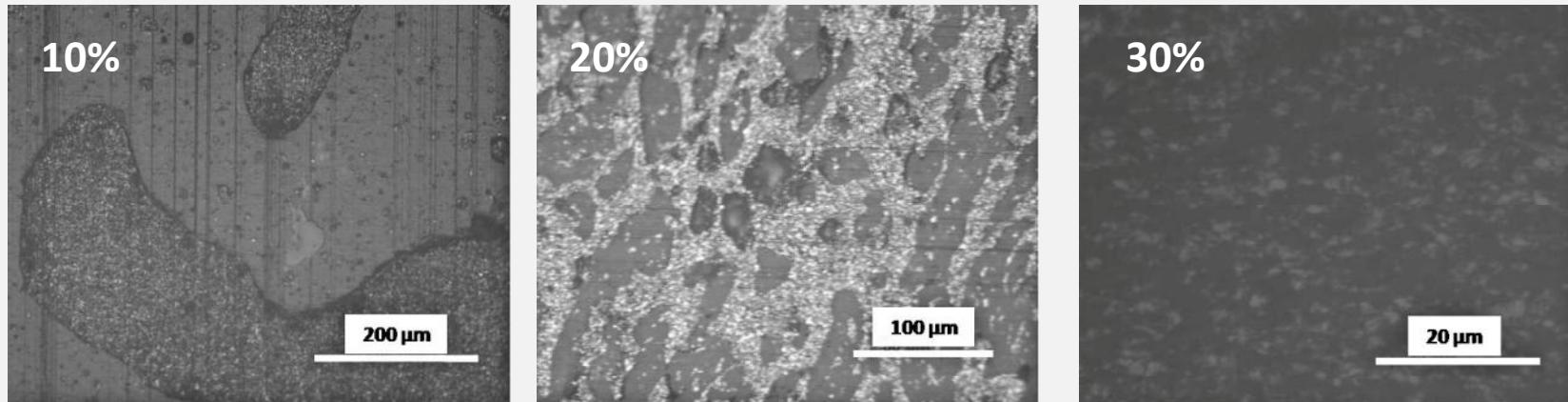


- Segregation in one continuous phase

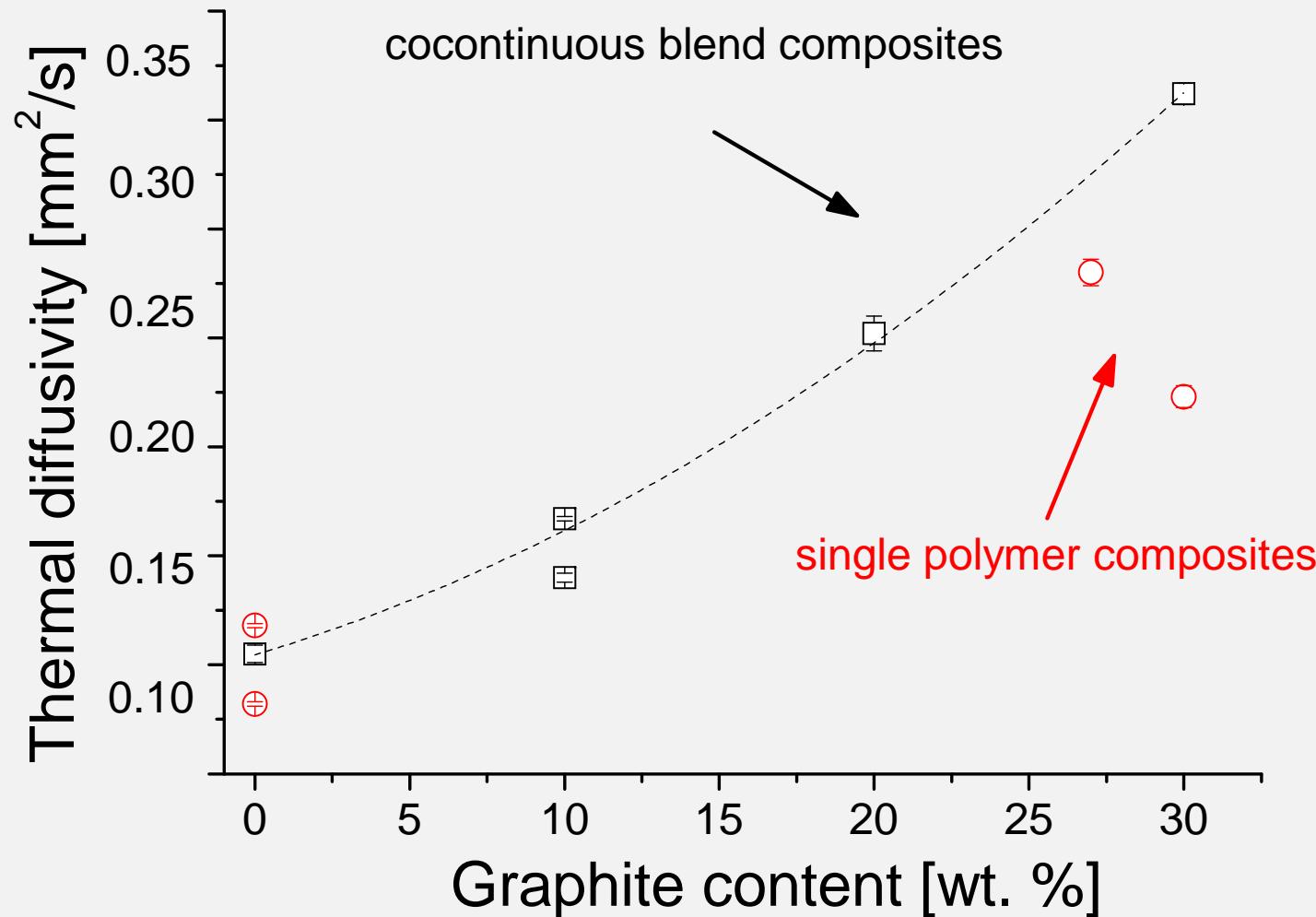
- Segregation at continuous blend interface

