Comparison of Graphite and Graphene Precursors in HNBR

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Why is Graphene Important?

- Thinnest platy filler known
  - One fourth as thick as montmorillonite platelet
  - One eighth as thick as typical nanoclay (including bound organic layer)
- “Graphene is the strongest material ever measured” C. Lee, et al. *Science (2008)* ***321, 385-388.***
- Young’s modulus ~ 1000 Gpa
- Best conventional electrical conductor at RT.
- Thermal conductivity > 3,000 W/mK

Major Platy Filler Options

- Conventional, not possible to exfoliate:
  - Talc, mica, metal flake, graphite, un-modified clays
- Clearly capable of exfoliation:
  - Organocation-modified clay (nanoclay)
  - Graphene (produced by oxidation/reduction)
  - Fluorographite
- May be capable of exfoliation:
  - Expanded graphite
  - Expanded mica (vermiculite)

Why is Exfoliation Important?

- Nanoscale particulates better for reinforcement
- Very high D/t ratios decrease permeability
- Bending stiffness of platelet ~ $1/\text{thickness}^4$
- Lower bending stiffness means greater elongation
- High stiffness coupled with high elongation occur for very thin, flexible sheets

Platy Fillers Reduce Permeability

- Create a "tortuous path"
  - Increases the path length for diffusion
  - Must consider if an adhered film layer at the surface of the plates is a "superhighway" for some permeants
- Swelling increases permeability
  - Swelling reduces the volume fraction platy filler
  - Swelling increases diffusivity
  - Swelling may enable aggregation of platelets
- Used a low swelling solvent (trimethylpentane) to probe effect of platy fillers

Approximate Organic Cation Content for 2 Common Grades of Ion-exchanged Nanoclays

Nanoclay type	*Quaternary ion concentration*	*Weight % organic*	*Volume % organic**
Cloisite ™ 15A	1.25 mEq/gram	43%	65%
Cloisite ™ 30B	0.90 mEq/gram	30%	52%

(*Based on density of the clay platelets of 2.75 g/ml.)

Problems:

- Organic cationic layer is highly permeable to typical solvents and water
- Poor thermal stability for organo-cations

Comparison of Graphene to Nanoclay

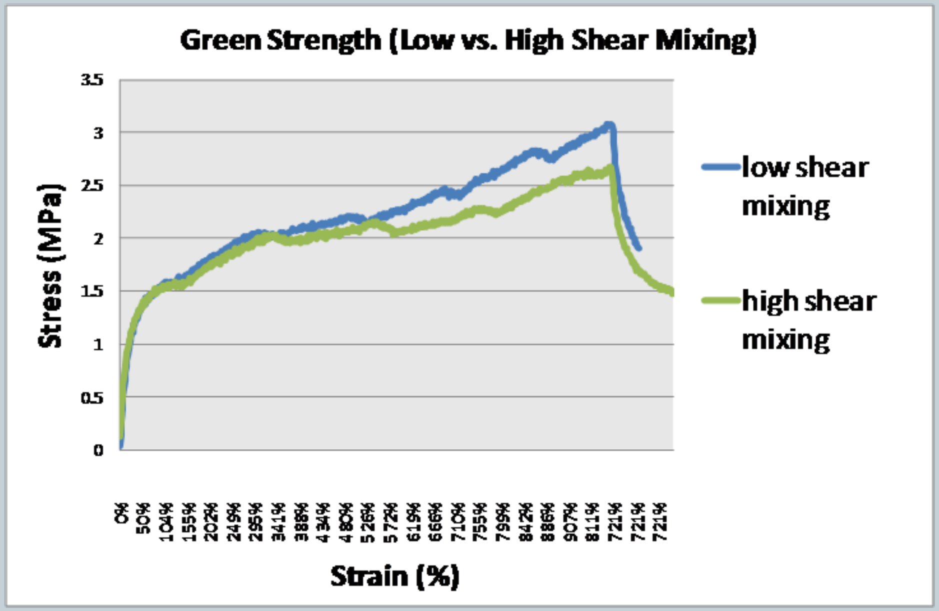
	Nanoclay	Graphene
Thickness of core particle	1 nm	.25 nm
Total thickness including ionically attached layer	2-3 nm	.25 nm
Electrical conductivity	semiconductor	very good conductor
Particles per cm^3, theoretical (based on D/t ratio =500)	$5x10^7$	$2.5x10^{10}$
Mechanical agitation effect	large	small
Effect on Moisture permeation (information from Navy SBIR)	small	big reduction

