



Graphene & Nanocomposites

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Ingénierie des Matériaux Polymères

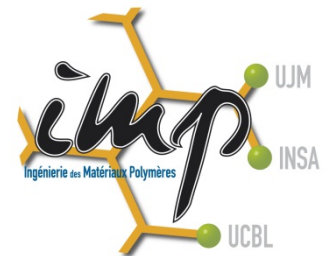
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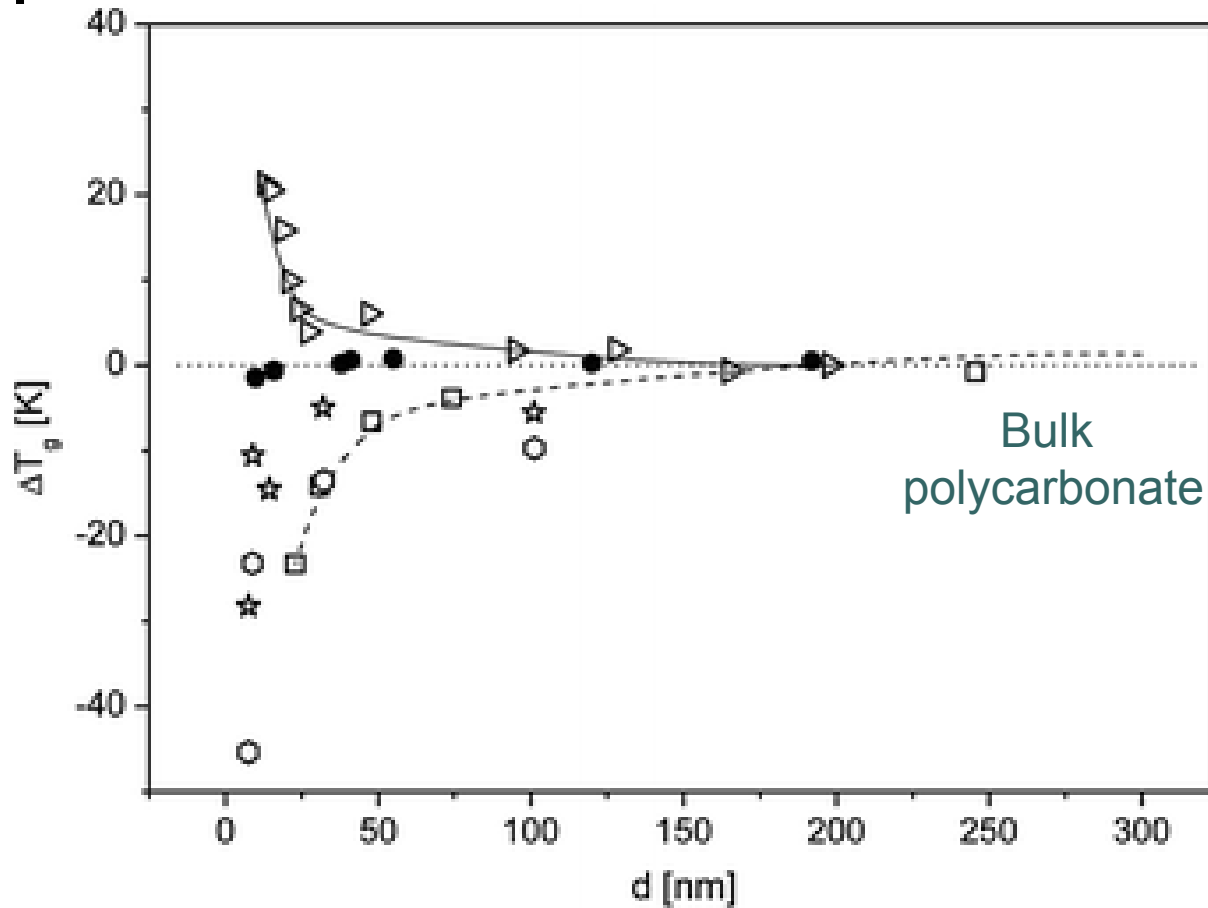
Journée V2P



<http://www.imp.cnrs.fr>

WHY NANOCOMPOSITES ?

- New physical behaviour from nanoscale

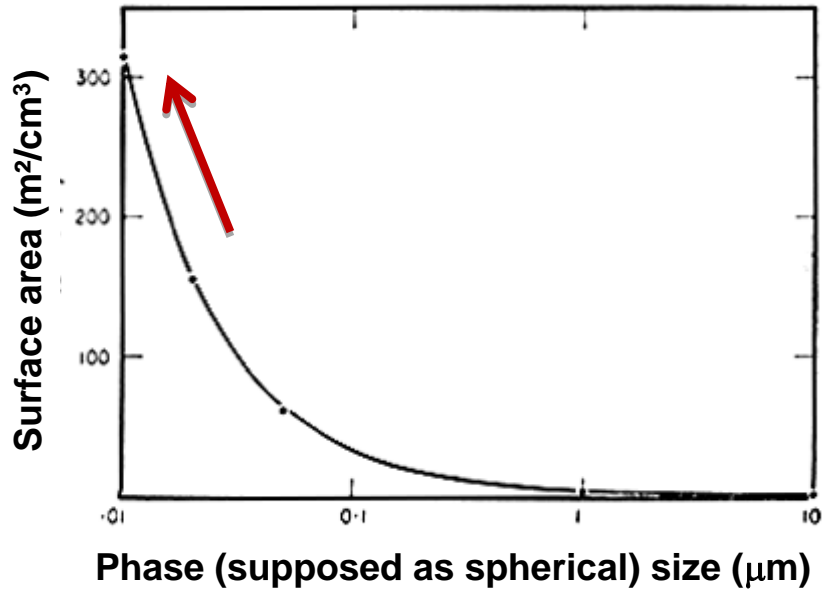


Confinement effects on molecular dynamics

Nanoscale comparable to radius of gyration in polymers

WHY NANOMATERIALS ?

Interface vs. Interphase



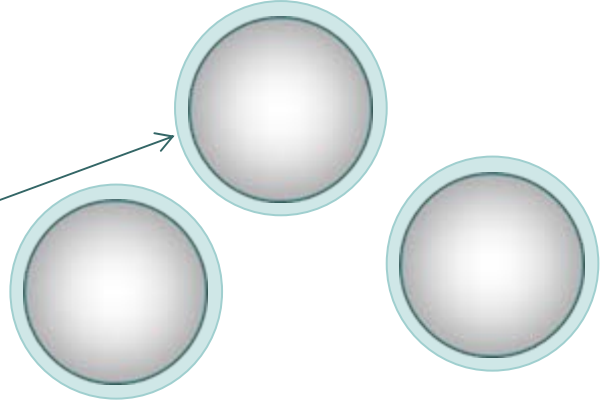
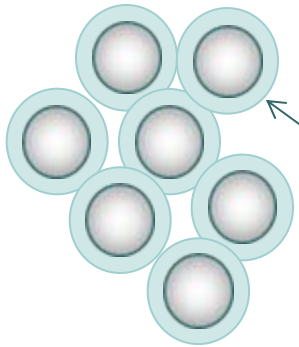
P.J. Sereda and R.F. Feldman, CNRC-NRC CA (2011)

Developed interfacial area between phases as a function of size

Nanomaterials

vs.

Micromaterials



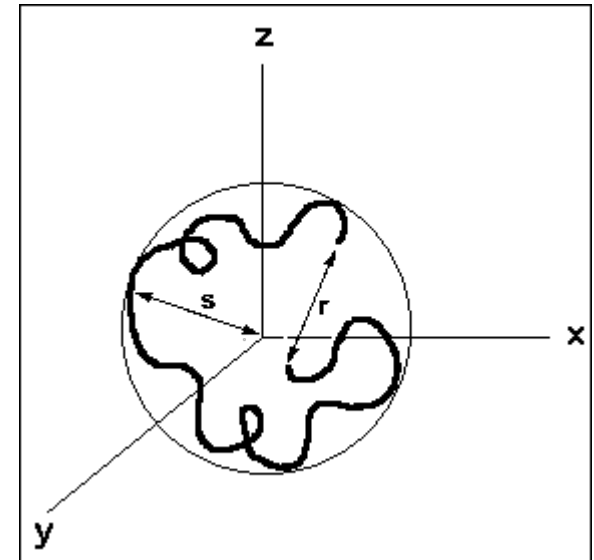
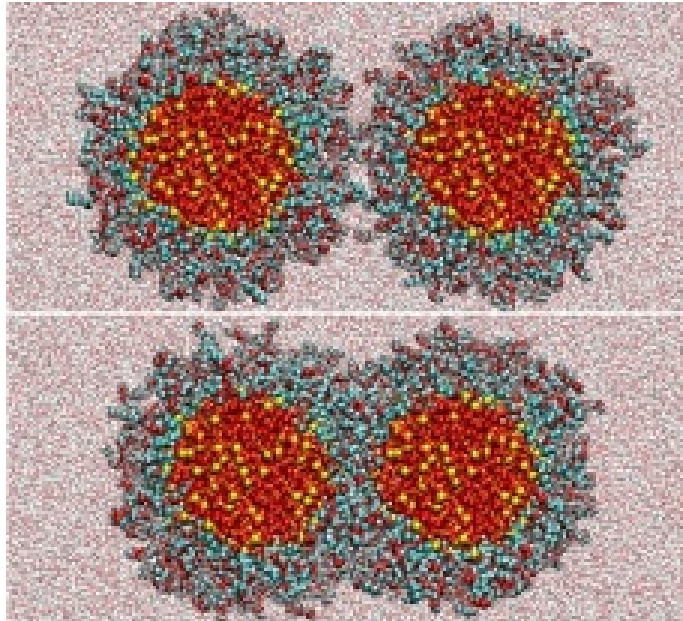
All is interface!

Polymer chains in interaction between phases



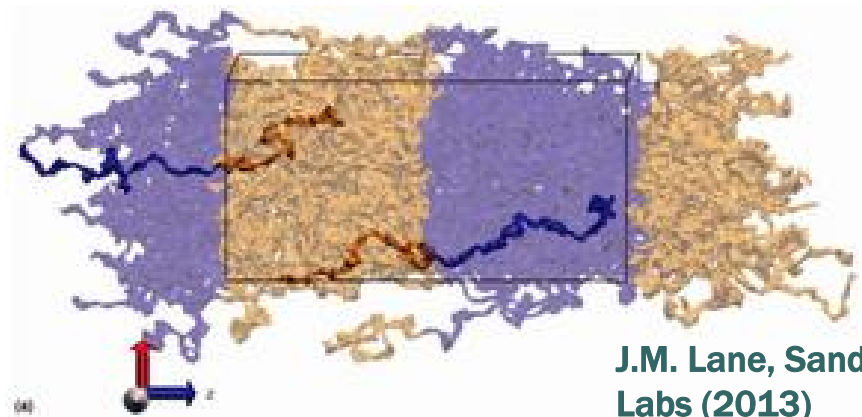
WHY NANOCOMPOSITES ?

All is interface - 'Interfaces-based materials



Interphases from changes of segmental Mobilities

Interphase dimension vs. phase sizes

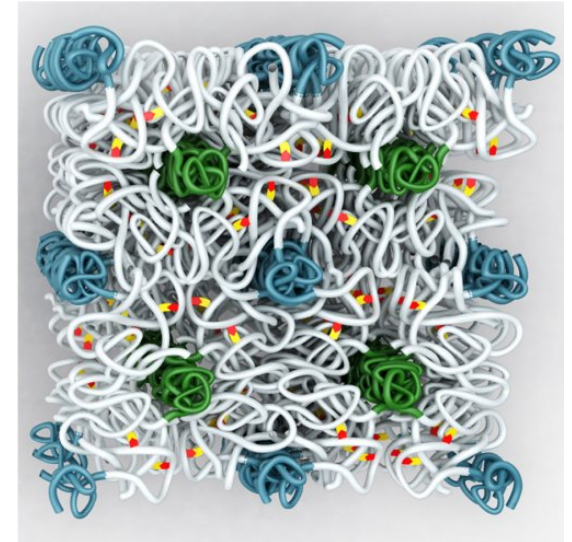


J.M. Lane, Sandia Nat. Labs (2013)

WHY NANOCOMPOSITES ?

‘Self-assembly’ of
Nano-objects/Nanofillers

In-situ generation of
structures at nanoscale (percolated,
oriented, etc)/ Morphology



S.B. Darling, Prog. Polym. Sci (2007)

**Large influence of the spacial arrangement
and assembling of nanofillers on nanocomposite
behaviours (mechanical, electrical, barrier, optical, ...)
Combination with other approaches for
tailoring at larger scales**

- Balance between particle-particle and particle-polymer matrix interactions:
- management of interfacial interactions
- Processing conditions : applied shear stresses, etc ... (shape factor)

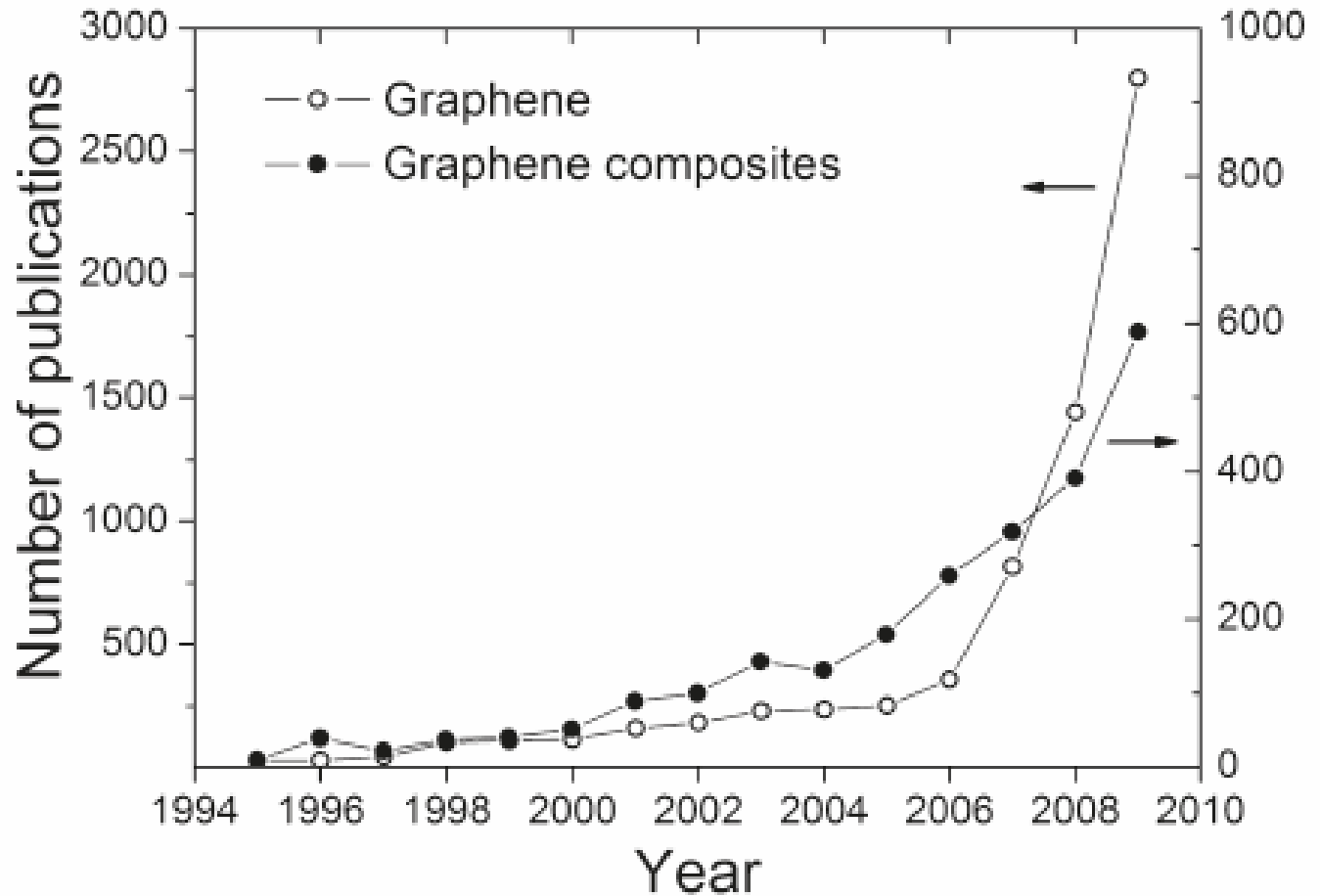


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- 1.- Introduction – Why nanocomposites ?
- 2.- Processing Graphene-Based Nanocomposites
- 3.- Expected Graphene-Based Nanocomposites
- 4.- Conclusions