Graphite in co-continuous blend

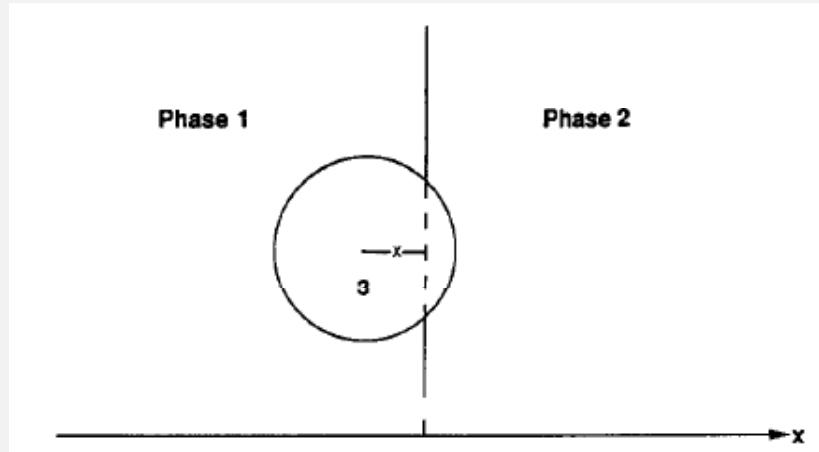
- 70% PVDF 30% PPgMA demonstrated cococontinuity
- Addition of graphite refines the phase separation and preserves cocontinuity



Structure stable
upon annealing
and melt
processing



Possible under suitable thermodynamic and kinetics conditions



$$\frac{x}{R} = \frac{\gamma_{13} - \gamma_{23}}{\gamma_{12}}$$

Cheng TW, Keskkula H, Paul DR.
Polymer 1992;33:1606-19

CNT in Blend	Theory x/R
PA6/EA*	-0,8
PA6/PVC	-0,5
PVDF/PA6	0,3
PVDF/PVC	-0,7

Experimental

- Carbon particles at interface
- Carbon particles in one phase

*copolymer of ethylene and methyl acrylate.

Improving the quality of thermal contacts by particle functionalisation



Supramolecular chemistry can be used to obtain self-assembling interfaces showing:

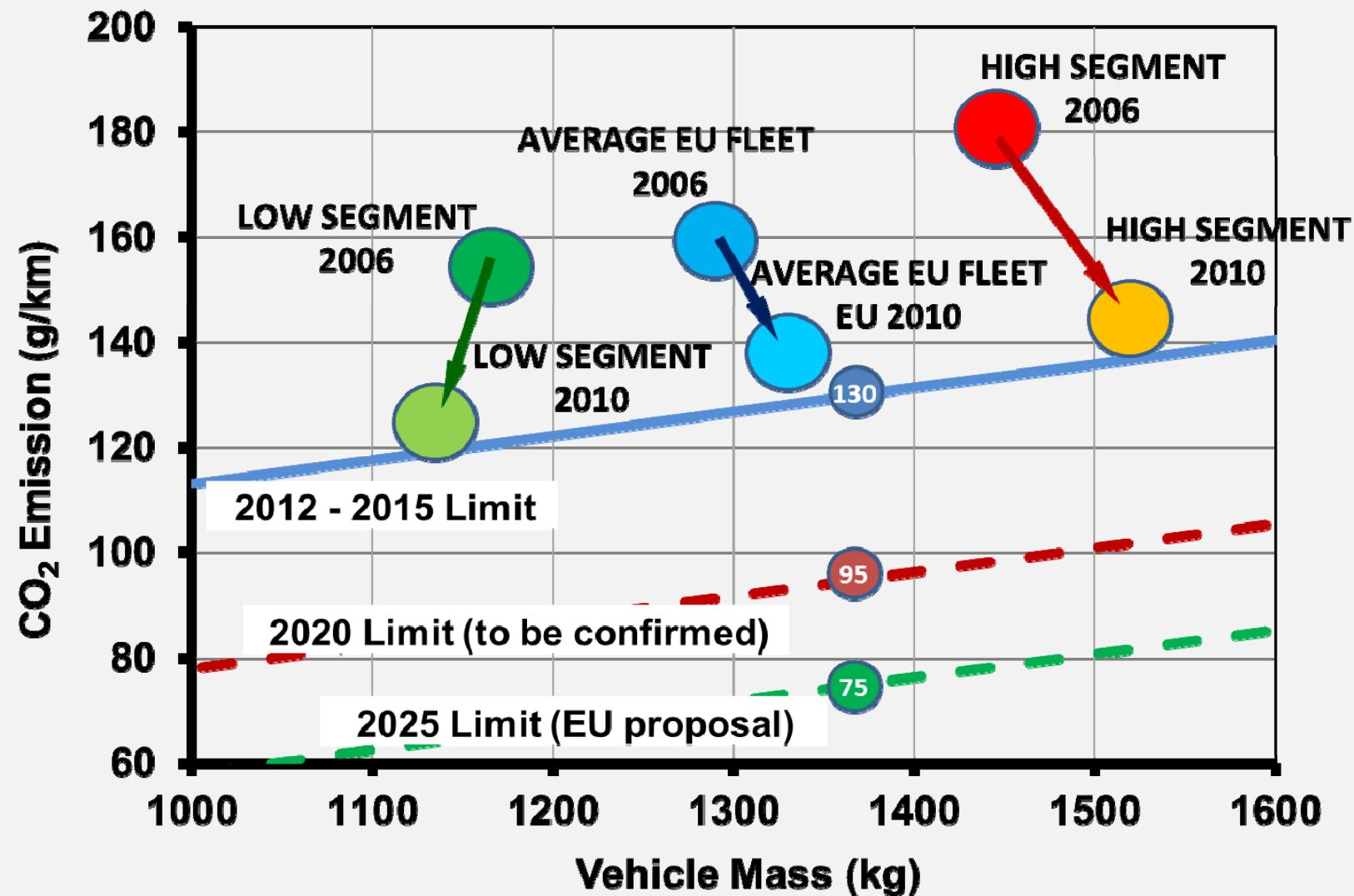
- High stiffness to avoid phonon damping
- Phononic vibration spectrum overlapped with graphene spectrum