Table 1: Non-Curing Masterbatch Formulations Used in the Study

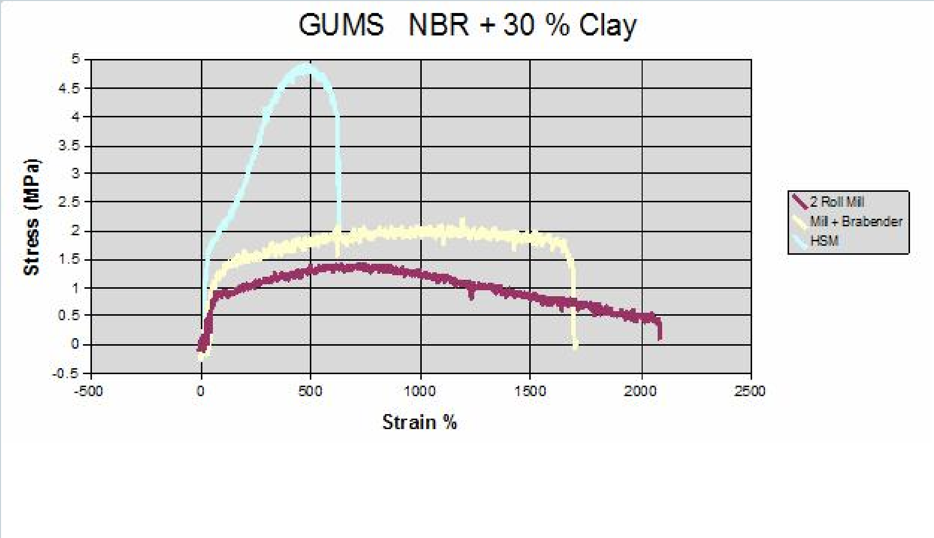
Masterbatch (First-Stage Mix) Recipe		
Ingredient	***Control***	***Graphite***
HNBR (Zetpol 2010)	100	100
antioxidant (Naugard 445)	2	2
N-550 carbon black	16.73	
Graphite (various types)		20.50
Total	**118.73**	**122.50**

Used in High Shear Experiments prior to adding Curative

Green Strength Effect of High Shear Mixing



HNBR + Expanded Graphite



NBR + Nanoclay

Table 2: Formulations for Final Stage Thermosetting Compounds

Ingredient	***Graphite***	***Control***
First stage graphite masterbatch	122.50	
First stage control (N-550) masterbatch		118.73
Peroxide (40% dicumyl peroxide)	8.00	8.00
Total parts	**130.50**	**126.73**

Graphite types and carbon black compared at equal volume fraction (7.6%) …(9.06% total filler)