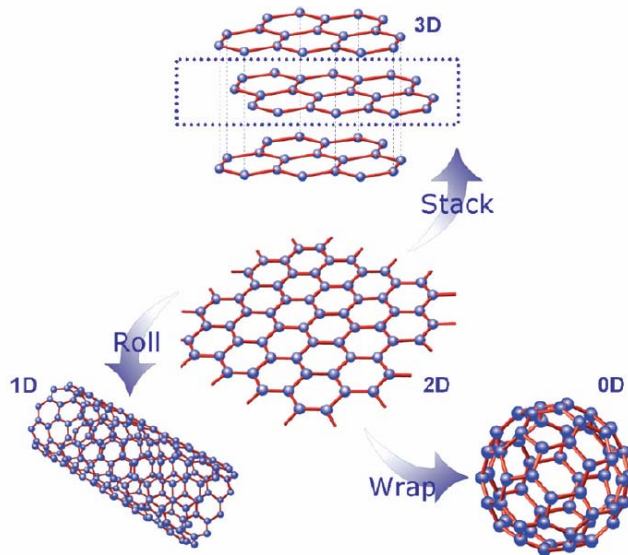


GRAPHENE 'FASHION'



Kim & C.W. Macosko, *Macromolecules* (2010)

GRAPHENE AS A NANOFILLER



- atomically thick
- two-dimensional (2-D) sheet (sp² carbon atoms/ honeycomb)
- building block of all other graphitic carbon allotropes of different dimensionality

Eizenberg, M.; Blakely, J. M. Surf. Sci. 1970

X. Wan, Accounts of Chemical Research (2012)

Materials	Tensile strength	Thermal conductivity (W/mk) at room temperature	Electrical conductivity (S/m)
Graphene	130 ± 10 GPa	(4.84 ± 0.44) × 10 ³ to (5.30 ± 0.48) × 10 ³	7200
CNT	60–150 GPa	3500	3000–4000
Nano sized steel	1769 MPa	5–6	1.35 × 10 ⁶
Plastic (HDPE)	18–20 MPa	0.46–0.52	Insulator
Rubber (natural rubber)	20–30	0.13–0.142	Insulator
Fiber (Kevlar)	3620 MPa	0.04	Insulator

High surface area (theoretical): 2,630 m²/g)

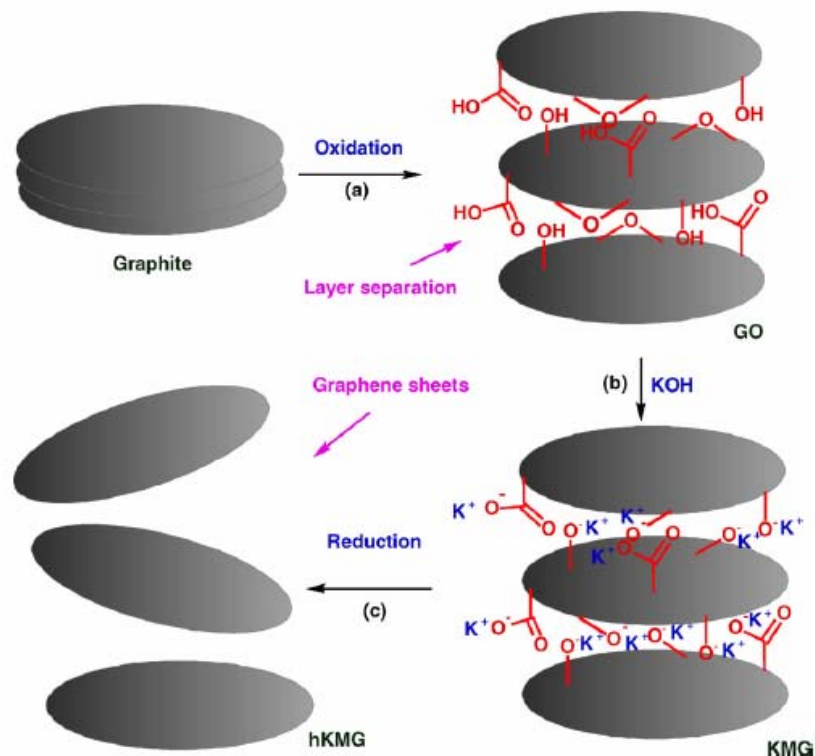
T. Kuilla et al., Progress Polym. Sci. (2010)

REQUIRED SURFACE FUNCTIONALIZATION ?

Improvement of the solubility for further processing
Enhancement of the interactions with organic polymers

- Amination
- Esterification
- Isocyanate-funct.
- Polymer wrapping
- Ionic liquids

Reduction of graphite oxide (GO) in a stabilization medium.

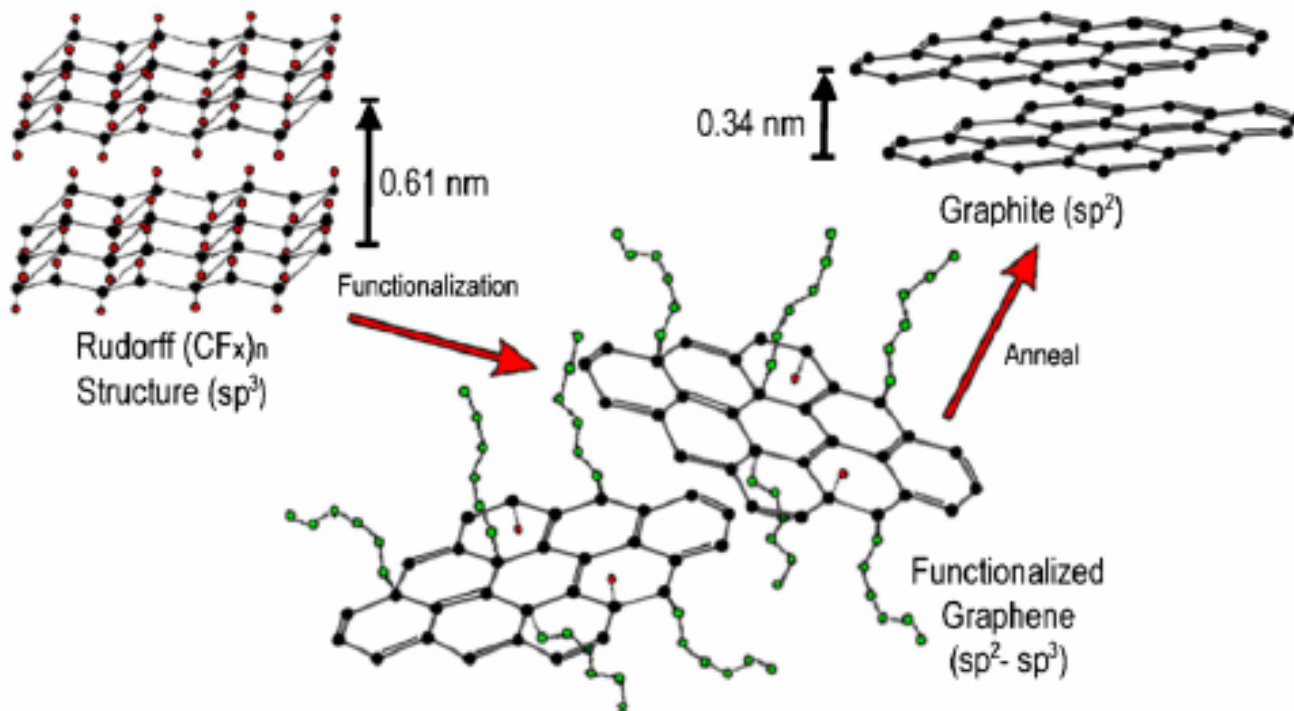


Park S. et al. Aqueous, suspension and characterization of chemically modified Graphene sheets. Chem Mater 2008;20:6592-4.



REQUIRED SURFACE FUNCTIONALIZATION ?

Covalent modification of graphene.



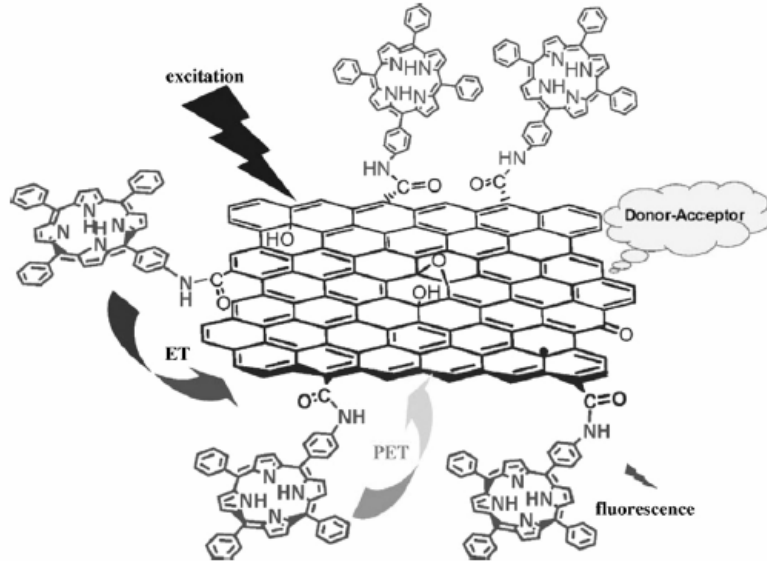
Amide coupling reaction between the carboxyl acid groups of graphene oxides and octadecylamine (ODA).

A.A. Worsley;
Chem. Phys. Lett. (2007)



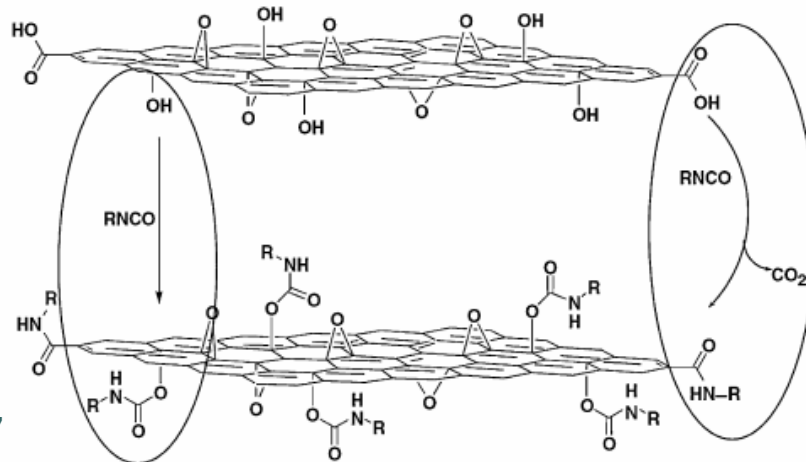
REQUIRED SURFACE FUNCTIONALIZATION ?

Covalent modification of graphene.



Covalent attachment of a porphyrin ring on the GO surfaces
(Thionyl chloride used to activate the carboxylic acid group in the presence of porphyrin using DMF as a solvent).

X.Y. Liu et al, Adv. Mater. (2009)



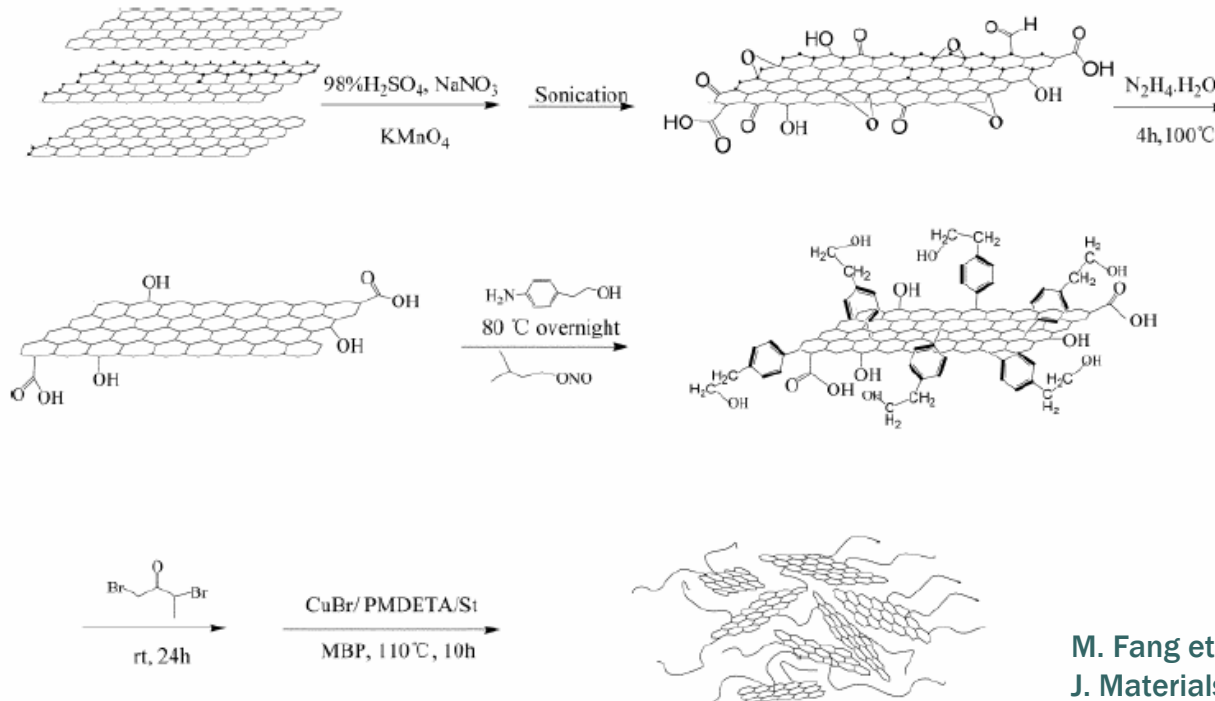
Isocyanate-modified graphene oxide : stable colloidal dispersion in all polar aprotic solvents, DMF, NMP, DMSO, hexamethylphosphoramide (HMPA).