**Conceptual
model**



Automotive sector needs for efficiency

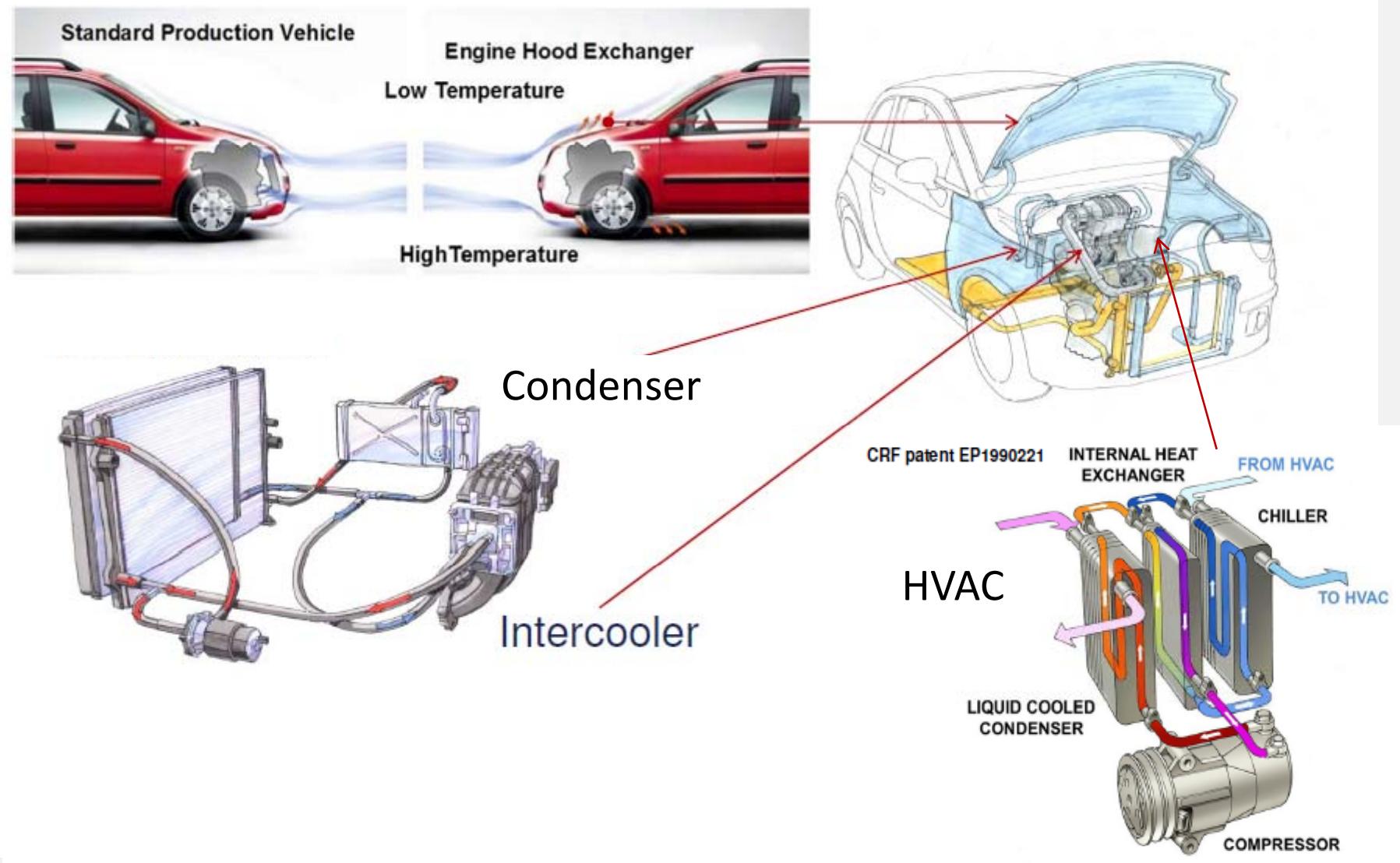


Aerodynamics is crucial for fuel saving (i.e. CO₂ emission reduction)