Table 3: ODR Cure Differences due to High Shear Mixing Prior to adding Curatives

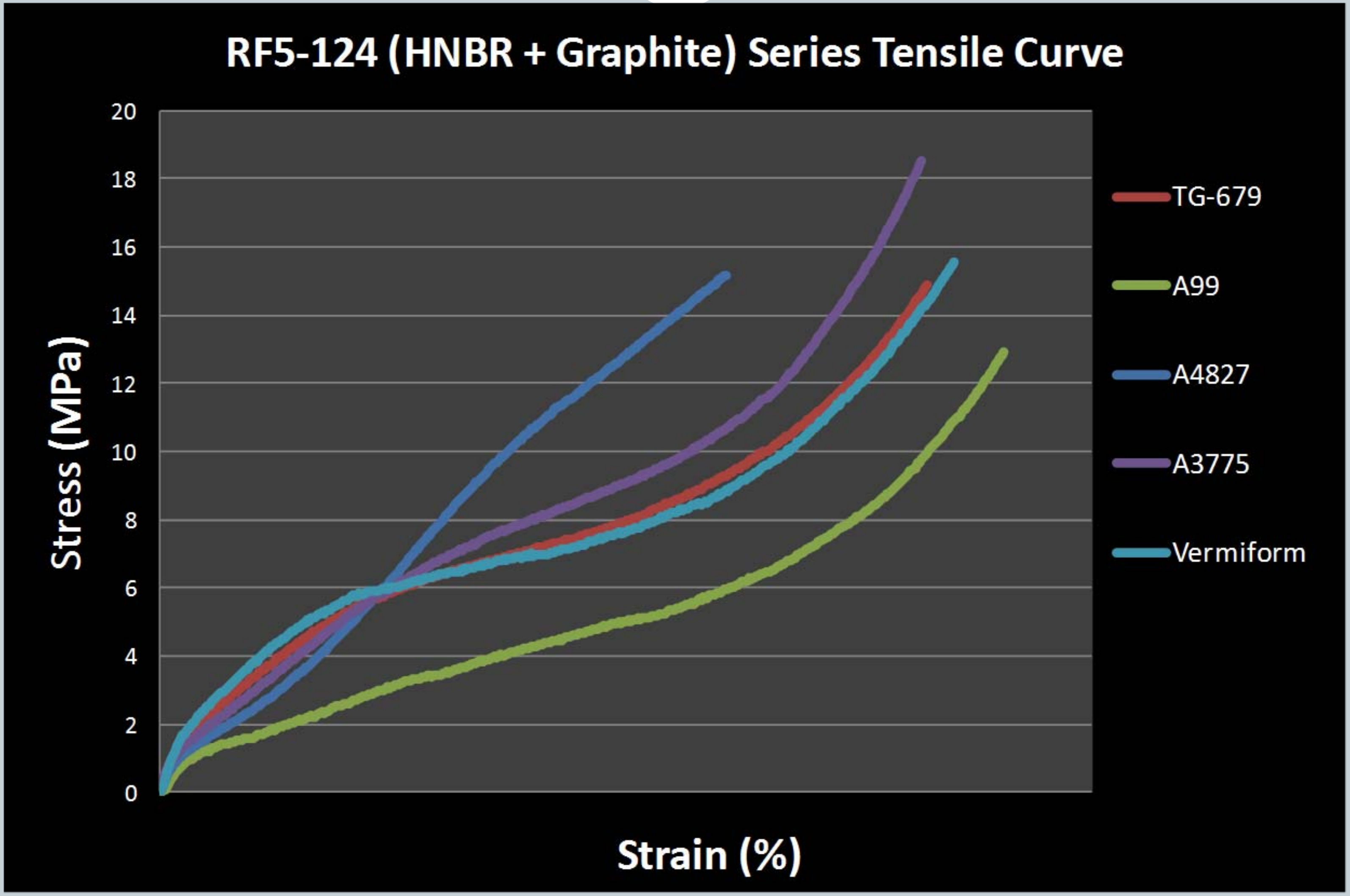
ODR parameter (177^o C, 3^o arc)	*Compound #6 (Brabender mix)*	*Compound #15 (High shear mixed)*
ML (dN-m)	13.6	10.2
MH (dN-m)	93.7	88.7
ts2 (minutes)	.77	.80
t'90 (minutes)	3.89	2.78