S. Stankovich et al,
Carbon (2006)



GRAPHENE DISPERSION IN POLYMER MATRICES

Grafting from polymerization for modification of graphene



M. Fang et al.,
J. Materials Chem. (2009)

Atom transfer radical polymerization (ATRP)

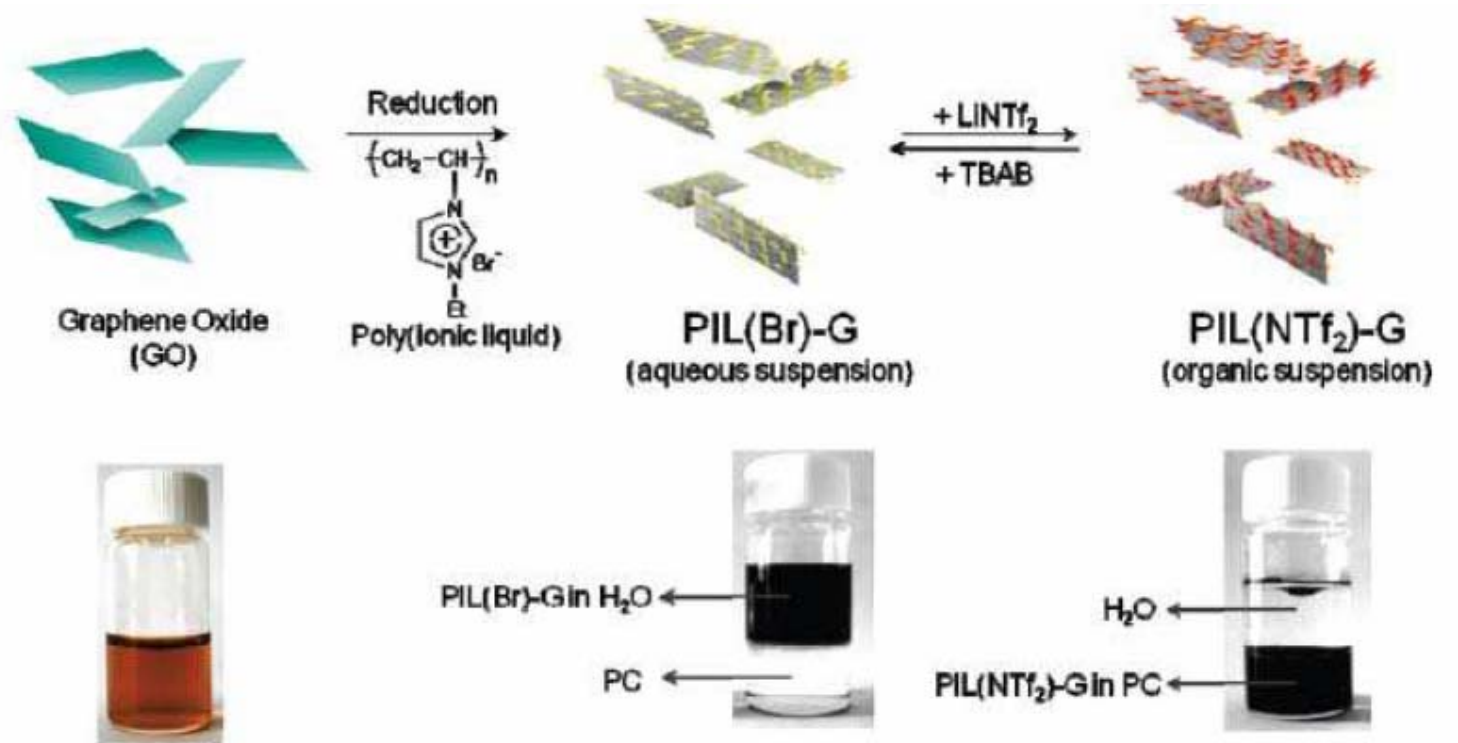
- *r*-GO treated with 2-(4-aminophenyl) ethanol and isoamyl nitrite (diazonium functionalization)
- modified *r*-GO reacted with 2-bromopropionyl bromide to be used as the initiator for styrene polymerization





REQUIRED SURFACE FUNCTIONALIZATION ?

Electrochemical modification of graphene



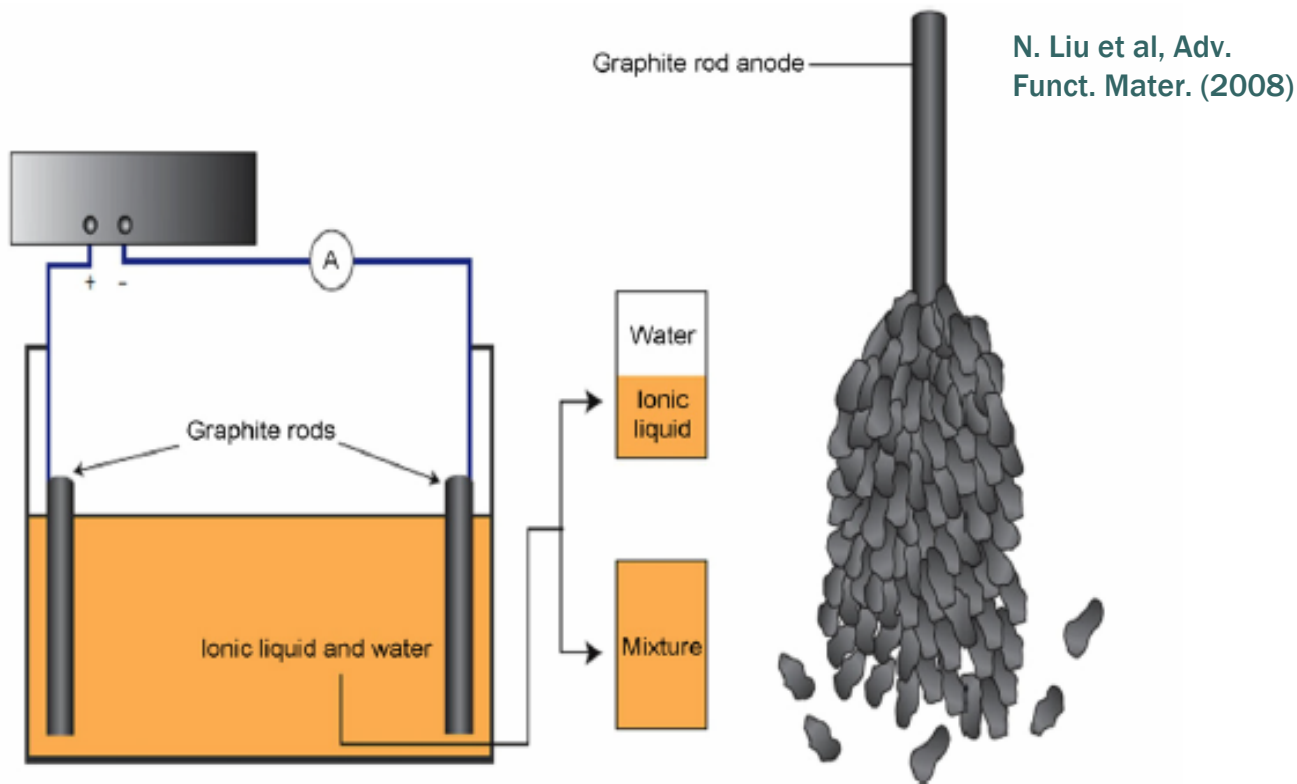
Hydrophilic-to-hydrophobic reversible switching of graphene sheets by simply exchanging the anions associated with polymeric ionic liquids (PIL)

H. Kim et al, Chem. Mater. (2010)



REQUIRED SURFACE FUNCTIONALIZATION ?

Electrochemical modification of graphene

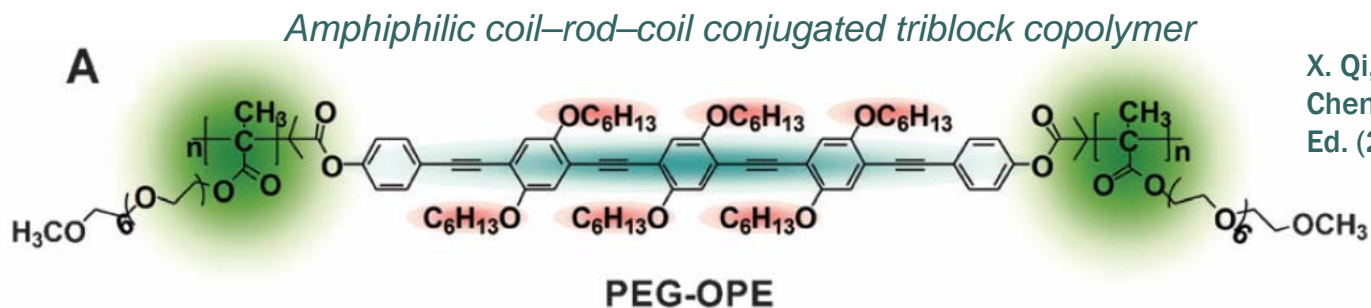


water and imidazolium-based ionic liquids

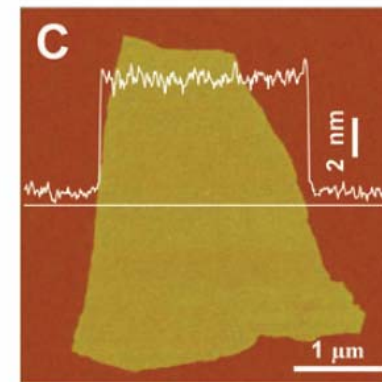
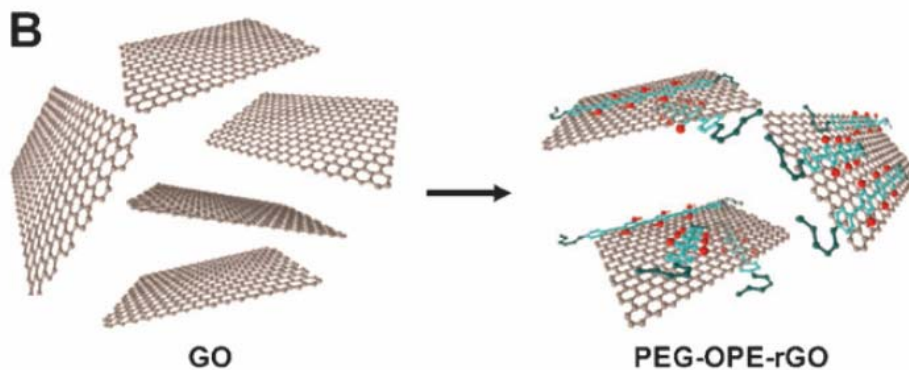
*Ultrasonication of dried GNPIL in DMF
⇒ homogeneous dispersion*

REQUIRED SURFACE FUNCTIONALIZATION ?

Non-covalent functionalization from van der Waals force, electrostatic interaction or π - π stacking



X. Qi, *Angew. Chem. Intern. Ed.* (2010)



(PEG-OPE) to improve the solubility in both high and low polar: conjugated rigid-rod backbone of PEG-OPE bound to the basal plane of the in situ reduced GO via the π - π interaction, whereas the lipophilic side chains and two hydrophilic coils of the backbone form an amphiphilic outer-layer surrounding the rGO sheet (solubility organic low polar (such as toluene and chloroform) and water-miscible high polar solvents (such as water and ethanol)).



REQUIRED SURFACE FUNCTIONALIZATION ?

Numerous methods for graphene modification

Method of modification	Modifying agent	Dispersing medium
Reduction in stabilization medium	KOH	Water
	Octadecyl amine	THF/CCl ₄ /1,2 dichloroethane
	Alkyl lithium	THF
Covalent modification	Organic isocyanate	DMF/NMP/DMSO/HMPA
	Organic diisocyanate	DMF
	PVA	Water/DMSO
	Porphyrin	DMF
	Poly-L-lysine	Water
Non-covalent modification	Poly(sodium 4-styrenesulfonate)	Water
	TCNQ	Water/DMF/DMSO
	PBA	Water
	SPANI	Water
Nucleophilic substitution	Alkyl amine/amino acid	CHCl ₃ /THF/toluene/DCM
Diazonium salt coupling	Aryl diazonium salt	DMF/DMAc/NMP
Electrochemical modification	Imidazolium based ionic liquids	DMF
Thermal treatment	-	NMP
π - π interaction	PNIPAAm	Water

T. Kuilla et al., Progress Polym. Sci. (2010)



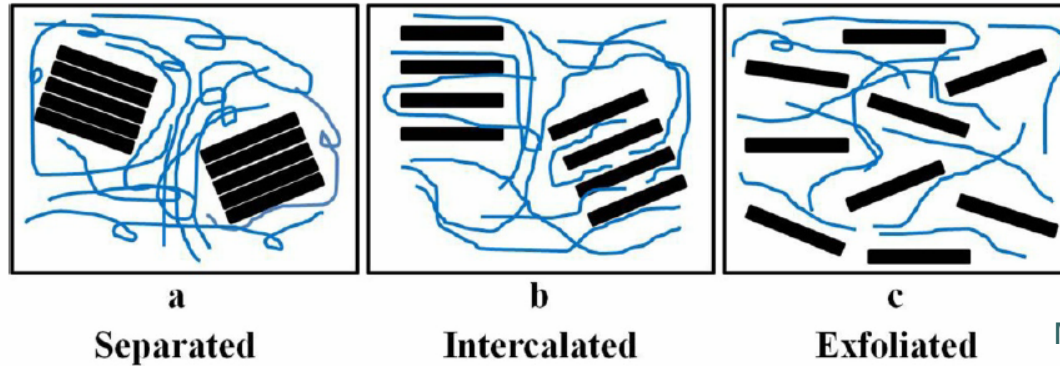


X. Huang et al,
Chem. Soc. Rev. (2012)

Methods	Conditions	Yield and properties
<i>Bottom-up approaches</i>		
CVD	Carbon sources: CH ₄ , H ₂ Substrate: Ni, Ru, Cu Temperature: 1000 °C	Sheet size of up to a few tens of micrometres.
PECVD	Carbon source: CH ₄ , H ₂ Substrate: Cu Temperature: 650 °C	Large area of more than 1 cm of monolayer graphene
Graphitization	Substrate: 6H-SiC(0001) Temperature: 1280 °C	Grain size: up to 50 µm long, 1 µm wide
Solvothermal	Reagents: Na and ethanol Temperature: 220 °C	Folded graphene structures Bulk conductivity: ~0.05 S m ⁻¹
Organic synthesis	Thermal fusion of polycyclic aromatic hydrocarbons at 1100 °C	For a 30 nm thick film on quartz, conductivity: 20 600 S m ⁻¹ , sheet resistance: 1.6 kΩ m ⁻²
<i>Top-down approaches</i>		
Liquid exfoliation of graphite	Intercalate: NMP Intercalate: SDBS	Single-layer yield: 7–12 wt% after purification Film conductivity: ~6500 S m ⁻¹ Film conductivity: ~35 S m ⁻¹ Single-layer yield: ~3% with a size of ~1 µm Graphene ribbons with lengths of ~40 µm. Single-layer yield: ~90% after purification Size: ~250 nm Resistance of single sheet with 100 nm in width: 10–20 kΩ Sheet size: 500 × 700 nm
Thermal exfoliation and liquid intercalation	Intercalate: ternary potassium salt Thermal exfoliation at 1000 °C Intercalates: oleum and TBA	Resistance of single sheet with 100 nm in width: 10–20 kΩ Sheet size: 500 × 700 nm
Electrochemical exfoliation	1-Octyl-3-methyl-imidazolium hexafluoro-phosphate as electrolyte; graphite rods as electrodes	
Chemical reduction of GO	Reduction agent: hydrazine Deoxygenation agent: KOH or NaOH Temperature: 50–90 °C Reduction agent: bovine serum albumin Reduction agent: vitamin C Temperature: 95 °C Reduction <i>via</i> bacteria respiration Reduction agent: hydriodic acid and acetic acid	Sheet resistance of graphene paper: 7200 S m ⁻¹ Incomplete removal of oxygen-containing groups To be used as template for nanoparticle synthesis Film conductivity: up to 7700 S m ⁻¹ Film resistance decreased up to 10 ⁴ after reduction Sheet resistance: pellets dried after solution reduction: 30 400 S m ⁻¹ Thin film after vapor reduction: 7850 S m ⁻¹
	In solution at room temperature or in vapor at 40 °C Sonolytic reduction: ultrasonication at 211 kHz for 30 min Microwave-assisted reduction in the presence of hydrazine	Formation of 1–4 layers of rGO Formation of 1–8 layers of rGO with size up to a few micrometres
Thermal reduction of GO	220 °C in air for 24 h 150 °C in DMF for 1 h	Film sheet resistance: 8 kΩ sq ⁻¹ Film resistance: 6 kΩ
Photothermal reduction of GO	High pressure Hg lamp with H ₂ or N ₂ flow Pulsed xenon flash	Sheet size: ~1 µm Single-sheet conductivity: 2000–20000 S m ⁻¹ Able to prepare a GO/rGO patterned film with a photomask Sheet resistance of rGO area: ~9.5 kΩ sq ⁻¹