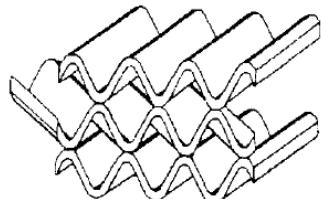


A redesign of the front part of the car is needed, by the substitution of the front radiator or with higher efficiency systems

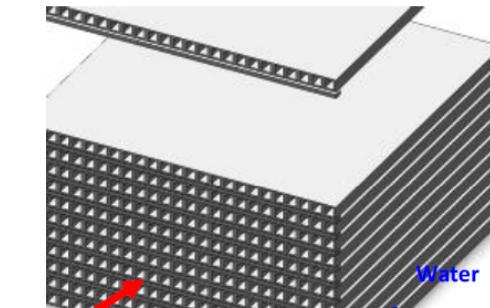
Aerodynamics & polymer heat exchange



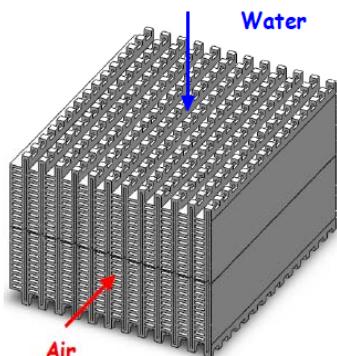
Our polymer heat exchangers designs



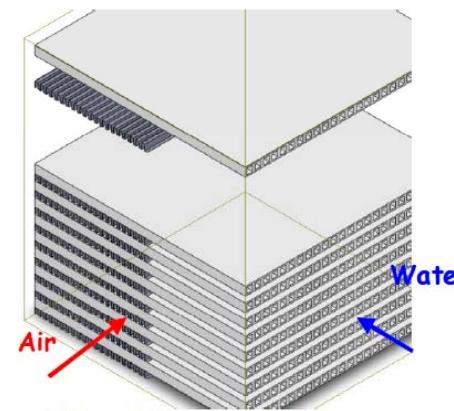
Corrugated plates



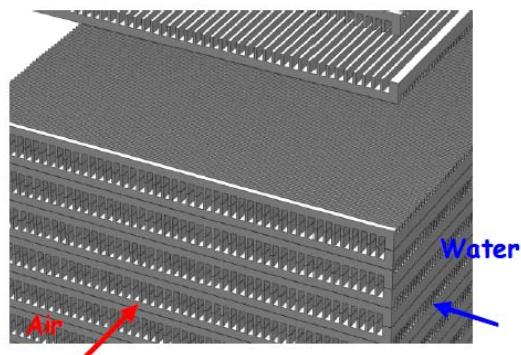
Hollow plates and gaps



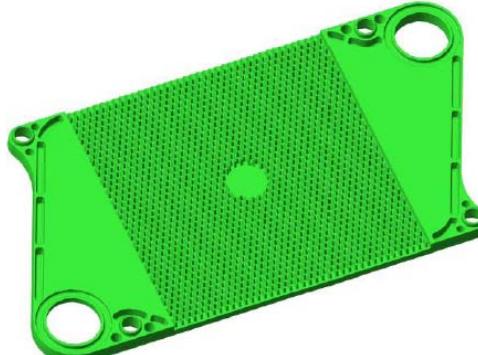
Integrally extruded hollow plates



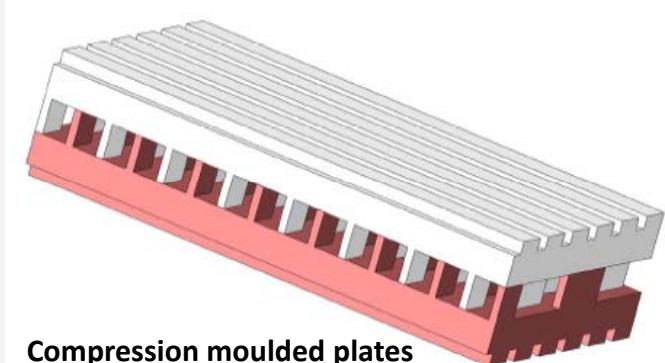
Hollow plates and straight fins



Double sided inject or compression moulded plates



High design flexibility
is allowed thanks to
the easy processing
of thermoplastic
polymers