No evidence of increased surface area for graphite

Some polymer degradation has occurred due to high shear

In nanoclay, both ML and MH increase with high shear treatment

Tensile Overlay for Different Graphites



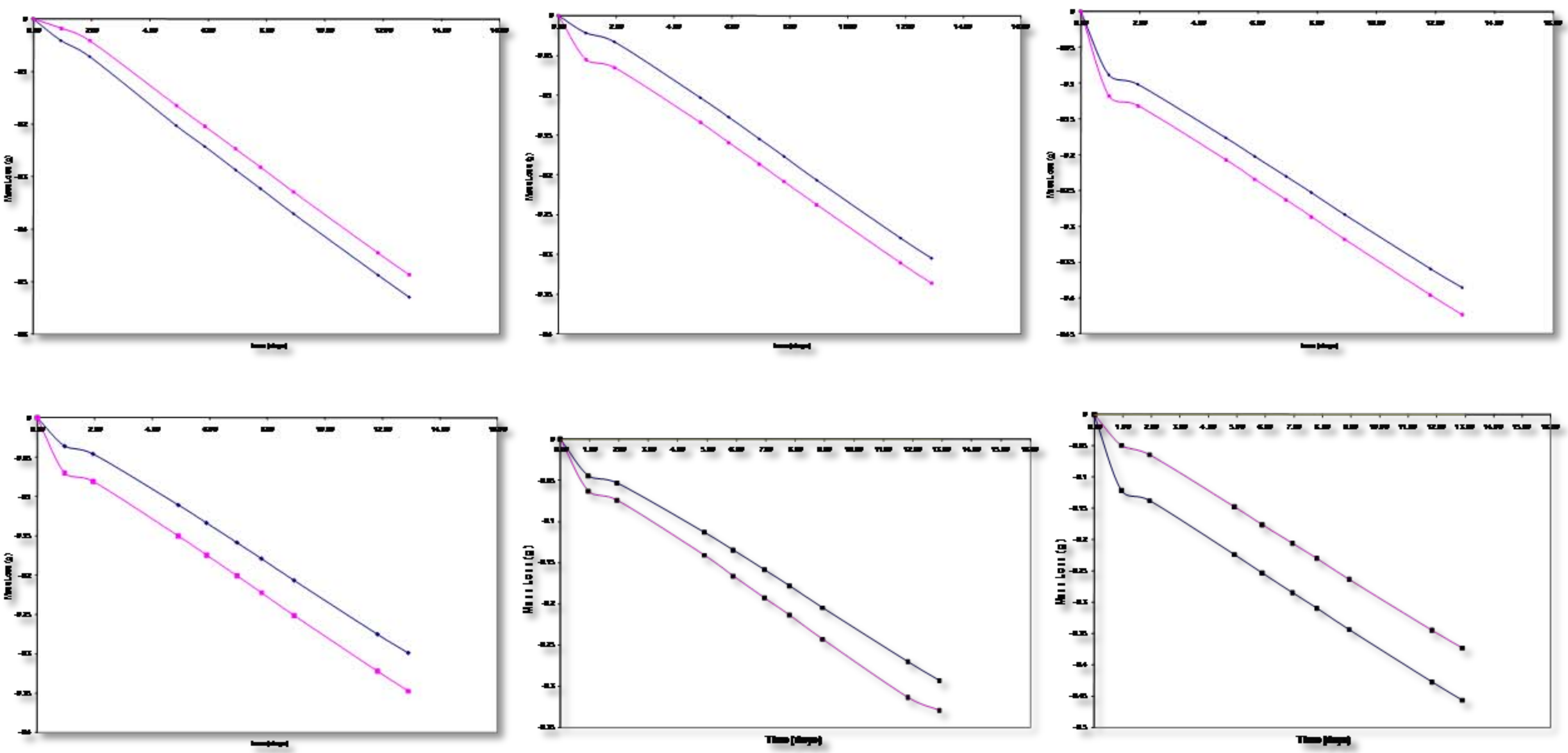
Highly Reproducible Permeation Tests

- Permeation tests were more reproducible than tensile tests!
- Permeation is a sensitive probe of the state of dispersion & delamination
- Choosing a low affinity, low swelling, high mobility solvent makes permeation into a very sensitive test to probe delamination

Permeation Results vs. Control

Graphite type:	vermiform	TG-679	A-3775 + high shear	A-3775	A-4827 micronized	Control N-550
Compound Number:	#124-1	#124-4	#124-15	#124-6	#124-3	#124-20
Relative permeability	0.436	0.453	0.503	0.519	0.578	1.000

Thumbnails of the raw permeation data:



Every single permeation result different at 95% confidence level
(color coded samples do not reach 99% conf. level as to being different)

Conclusions

- No evidence of exfoliation in HNBR-expanded graphite compounds with high mixing intensity
- Expanded graphite was significantly better than micronized graphite in resisting permeation
- Present grades of expanded graphite cause blistering at phr levels that are desirable for low permeability compounds
- There is a need for a grade of expanded graphite and/or masterbatches of expanded graphite that are optimized for elastomers