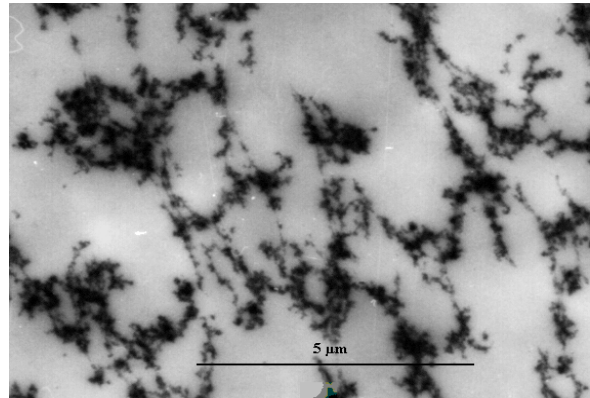
GRAPHENE DISPERSION IN POLYMERS

Layered nanofillers in polymer matrices

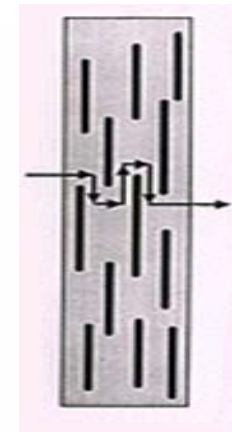


M. Wang, InTech (2012)

Morphology needs to be designed from the expected behaviour



Generation of nanofiller network (percolation)

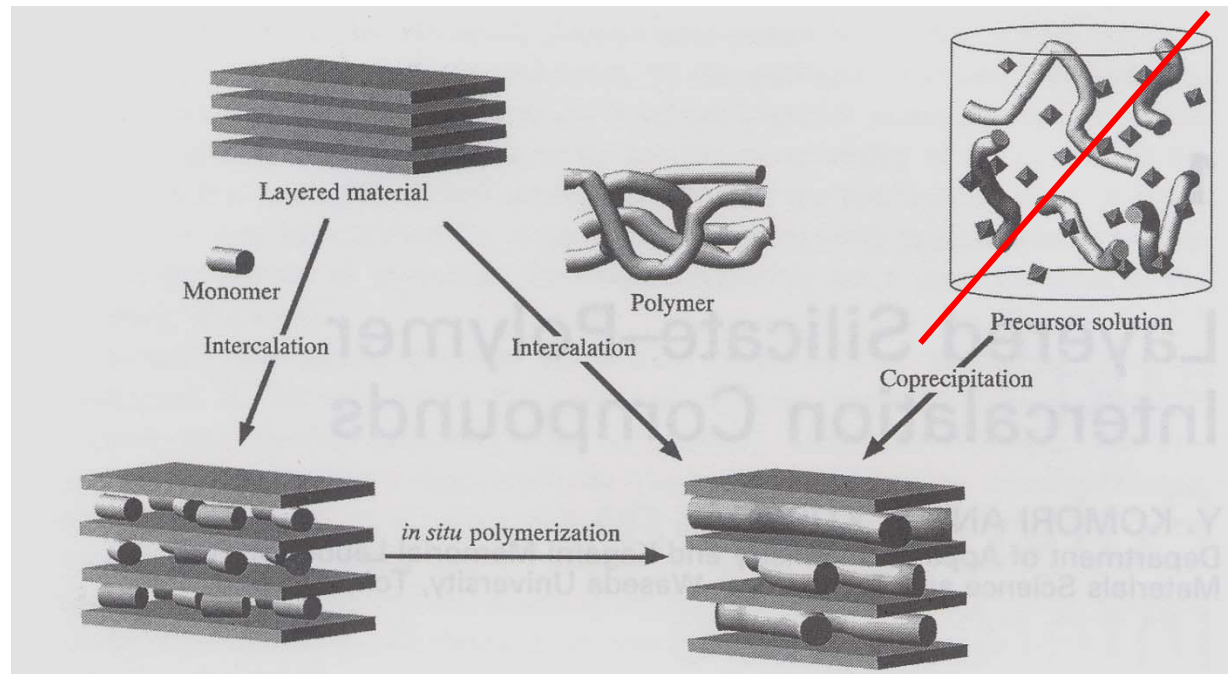


Ordered / Individual nanofillers



GRAPHENE DISPERSION IN POLYMERS

Similar routes as layered silicate-based nanocomposites processing



Numerous
polymer
matrices

Epoxy, PMMA

Polypropylene, LLDPE, HDPE, polystyrene, PPS], polyamide

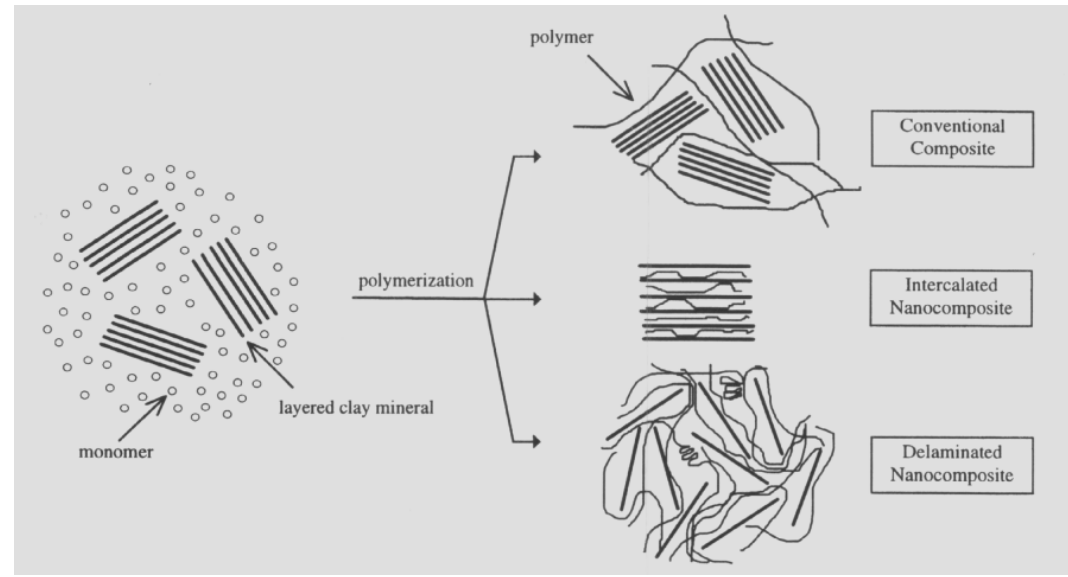
Polyaniline, phenylethynyl-terminated polyimide

Silicone rubber

GRAPHENE DISPERSION IN POLYMERS



Nanocomposites processing via in-situ polymerization



Berlung (1999)

Large variety of polymer nanocomposites:
Polystyrene, poly(methyl methacrylate), polystyrene sulfonate (PSS), polyimide (PI), poly(ethylene terephthalate) (PET), etc
Epoxy-amine, polyurethane (OH/NCO), etc

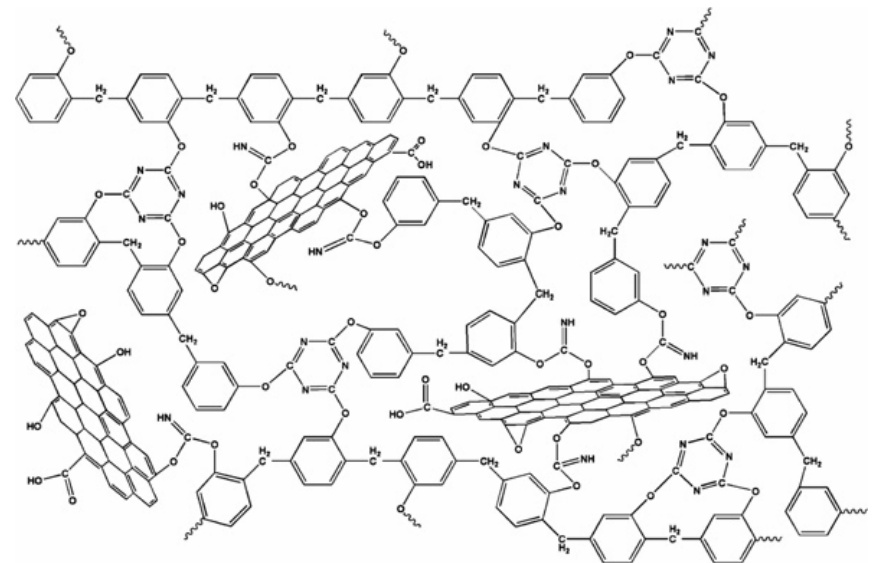
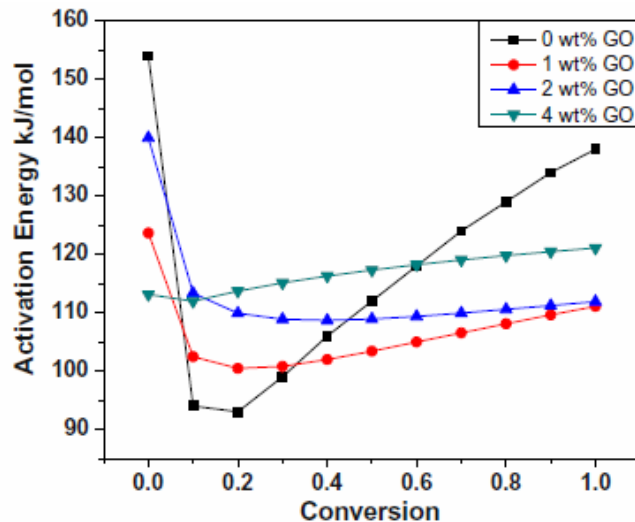
GRAPHENE DISPERSION IN POLYMERS

Nanocomposites processing via in-situ polymerization

- . Influence of the presence of graphene nanosheets on polymerization
Catalytic effect of free hydrogen species, bonding, ...
- . Influence on gelation time (polymer networks)

Cyanate ester / graphene

X. Wang et al, Europ. Polym. J. (2012)

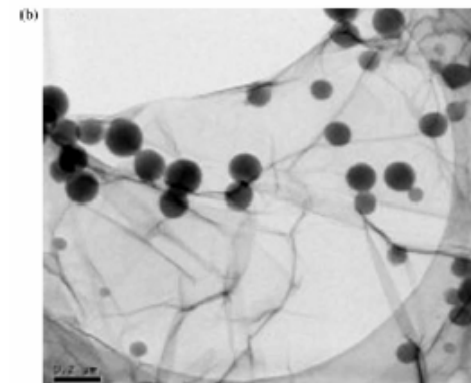
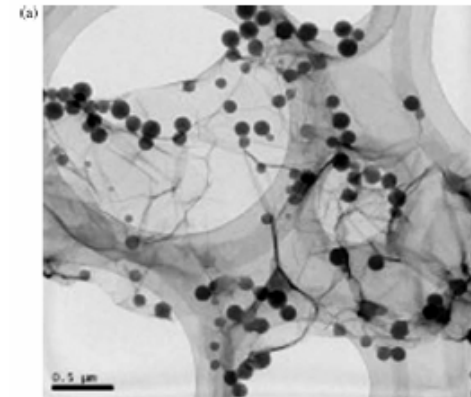
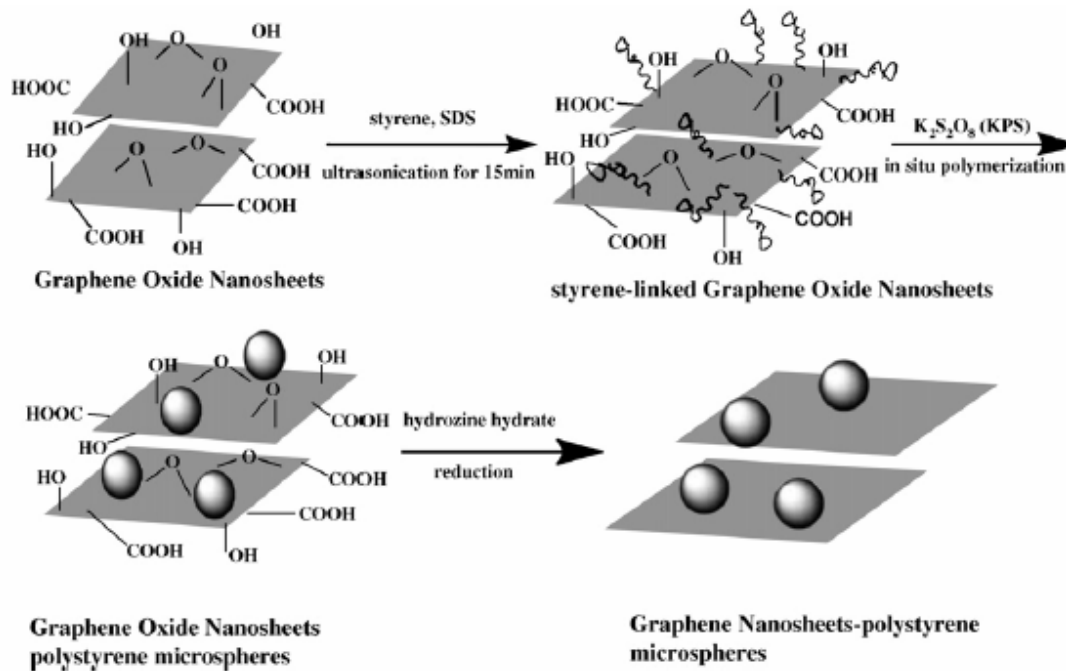


Crosslinked network formation through triazine ring and $-O-(C=NH)-O-$ bond for the PT-30/GO nanocomposites



GRAPHENE DISPERSION IN POLYMER MATRICES

Nanocomposites processing via in-situ emulsion polymerization



J. Lianga et al., Carbon (2009)



GRAPHENE DISPERSION IN POLYMERS

Solution-based nanocomposites processing

Graphene or modified graphene dispersed in a suitable solvent, such as water, acetone, chloroform, tetrahydrofuran (THF), dimethyl formamide (DMF) or toluene, owing to the weak forces that stack the layers together.

Solvent removal as a critical step for processing

Driving force for polymer intercalation from solution is the entropy gained by the desorption of solvent molecules, which compensates for the decrease in conformational entropy of the intercalated polymer chains.

Synthesis of intercalated nanocomposites based on polymers with low or even no polarity.