Compression moulded plates

Polymer heat exchangers benchmarking



	Criteria weight	Plain sheets	Plain sheets with corrugations	Hollow plates	Hollow plates and aluminum fins	Integrally extruded	Hollow plates and sandwich polymer film	Injected plates	Compressed plates
Technical									
Thermal performance	10	1	1.5	2	3	2	3	2.5	3
Mechanical performance	7	1	1	2	2.5	3	2	3	3
Assembling cost	5	3	3	3	3	2	2.5	3	3
Modularity	3	3	3	3	3	2	3	1.5	1.5
Material cost	5	2	2.5	2	2.5	2	2	2	2
Total weighted		41	46	58	72	57	66	66	71
Feasibility									
Development cost	3	3	2	3	1	1	2	3	3
Development risk	5	3	2	3	1	1	2	2	2
Intellectual property risk	5	3	3	2	3	3	2	3	3
New intellectual property	5	1	2	1	3	3	3	2	2
Skill available in consortium	5	3	3	1	1	1	2	3	3
Total weighted		44	41	34	28	43	41	44	59
Grand Total		85	87	92	100	100	107	110	130

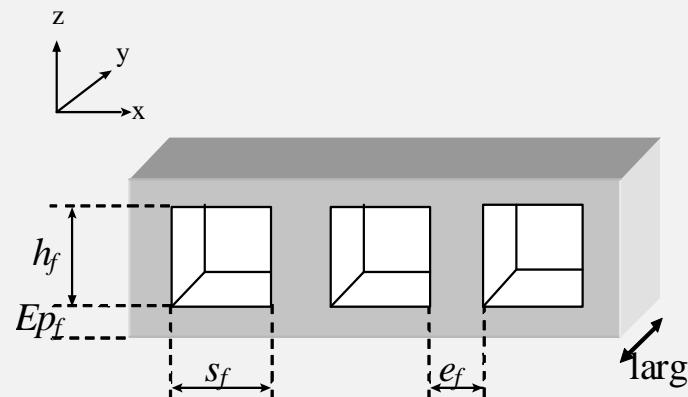
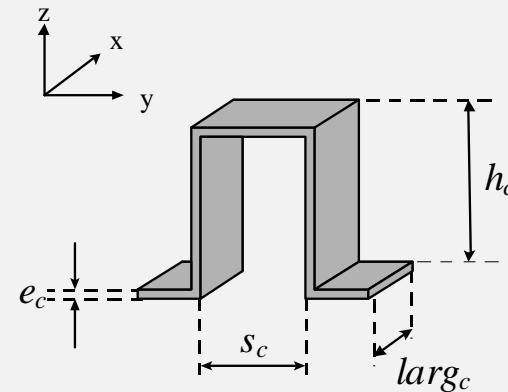
Hollow Plates & Straight Fins Design Parameters

Straight fins parameters

Total height $h_c + e_c$

Total step width $s_c + e_c$

Thermal conductivity k_c



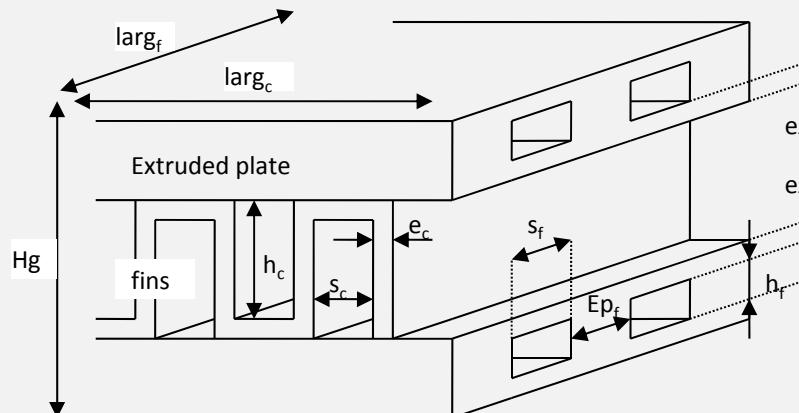
Global scheme

Extruded plate parameters

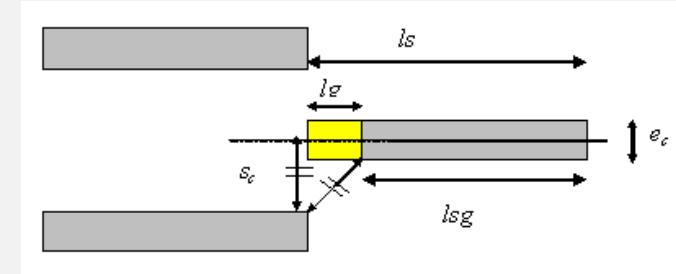
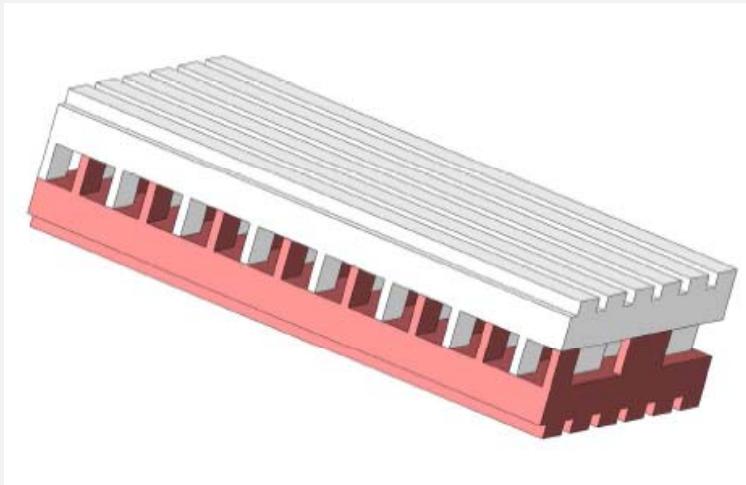
Total height $h_f + 2Ep_f$