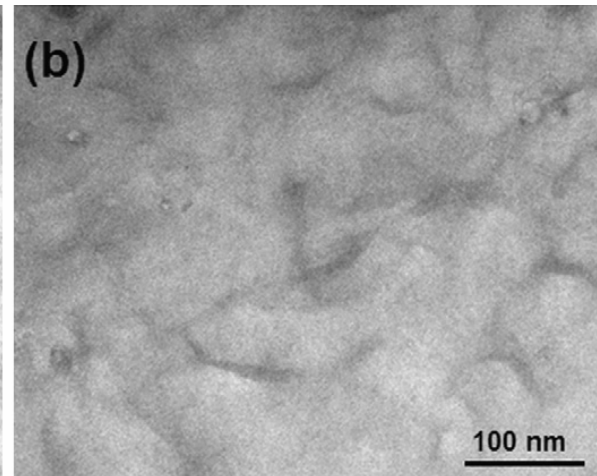
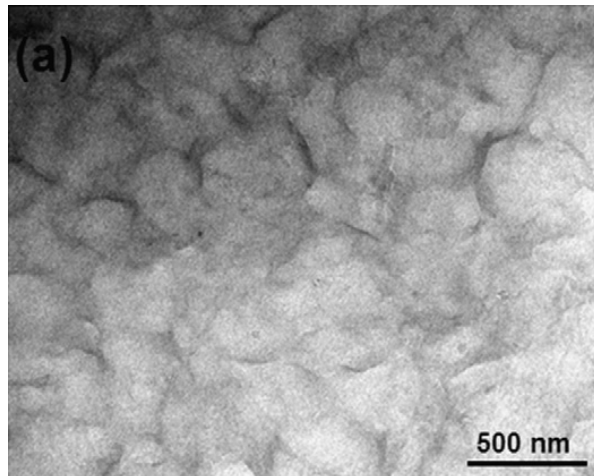
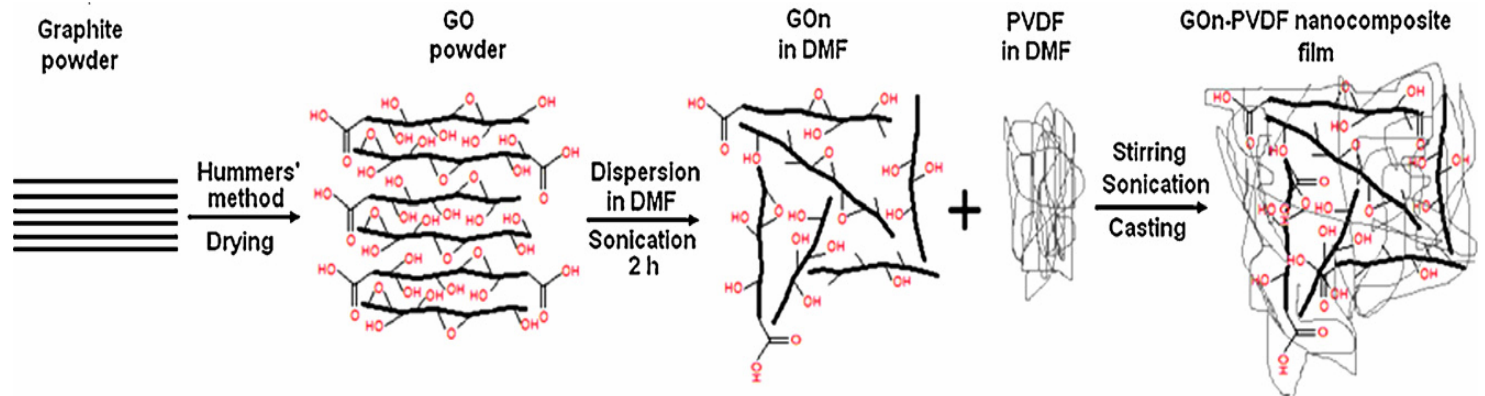
maleic anhydride grafted polyethylene (PE-g-MA), epoxy, PS, polypropylene (PP), poly(vinyl alcohol) (PVA), poly(vinyl chloride) (PVC), ethylene vinyl acetate (EVA)



GRAPHENE DISPERSION IN POLYMERS

Solution-based nanocomposites processing

PVDF-graphene nanocomposites

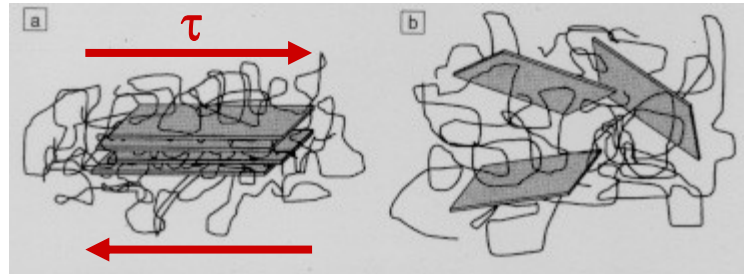


GRAPHENE DISPERSION IN POLYMERS

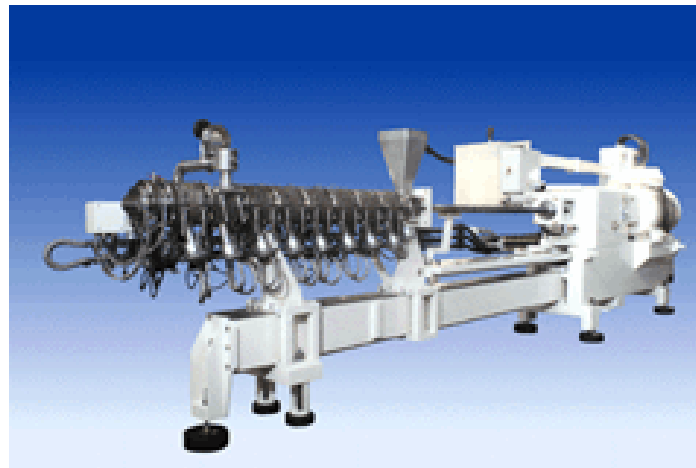
Nanocomposites melt processing



Applying shear



Dispersion tools
(high viscosity medium)



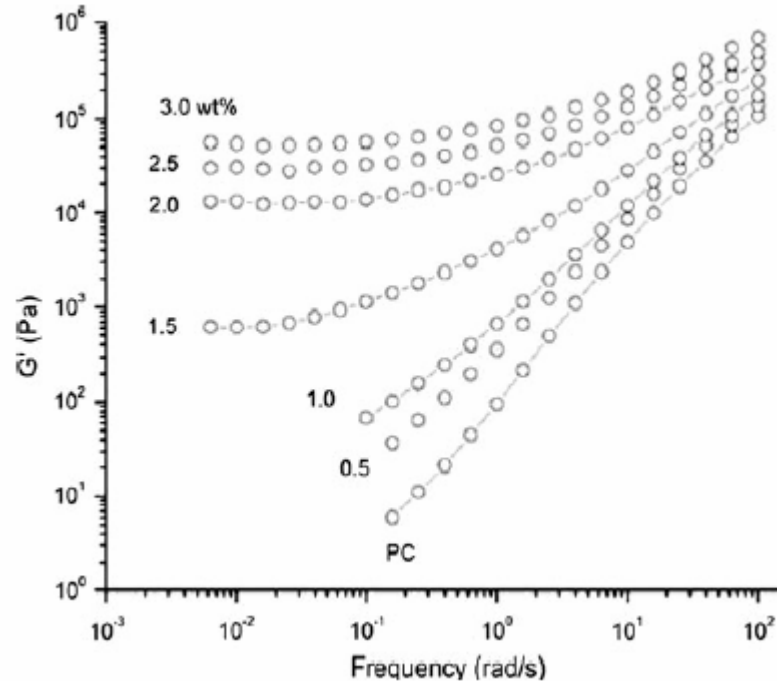
Twin-screw extrusion

Large dependence of morphology with the tool used

Thermoplastic matrices such as PP/EG, HDPE/EG, PPS/EG, PA6/EG, etc.

GRAPHENE DISPERSION IN POLYMERS

Nanocomposites melt processing



Polycarbonate/
Graphene @ 210°C

B. Li et al., J. Mater. Sci. (2011)

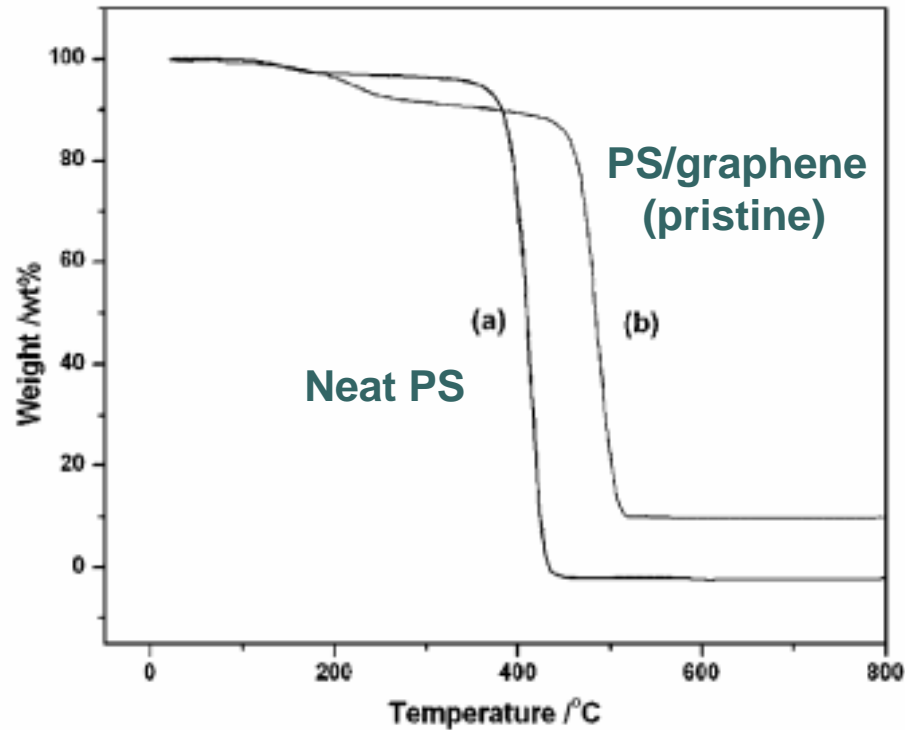
Large increase of the molten state viscosity with increasing graphene volume fraction and state of dispersion

⇒ Processing using conventional tools (extrusion, injection, ...)...

GRAPHENE-BASED NANCOMPOSITES

Thermal stability

PS/graphene nanocomposites under N₂ atmosphere



N. Liu et al,
Adv. Funct. Mater. (2008)

Hindering segmental motions of polymer chains via

- mechanical interlocking
- hydrogen bonding with surface oxygen functionalities

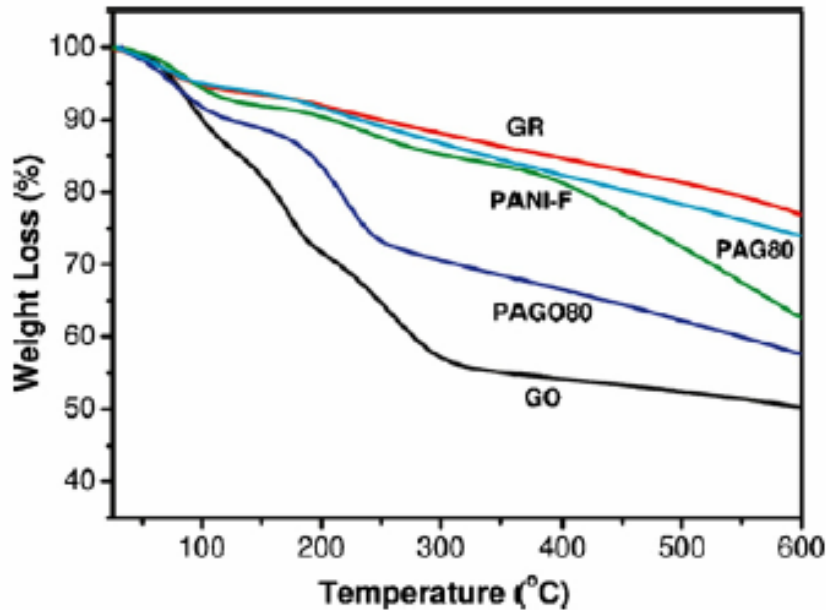


GRAPHENE-BASED NANCOMPOSITES

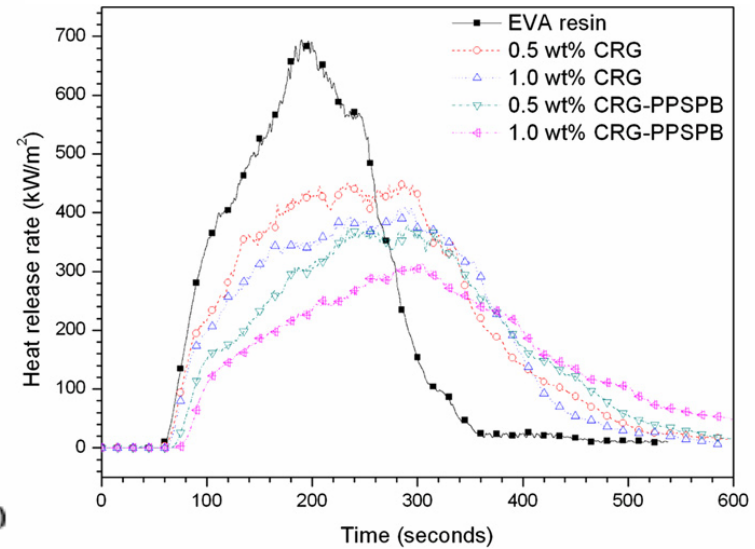
Thermal stability



Graphene as flame retardant



H. Zhang et al.,
Electrochim. Acta (2009)

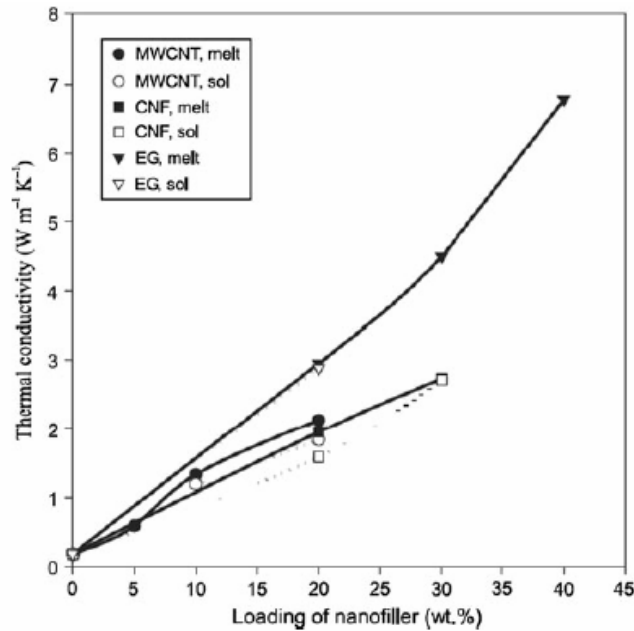


G. Huang et al., Materials Chemistry
and Physics (2012)

During combustion, inflammable anisotropic nanoparticles form a jammed network of char layers that retards transport of the decomposition products.