Total step width $s_f + e_f$

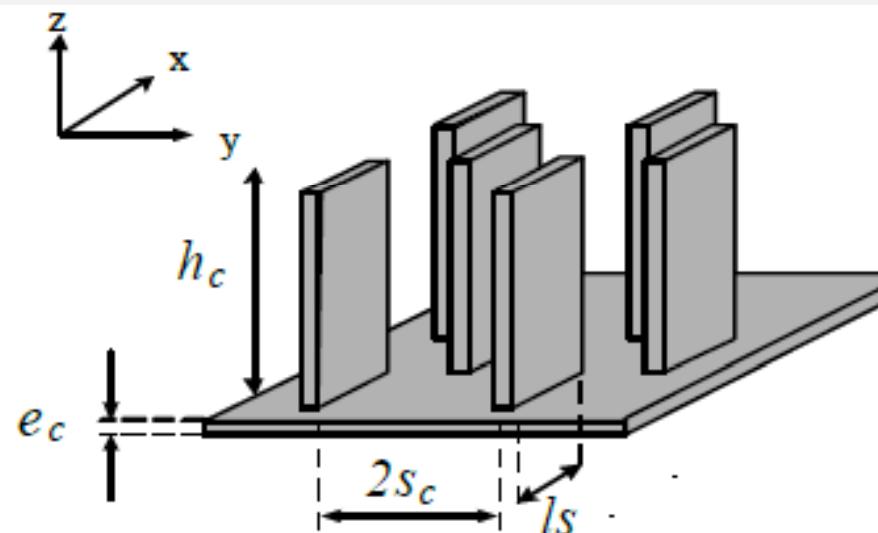
Thermal conductivity k_f



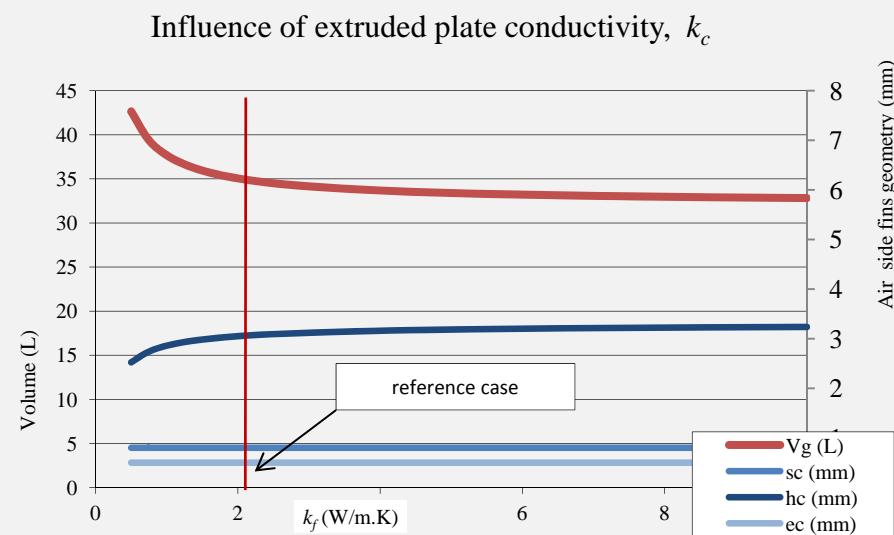
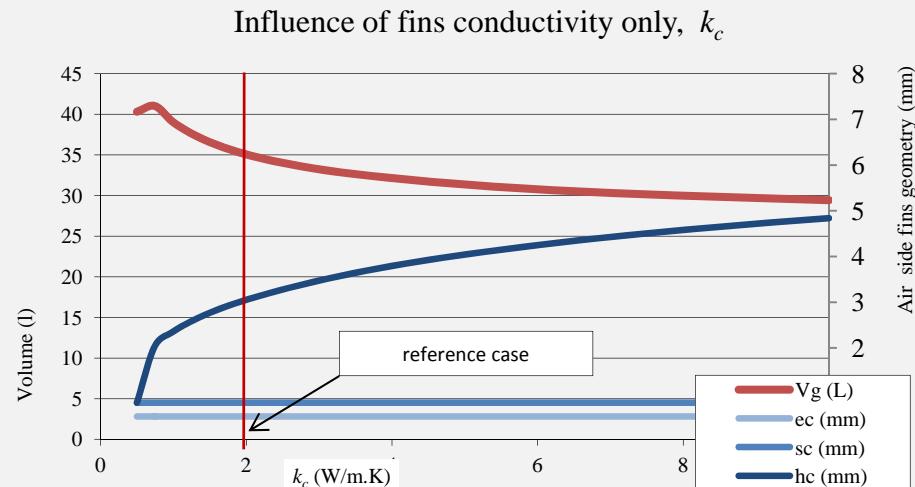
Finned plates Design Parameters



Total height $h_c + e_c$
Total step width $s_c + e_c$
Serrated length l_s
Thermal conductivity k_c



Hollow plates and straight fins parameters impact



The thermal conductivity impacts a lot the fin efficiency. To optimize the heat exchanger, the fin height must be adapted to the material conductivity.

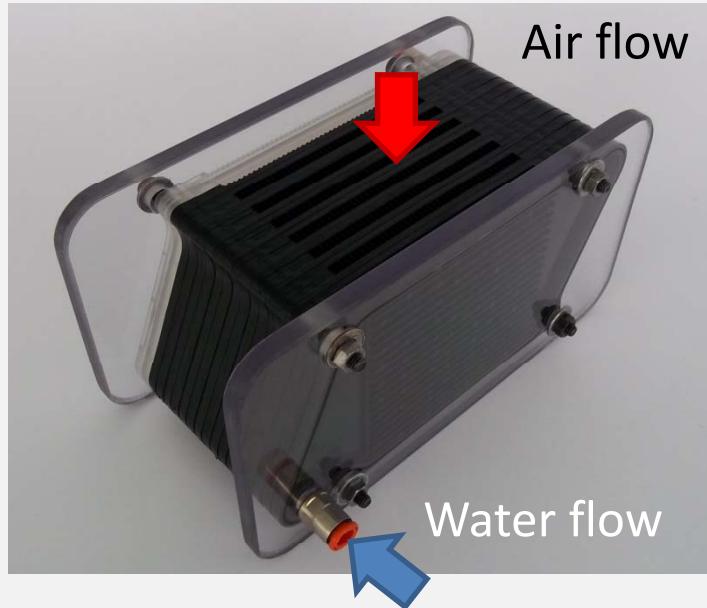
The air side fins conductivity has a larger impact on the final volume than that of the extruded plate

High-conductivity specific materials can be used for these fins only

Heat Exchangers performance

All @ 8/400 mbar	Metallic reference	Hollow plates and straight fins	Injected plates	Compression molded plates
Technology	CuNi Tube and aluminum fins	Sandwich	Overlapped fins	Overlapped fins
Material conductivity	380 / 220 W/(mK)	1 / 10 W/(mK)	1 W/(mK)	20W/(m K)
Width x Depth x Height	0.26 x 0.42 x 0.33 m	0.55 x 0.28 x 0.24m	0.60 x 0.08 x 0.65m	0.45 x 0.15 x 0.45m
Core Volume	35.7 l	36.8 l	32.9 l	30.5 l
Fin thickness		0.5mm	0.5mm	1mm
Fin height		4.9mm	0.8mm	3.9mm
Fin passage		0.8mm	1.6mm	1.6mm
Plate thickness		0.5mm	1mm	1mm

Polymer heat exchanger prototype

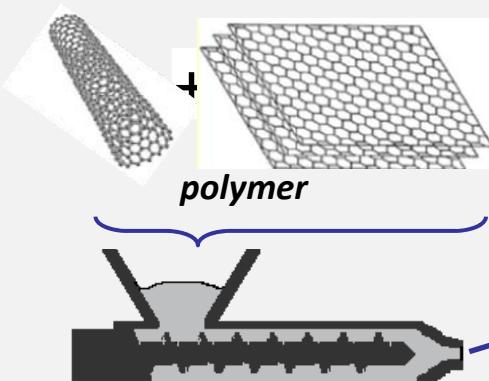


$K = 2 \text{ W/mK}$

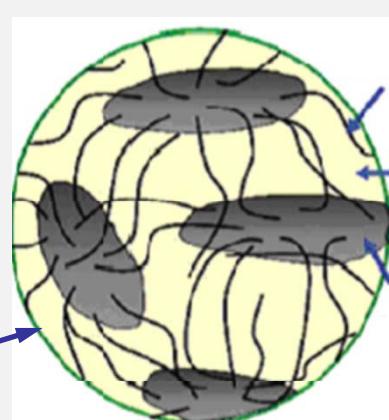
Target performance achieved

Best cost effectiveness with 10% graphite-CNT blend according to the below manufacturing route