GRAPHENE-BASED NANCOMPOSITES

Thermal behaviour



Thermal conductivity

⇒ *Processing*

PEI nanocomposites

S. Goshe et al., High Perf. Polym. (2006)

Dimensional stability

⇒ *CTE, HDT*

Polymer	Types of GNPs	Concentration of GNP	Increase of T_g (°C)
PVA	GNP	5 wt%	45
PMMA	GNP	5 wt%	35
PMMA	As-received graphite	5 wt%	20
PLA	Exfoliated graphite	3.0 wt%	14
PANI	GNP	N/A	40
Flouroelastomer	GNP	7 phr	7
PS	GIC-220N	5 wt%	80
HIPS	GIC-220N	5 wt%	None
ABS	GIC-220	5 wt%	10
Nylon-6	Foliated graphite	5 wt%	24

B. Li et al, J. Mater. Sci (2011)



GRAPHENE-BASED NANCOMPOSITES

Mechanical Behaviour

Matrix	Filler type	Filler loading (wt.% ^a , vol.% ^b)	Process	% Increase E	% Increase TS	% Increase flexural strength
Epoxy	EG	1 ^a	Sonication	8	-20	
	EG	1 ^a	Shear	11	-7	
	EG	1 ^a	Sonication and shear	15	-6	
	EG	0,1 ^a	Solution			87
PMMA	EG	21 ^a	Solution	21		
	GNP	5 ^a	Solution	133		
PP	EG	3 ^b	Melt			8
	xGnP-1	3 ^b	Melt			26
	xGnP-15	3 ^b	Melt			8
	Graphite	2,5 ^b	SSSP		60	
LLDPE	xGnP	15 ^a	Solution		200	
	Parrafin coated xGnP	30	Solution		22	
HDPE	EG	3 ^a	Melt	100	4	
	UG	3 ^a	Melt	33		
PPS	EG	4 ^a	Melt			-20
	S-EG	4 ^a	Melt			-33
PVA	GO	0,7 ^a	Solution		76	
	Graphene	1,8 ^b	Solution		150	
TPU	Graphene	5,1 ^b	Solution	200		
	Sulfonated Graphene	1 ^a	Solution		75	
PETI	EG	5 ^a	<i>In situ</i>	39		
		10 ^a	<i>In situ</i>	42		

GRAPHENE-BASED NANCOMPOSITES

Mechanical Behaviour

Table 4. Mechanical Properties of Graphene/Polymer Nanocomposites

polymer ^a	reinforcements	processing	E_{matrix} (MPa)	graphene concentration (vol %)	modulus increase (%)	tensile strength increase (%)	ultimate strain increase (%)
PVA	GO	solvent	2100	2.5	128	70	32
PVA	GO	solvent	2130	(0.49) ^b	62	76	-70
PMMA	GO	in situ polymerization	520 ^c	(1.7)	54 ^c	N/A	N/A
PCL	GO	solvent	340	(2.4)	108	36	-90
PCL	GO	solvent	260	(0.46)	50	N/A	N/A
epoxy	TRG	in situ polymerization	2850	(0.05)	31	40	N/A
PEN	TRG	melt	2350	2.4	57	N/A	N/A
PC	TRG	melt	2080	1.3	25	N/A	N/A
PMMA	TRG	solvent	2100	(0.005, 0.5)	33, 80	N/A	N/A
PVDF	TRG	solvent	1280	(3.1)	92	N/A	N/A
SAN	TRG	solvent + melt	2350	(2.3)	34	N/A	-58
PC			1480	(2.5)	52	N/A	-98
PP			980	(1.9)	43	N/A	-99
PA6			1650	(2.4)	32	N/A	-94
natural rubber	TRG	solvent/melt	1.3	(1.2)	750	N/A	N/A
PDMS		in situ polymerization	0.6	(2.2)	1100	N/A	N/A
styrene-butadiene rubber		-	10	(0.8)	390	N/A	N/A
TPU	TRG	solvent	458	(1.5)	43	-23	-15
silicone foam	TRG	in situ polymerization	250 ^d	(0.12)	200 ^d	N/A	N/A
PVA	acid functionalized TRG	solvent	660	(0.4)	35	N/A	N/A
PMMA	amine treated, acid functionalized TRG		2120	(0.3)	70	N/A	N/A
TPU	TRG	melt	6.1-7.1	1.6	250	N/A	N/A
		solvent		1.6	680	N/A	N/A
		in situ polymerization		1.5	210	N/A	N/A
PS	iGO	solvent	1450	1.6	490-900	N/A	N/A
	PS-functionalized, chemically reduced GO	solvent		(0.4)	57	N/A	N/A
TPU	chemically reduced sulfonated-graphene	solvent	9.8	(0.5)	120	75	N/A
TPU	GO	solvent	6	(2.4)	900	-19	-60
PAN	exfoliation of alkali intercalated graphite	electrospinning, solvent	2450	(2.1)	100	N/A	N/A



GRAPHENE-BASED NANCOMPOSITES

Mechanical Behaviour

Large increase of Young's modulus

PMMA 33% improvement for 0.01 wt %

Ramanathan, T et al., Nature Nanotechnol. 2008

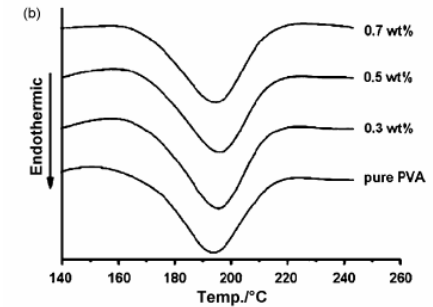
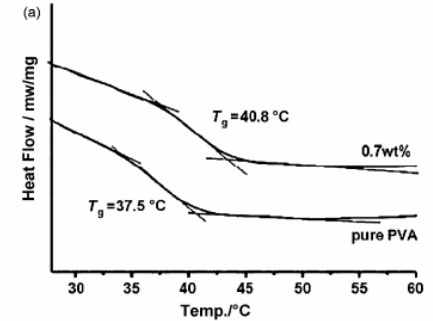
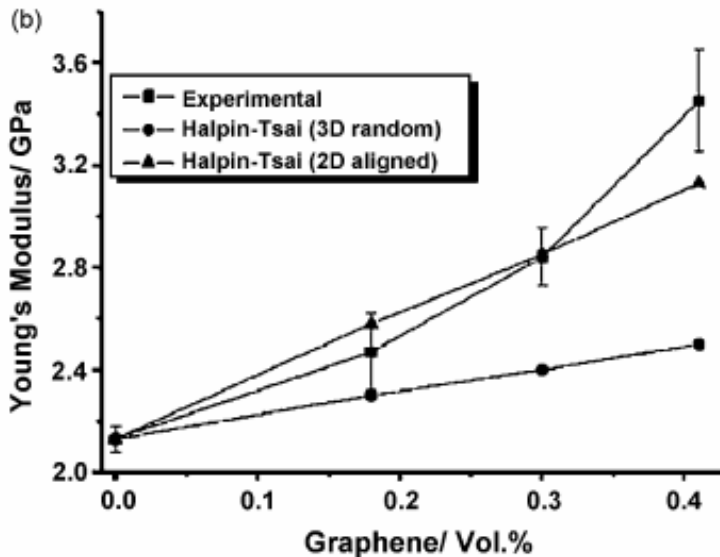
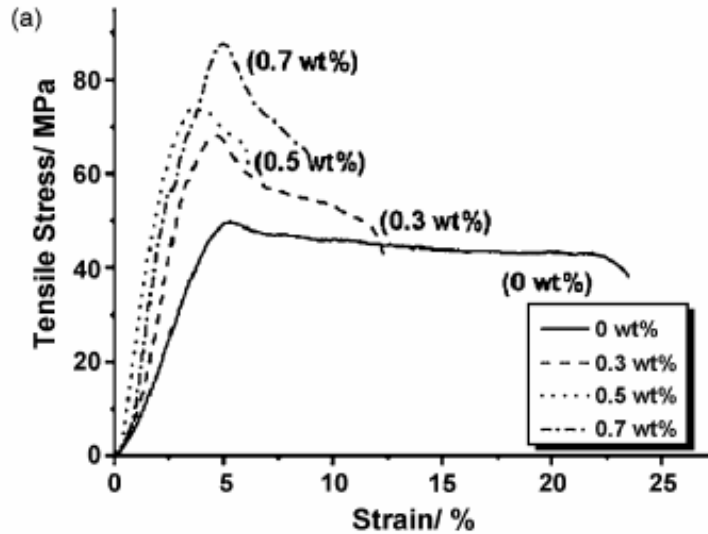
Epoxy 31% increase for 0.1wt %

Rafiee, M.A et al., ACS Nano 2009

- ⇒ strong hydrogen-bonding interaction of oxygen-functionalized graphene (thermally reduced graphene oxide)
- ⇒ mechanical interlocking at the wrinkled surface that may restrict segmental mobility of polymer chains near TRG surfaces

GRAPHENE-BASED NANCOMPOSITES

Mechanical Behaviour



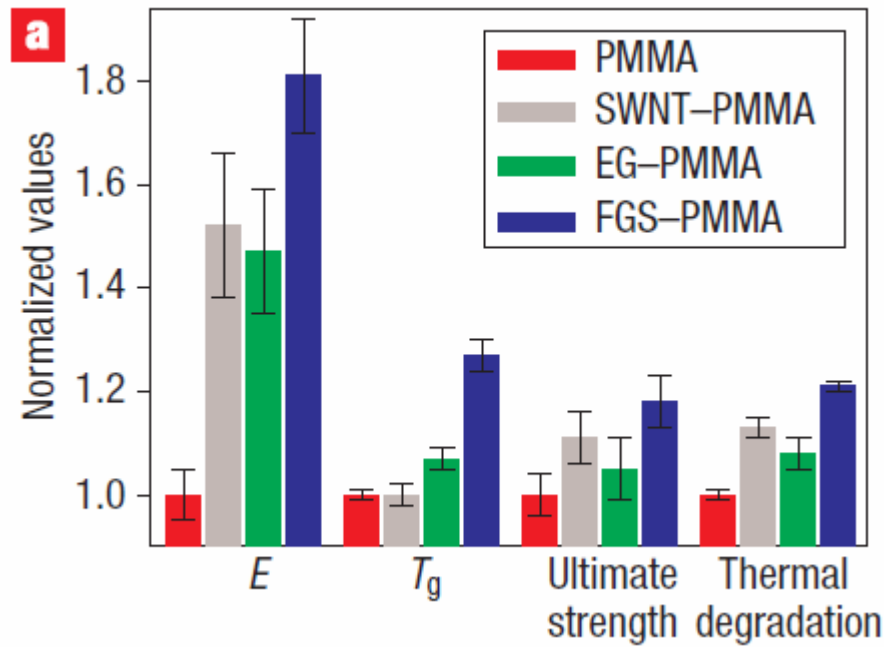
J. Liang et al, Adv. Funct. Mater. (2009)

PVA / graphene nanocomposites

GRAPHENE-BASED NANCOMPOSITES

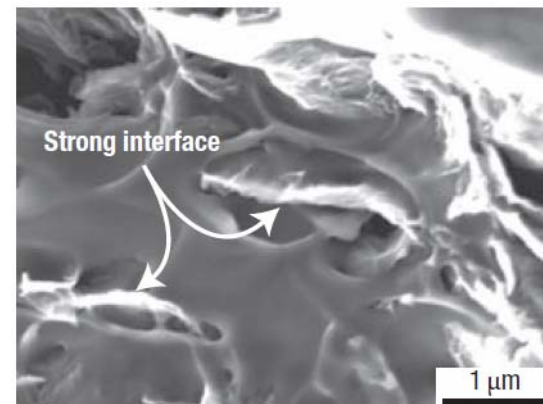
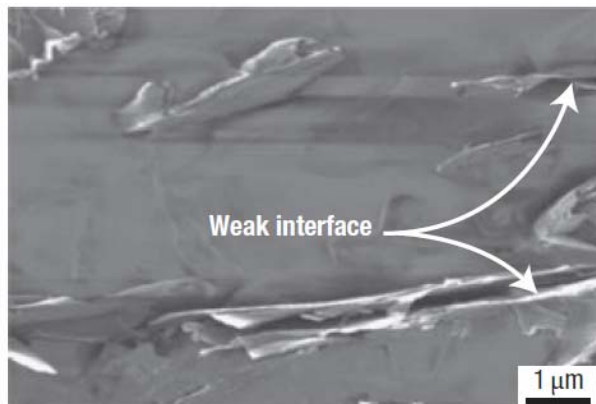
Mechanical Behaviour

Role of the interface

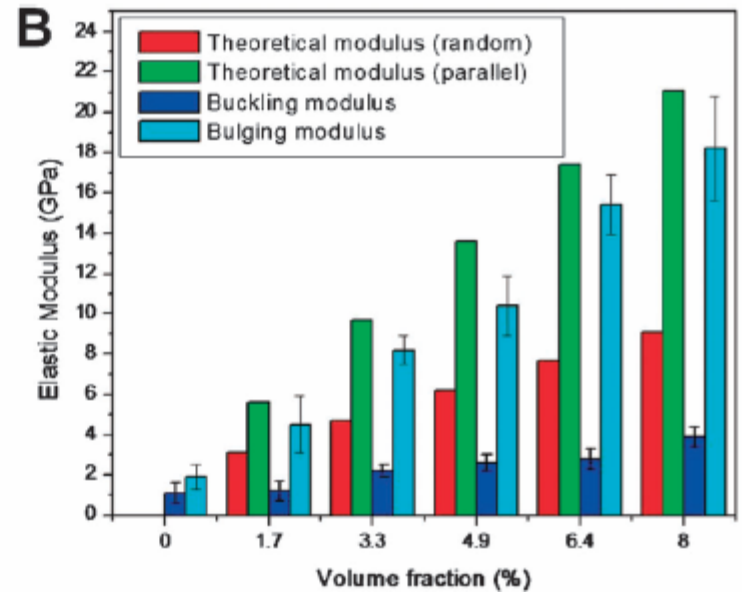
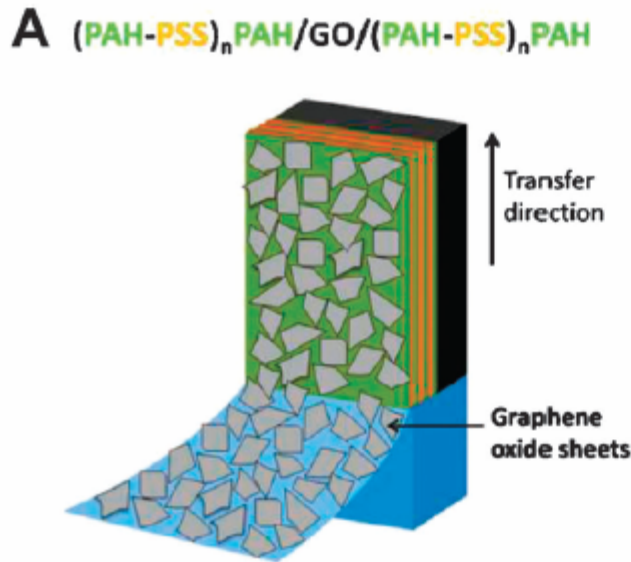


PMMA / graphene nanocomposites

T. Ramanathan et al.,
Nature Nanotechnology (2008)



GRAPHENE DISPERSION IN POLYMER MATRICES



D.D. Kulkarni et al, ACS Nano (2010)

Layer-by-layer (LbL) assembling via the Langmuir–Blodgett (LB) technique to deposit GO sheets onto films of polyelectrolyte poly(allylamine hydrochloride) (PAH) and poly(sodium 4-styrene sulfonate) (PSS) multi-layers