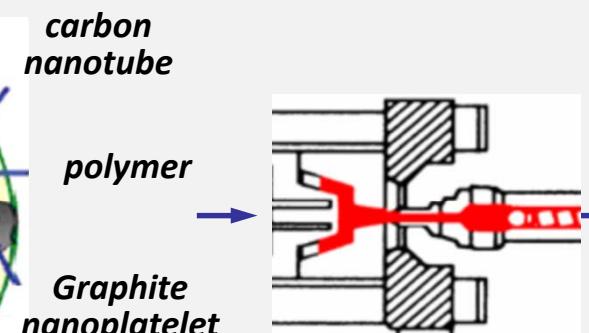
Bulk inclusion



Compound



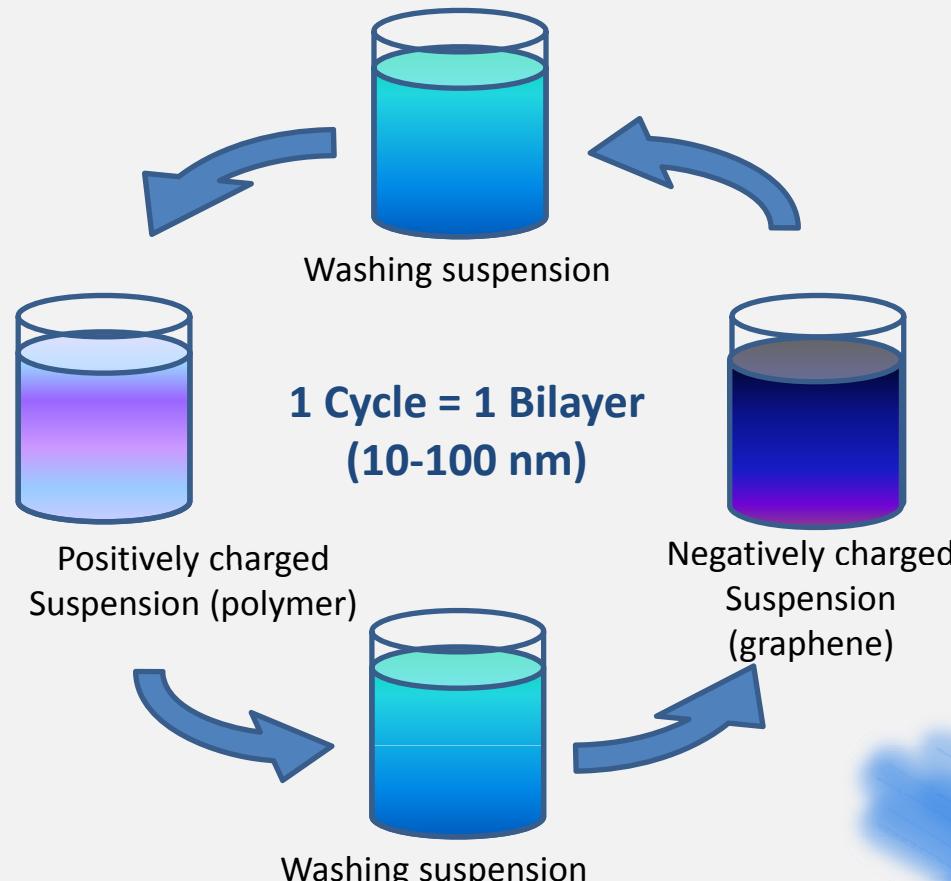
Moulding



Heat exchangers plates

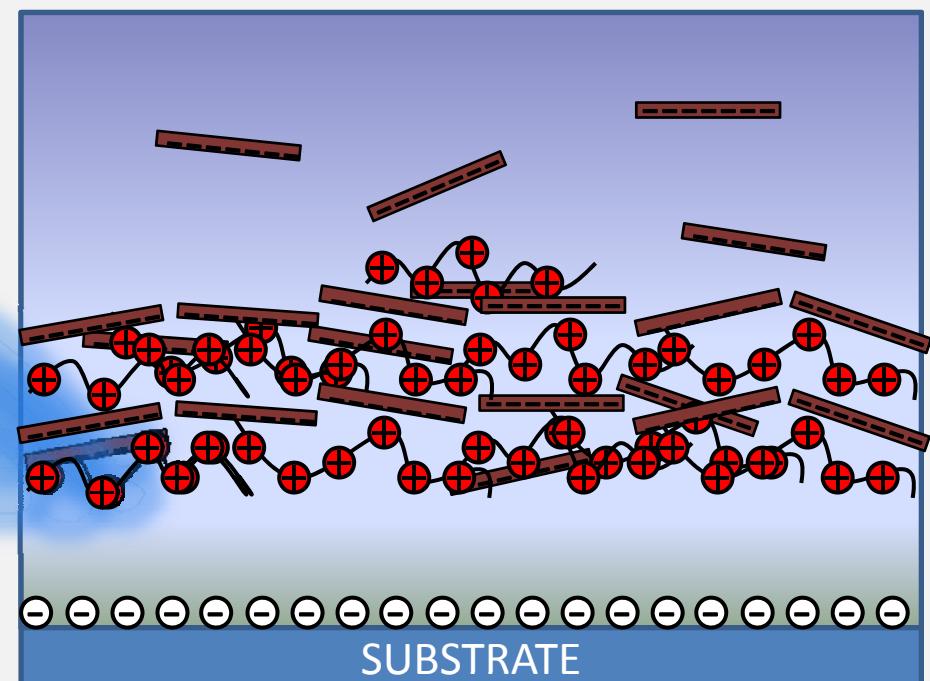


Antifouling surface functionalisation



Suitable for in-plane conductivity
Controls the platelets orientation and contacts (overlaps)

Layer by Layer Process outlook



A flourishing future can be foreseen for polymer heat exchangers in every application field where lightness and resistance to corrosion are an issue.

Polymer thermal conductivity can be increased by (nano)fillers whose critical parameters are cost (materials & manufacturing routes), capability of enabling effective thermal contact among nanoparticles, limited influence on polymer mouldability.

Graphene has definitely the highest potential in this context among carbon allotropes.

To fully exploit this potential materials costs must decrease and functionalisation must be accomplished to enable self-assembling of stiff interfaces to avoid phonon damping

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- Mr **Samuele Colonna** for specimen preparation and testing
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*Research group at the
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Alessandria branch*



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www.thermonano.org

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