GRAPHENE-BASED NANCOMPOSITES

Electrical Behaviour

Matrix	Filler	Filler loading (wt.% ^a , vol.% ^b)	Process	σ (S m ⁻¹) of matrix	σ (S m ⁻¹) of composite
Epoxy	EG	3.00 ^a	Sonication	1E-13	1E-4
	EG	2.50 ^b	Solution	1E-15	1E-2
	Graphene	0.52 ^b	Solution	1E-10	1E-2
PMMA	NanoG	0.68 ^b	<i>In situ</i>	1E-13	1E-3
	EG	1.00 ^a	Solution	1E-15	1E-3
	EG	10 ^a	<i>In situ</i>	-	77.65
PS	NanoG	1.00 ^a	<i>In situ</i>	1E-14	1E-4
	Graphene	0.10 ^b	Solution	1E-16	1E-5
	GNS ^{C4P}	0.40 ^b	Solution	1E-14	1E-5
	GNS ^{C4P}	0.10 ^b	Solution	1E-14	4
	GNS ^{8B}	0.20 ^b	Solution	1E-14	1E-5
	GNS ^{5D}	0.30 ^b	Solution	1E-14	1E-5
	Graphene	-	Solution	1E-16	24
	Graphene	2.0 ^a	<i>In situ</i>	1E-10	1E-2
	EG	1.50 ^b	<i>In situ</i>	1E-16	1E-4
K-GIC	8.20 ^a	Solution	NA	-	
Nylon-6	EG	1.50 ^b	<i>In situ</i>	1E-15	0.1
	FG	0.75 ^b	<i>In situ</i>	1E-15	1E-5
PP	xGnP-1	3.00 ^b	Coating	1E-12	0.1
	xGnP-1	3.00 ^b	Solution	1E-12	1E-2
	xGnP-15	7.00 ^b	Melt	1E-12	1E-3
	xGnP-15	5.00 ^b	Coating	1E-12	0.1
	EG	0.67 ^b	Solution	1E-16	0.1
HDPE	EG	3.00 ^a	Melt	1E-16	1E-8
	UG	5.00 ^a	Melt	1E-16	1E-10
PPS	EG	4.0 ^a	Melt	1E-12	1E-3
	S-EG	4.0 ^a	Melt	1E-12	1E-2
PANI	Graphite	1.5 ^a	<i>In situ</i>	5.0	3300.3
	GO	-	<i>In situ</i>	2.0	1000
PVDF	FGS	2.0 ^a	Solution	1E-11	1E-2
	EG	5.0 ^a	Solution	1E-11	1E-3
PVA-S PET	NanoG	0.2 ^a	Solution	1E-13	1E-3
	Graphene	0.47 ^b	Melt	1E-14	7.4E-2
Polycarbonate	FGS	2.0 ^a	Melt	1E-14	1E-9
	Graphite	12	Melt	1E-14	6.6E-11

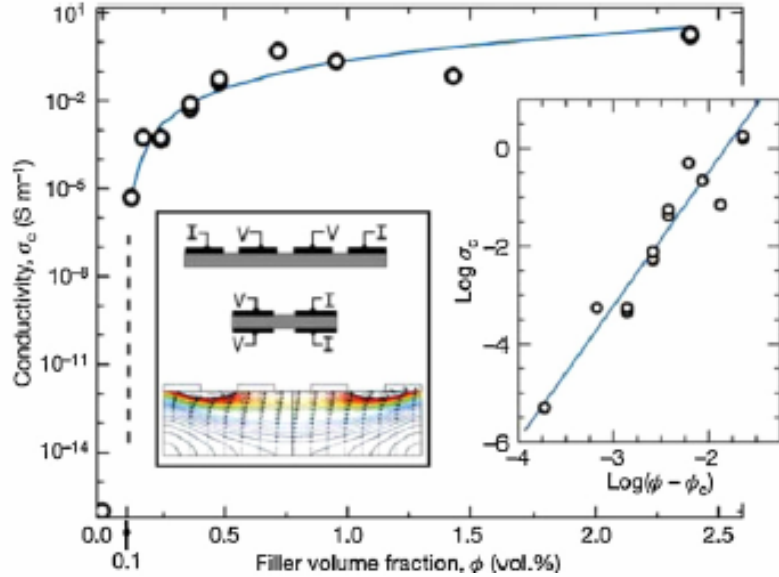


GRAPHENE-BASED NANCOMPOSITES

Electrical Behaviour



Polystyrene / graphene



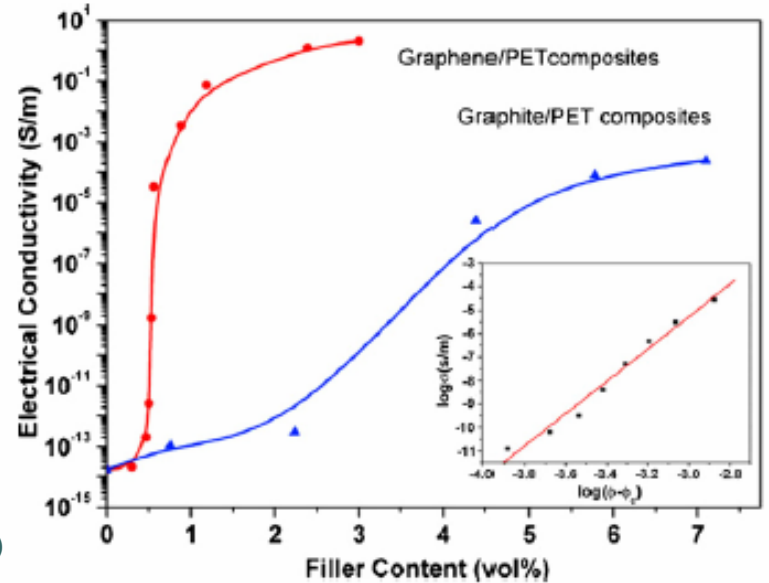
S. Stankovich et al., Nature (2006)

PBT/graphene

Critical phenomena around the percolation threshold:

$$\sigma_m = \sigma_h (\phi - \phi_c)^t$$

Antistatic criterion (10^{-6} Sm^{-1})



B.I. Halperin et al., Phys. Rev. Lett. (1985)

GRAPHENE-BASED NANCOMPOSITES

Electrical Behaviour



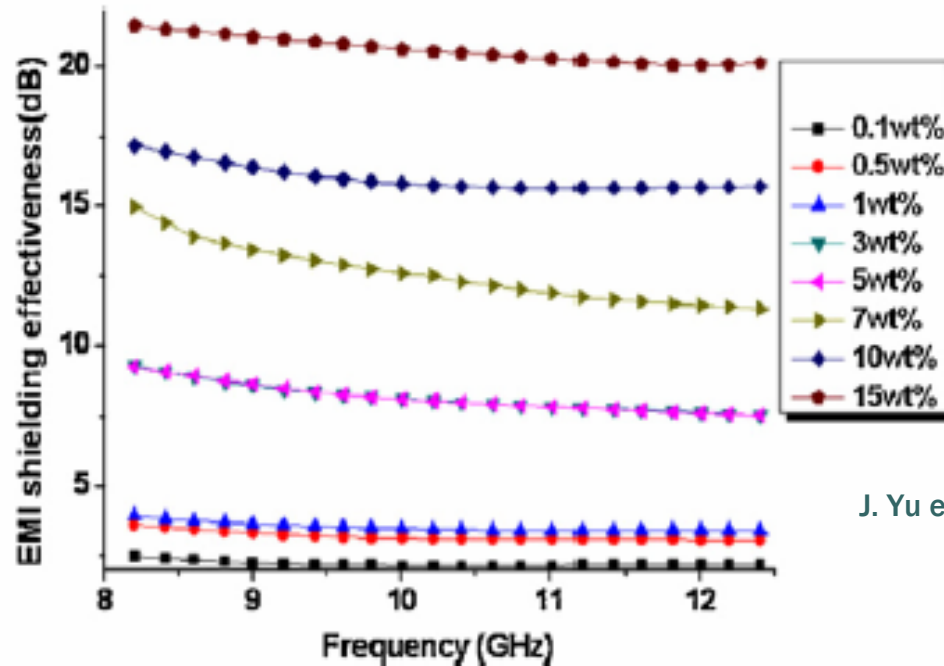
Table 3. Electrically Conductive Graphene/Polymer Nanocomposites

polymer ^a	graphene type	processing	electrical percolation threshold (vol %)
chemically modified			
PS	iGO ^b	solvent blending + hydrazine	0.1
vinyl chloride/vinyl acetate copolymer	GO	solvent blending + hydrazine	0.15
PS	electrochemically exfoliated graphite	solvent blending + ionic liquid	0.13–0.37
epoxy	partially reduced GO	in situ polymerization at 250 °C	0.52
PMMA	GO (17 mol % O)	in situ polymerization	(1.3) ^c
PMMA	GO (12 mol % O)	in situ polymerization	(1.6)
thermally exfoliated			
TPU	TRG, ~800 m ² /g, 4 mol % oxygen	solvent blending	0.3
		in situ polymerization	0.4
		melt compounding	0.8
PEN		melt compounding	0.5
PC		melt compounding	0.6
natural rubber	> 600 m ² /g, 5 mol % oxygen	melt or solvent blending + vulcanization	(0.8, solvent blend), (> 2.0, melt blend)
PS–PI–PS		melt or solvent blending	(0.6)
PDMS		oligomer blending + polymerization	(0.6)
TPU	apparent specific volume: 410 cm ³ /g, 5 mol % oxygen	solvent blending	(1.0)
TPU		solvent blending	(1.0)
TPU		in situ polymerization	(1.6)
PVDF	–	solvent blending	(1.6)
SAN	600–950 m ² /g, up to 14 mol % oxygen	preblending using solvents, followed by melt compounding	(1.9)
PC			(1.3)
PP			(2.0)
PA6			(3.8)

GRAPHENE-BASED NANCOMPOSITES

EMI Shielding

Electromagnetic interference (EMI) shielding



J. Yu et al, Carbon (2007)

EMI shielding effectiveness increased with increasing graphene loading, attributed to the formation of a conducting interconnected graphene-based sheet network in the insulating epoxy matrix.

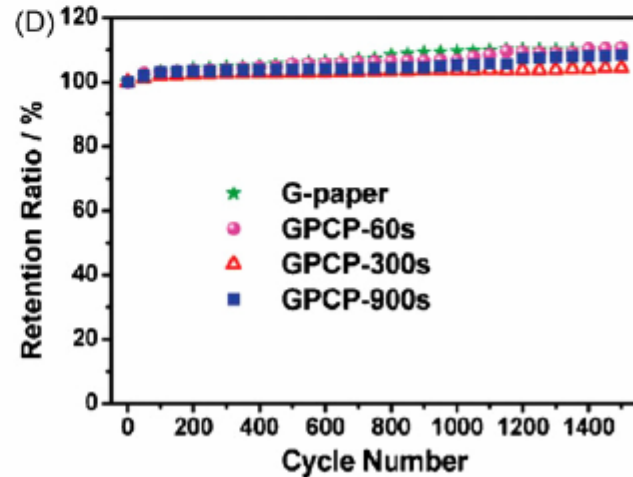
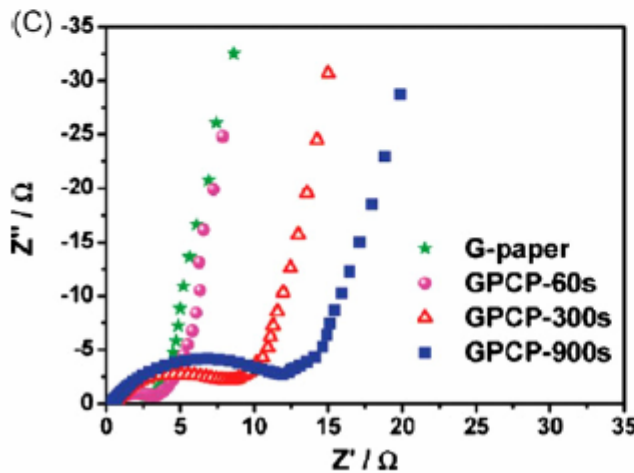
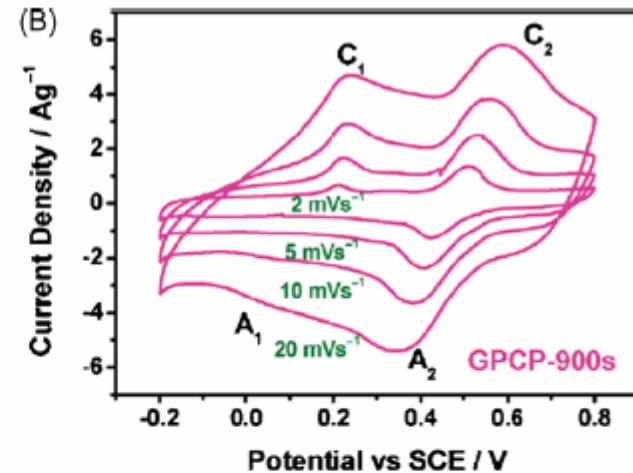
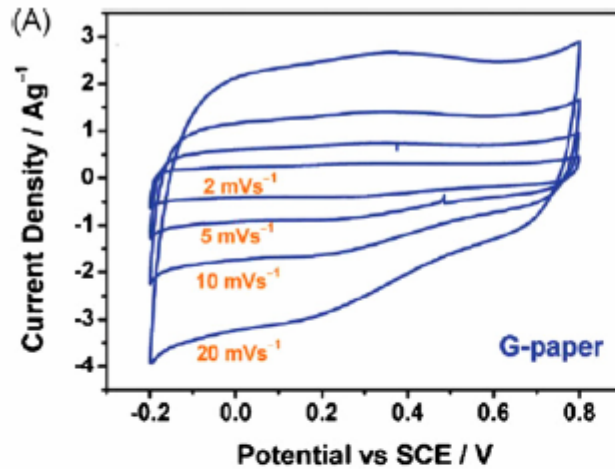


Effective light weight shielding materials for electromagnetic radiation.

GRAPHENE-BASED NANCOMPOSITES

Electrical Behaviour

PANI/graphene composite paper (GPCP)
In-situ electropolymerization of aniline



Cyclic voltametry

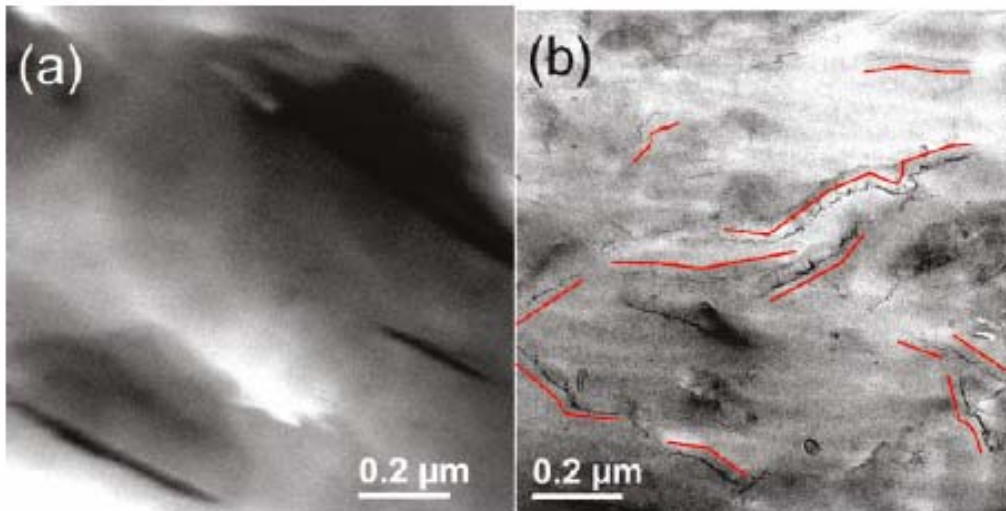
GP, only one pair of redox peaks due to the transition between quinone/hydroquinone groups. GPCP, two couples of redox peaks indicating the presence of pseudocapacitive PANI.

GRAPHENE-BASED NANOCOMPOSITES

Gas Transport / Permeability



polymer	filler	processing	permeant	relative reduction (%)	graphene loading (vol %)
PEN	TRG	melt	hydrogen	44	1.8
PC	TRG	melt	helium	32	1.6
TPU	TRG	melt	nitrogen	39	1.6
			nitrogen	52	1.6
			nitrogen	81	1.6
			nitrogen	71	1.5
			nitrogen	94–99	1.6
natural rubber	iGO	in situ polymerization	nitrogen	62	1.5
	GO	in situ polymerization	nitrogen	60	1.7
PS-PI-PS	TRG	melt/solvent/oligomer polymerization	air	~80	2.2
PDMS				~80	2.2



Defect-free graphene sheets are impermeable to all gas molecules.

GRAPHENE-BASED NANOCOMPOSITES

Gas Transport / Permeability



Tortuosity τ

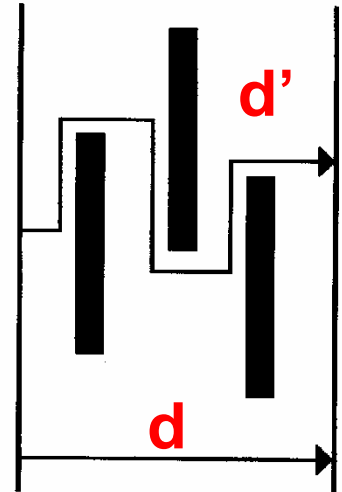
$$\tau = d' / d = 1 + \Phi_s L / 2 w$$

sheet dimensions

L length

w thickness

Volume fraction of nanosheets Φ_s

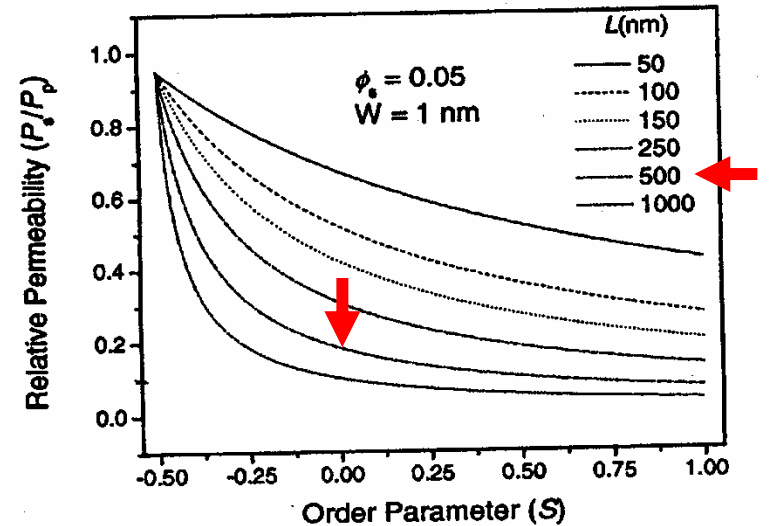
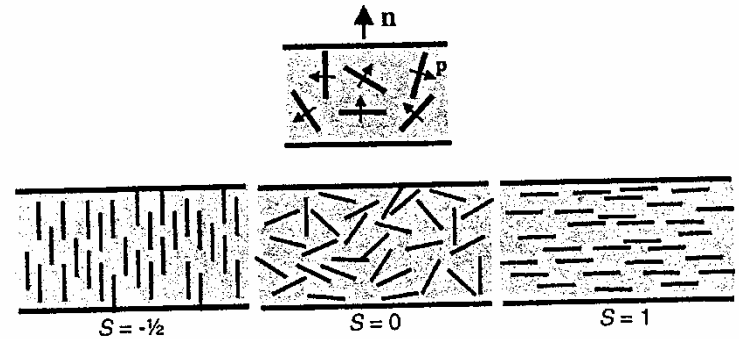
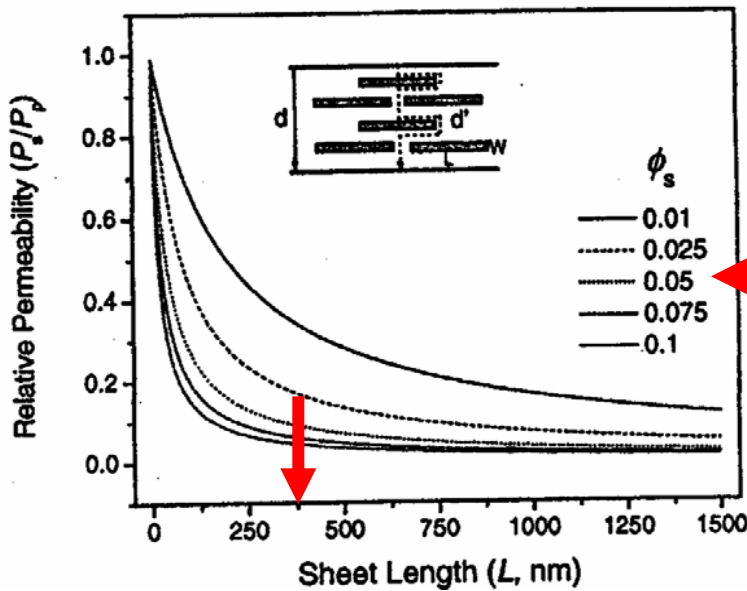


Tortuosity effect on gas permeability

$$P_s / P_p = 1 - \Phi_s / \tau$$

GRAPHENE-BASED NANOCOMPOSITES

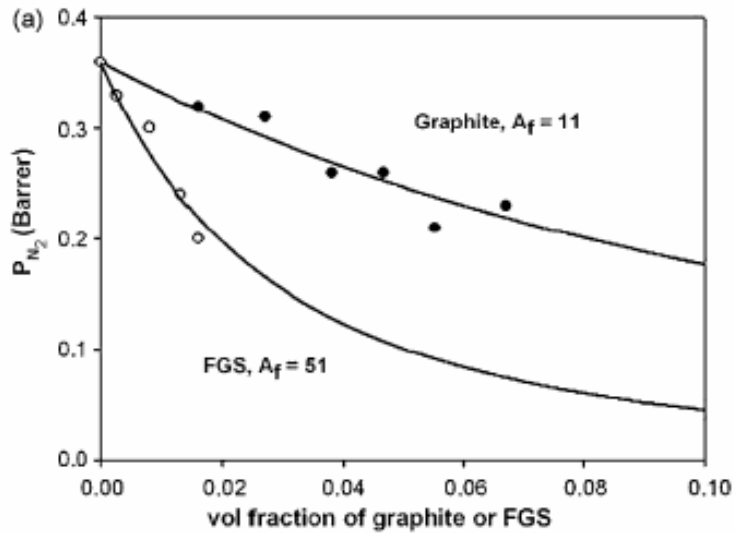
Gas Transport / Permeability



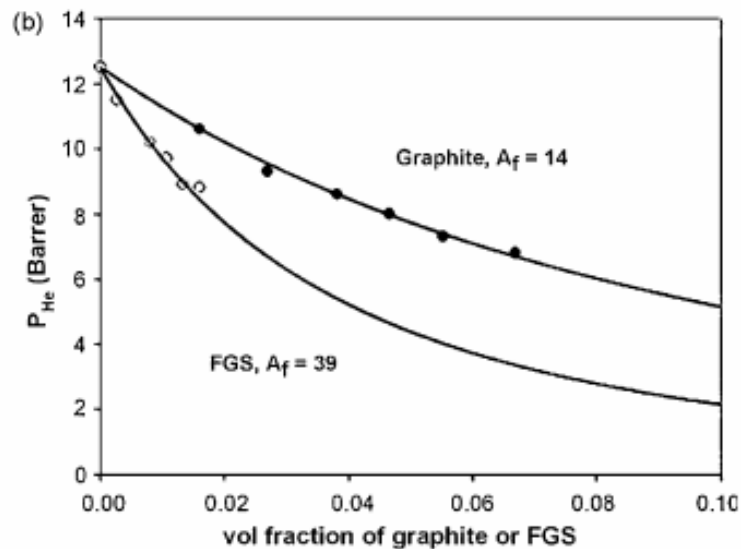
Strong dependence of gas barrier properties with processing conditions

GRAPHENE-BASED NANOCOMPOSITES

Gas Transport / Permeability



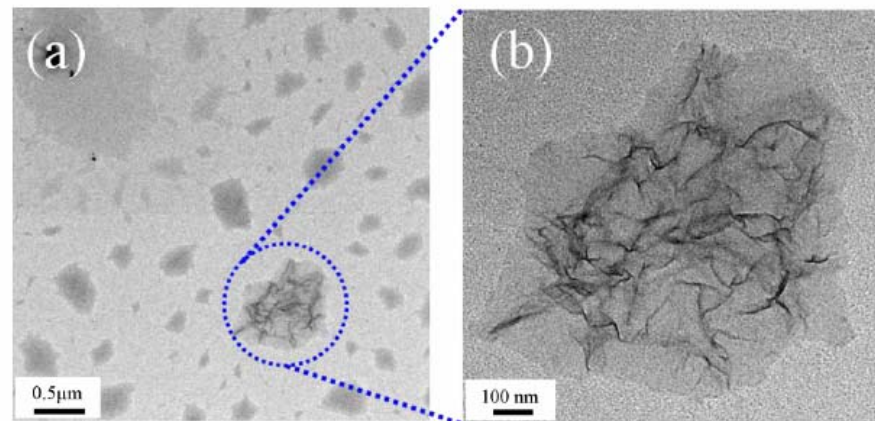
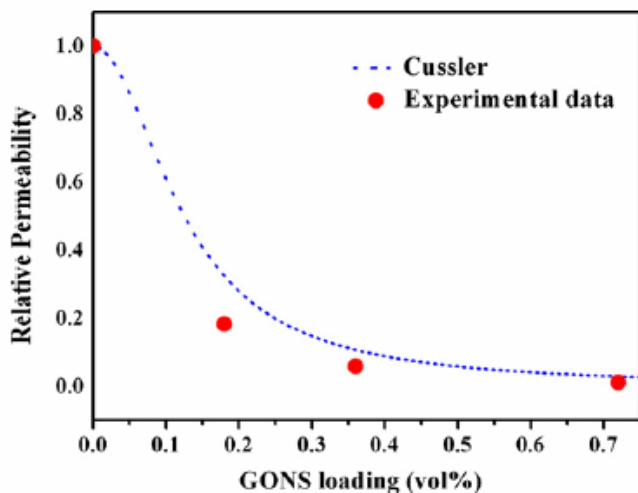
N_2 and He permeation
PC/graphite and PC/FGS
(functionalized graphite sheets)
nanocomposites composites
at 35 °C



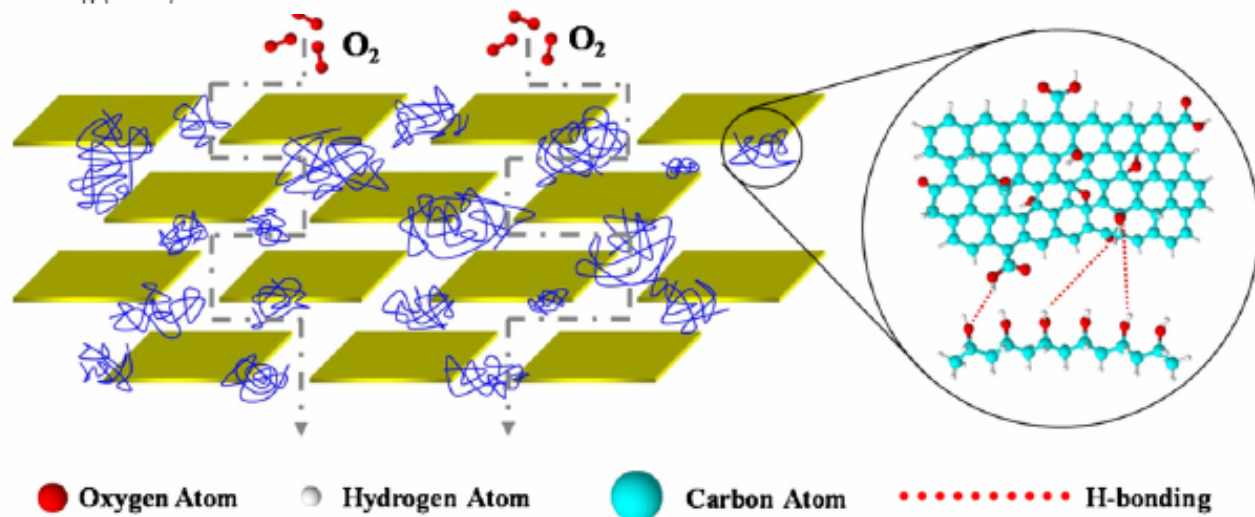
H. Kim & C.W. Macosko,
Polymer (2009)

GRAPHENE-BASED NANOCOMPOSITES

Gas Transport / Permeability



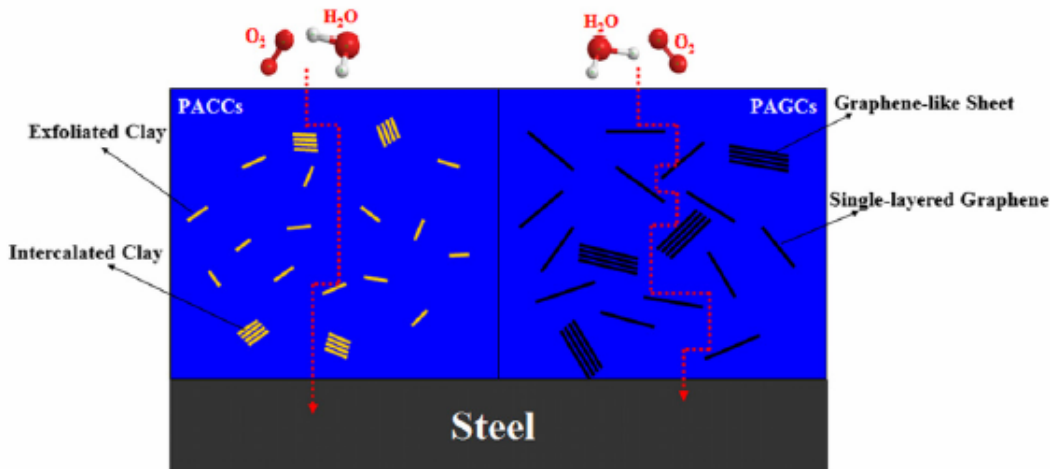
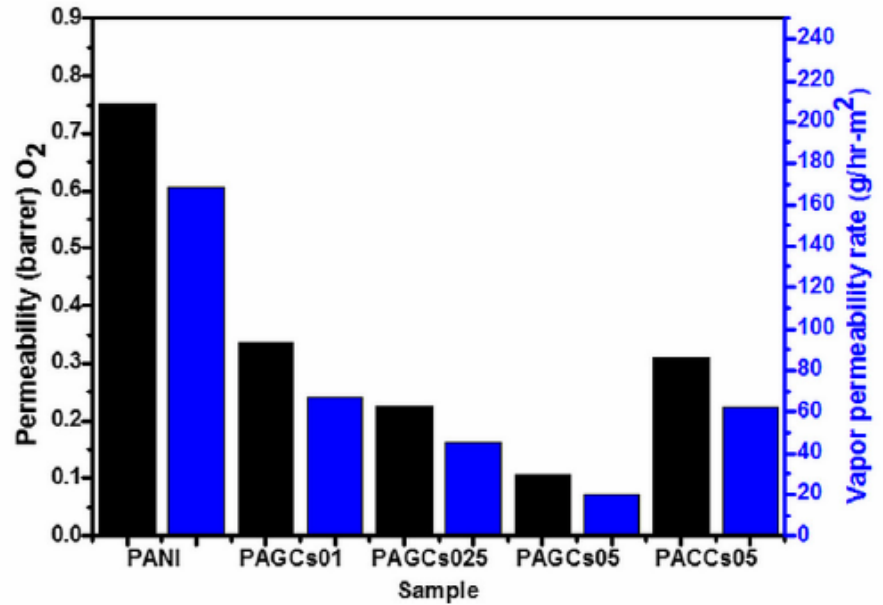
Tortuosity effect on gas path



GRAPHENE-BASED NANOCOMPOSITES

Gas Transport / Permeability

Polyaniline/graphene nanocomposites as protective coatings (anticorrosion)



. Chang et al, Carbon. (2012)



MAIN CONCLUSIONS



Graphene for nanocomposites

multifunctional nanofiller

electrical,
thermal,
mechanical,
gas barrier

acting from the same basic features as other nanofillers.

Graphene can provide a combination of the benefits achieved with layered silicates (gas permeation barrier and stiffness) and carbon nanotubes (electrical and thermal conductivity).