

COMPARISON OF GRAPHITE AND GRAPHENE PRECURSORS IN HNBR

By Roger W. Faulkner\*  
Kenneth J. Mumby  
Rethink Technologies, Inc.  
15 West Main Street  
Cambridge, NY 12816

Presented at the Fall 176th Technical Meeting of the  
Rubber Division, American Chemical Society  
Pittsburgh, PA  
October 13-15, 2009

ISSN: 1547-1977

\*Speaker: [roger\\_rethinker@yahoo.com](mailto:roger_rethinker@yahoo.com)

Website: [www.rethink-technologies.com](http://www.rethink-technologies.com)

## ABSTRACT

High shear mixing of expanded graphite produced a small but statistically significant reduction of permeability in HNBR at a shear rate of about 20,000 second<sup>-1</sup>, though the small reduction of permeability due to high shear mixing was less than the differences observed between different grades of graphite, and is not believed to indicate exfoliation to graphene. The research showed that high degrees of reinforcement and enhanced permeation resistance are seen with dispersions of expanded graphite compared to micronized graphite. The bulk density of expanded graphite as initially produced (“vermiform”) is extremely low, 0.004 g/cc in the sample used in this study. Vermiform expanded graphite was compared to four commercially available grades of graphite, including two commercially available grades of expanded graphite, at equal volume loading of graphite or carbon black (used in the control compound), in peroxide-cured HNBR. Permeation of an aliphatic permeant (trimethylpentane) was significantly lower for HNBR compounds containing all grades of graphite tested compared to N-550 carbon black. The expanded graphite grades produced significantly lower permeation than the micronized natural graphite, and the vermiform lab expanded graphite produced the lowest permeation rate of any of the fillers tested. Blistering is observed in HNBR, IIR, BIIR, and ethylene/octene copolymer elastomers when high levels of expanded graphite are used as a filler.

## INTRODUCTION

Expanded graphite has been used extensively in making flexible graphite sheets for gaskets since it was patented in 1915<sup>1</sup>, but it has not been used much in rubber until recently. Recent work has shown that graphite can be exfoliated all the way down to graphene (single molecular sheets of graphite, less than a nanometer thick) via wet chemistry<sup>2</sup>, where oxidation to graphite oxide leads to dispersed platelets that are only one atom thick, which may then be reduced back to graphene. Graphite exfoliation has also been shown to occur without oxidation of the graphite in dilute dispersions of expanded graphite in N-methylpyrrolidone<sup>3</sup>. Graphite exfoliation is also believed to occur in the production of fluorographite<sup>4</sup>, which has been shown to be useful in FFKM elastomer<sup>5</sup>; exfoliation of graphite during production of fluorographite is believed to occur because fluorination causes the graphite sheet to buckle, which is similar to what occurs during production of graphite oxide, but the fluorination is not readily reversible.

Laboratory bulk exfoliation of graphite typically starts from a previously expanded grade of graphite. This study examines whether expanded graphite per se can be exfoliated or partially exfoliated to graphene in high shear rate/shear stress polymer mixing equipment, similar to what has been shown to work for partial exfoliation of montmorillonite-based, organo-modified nanoclay<sup>6</sup>, and possibly also for mica in polypropylene composites<sup>7</sup>. This effort to mechanically exfoliate expanded graphite to graphene was not successful in HNBR at a shear rate of about 20,000 second<sup>-1</sup>, though the research did show that high degrees of reinforcement and enhanced permeation resistance are seen with dispersions of expanded graphite (also known as “graphite nanoplatelets”<sup>8</sup>).

When graphite is expanded, it is usually treated with concentrated sulfuric acid plus a small amount of an oxidizer (usually nitric acid), then after the acid intercalates between the graphite planes, the intercalated graphite is rapidly heated to ~850° C, whereupon the graphite expands rather like an accordion, as byproduct gases are released. The initially flat pieces of acid-treated graphite expand to many times their initial volume, and the expanded graphite looks like

worms; in fact the expanded graphite is described as "vermiform," which means "worm-like." The expansion process fails if the intercalated graphite flakes are too small; apparently in this case the gas escapes out the edges of the intercalated graphite layers rather than blowing the planes apart into the expanded form. It is possible that the expansion of intercalated graphite at 850° C involves reduction of the previously oxidized graphite; if so, the graphite expansion process is fundamentally similar to the oxidation/reduction of graphite in solution, which is one of the recognized routes to producing bulk graphene from graphite. It therefore seems reasonable to consider whether expanded graphite may contain graphene. The experiments we have performed so far cannot answer this question.

The bulk density of vermiform expanded graphite is extremely low; in the laboratory expanded sample we used, the bulk density (as received from Asbury Graphite Mills, where the laboratory expansion was performed) was 0.004 g/cc, comparable to aerogel. Because of the extremely low bulk density of vermiform expanded graphite, it has rarely if ever been used before in polymer dispersions. Vermiform expanded graphite was compared to four commercially available grades of graphite, including two commercially available grades of expanded graphite, at equal volume loading of graphite or carbon black (used in the control compound), in HNBR. One of the commercially available expanded grades, Asbury Graphite Grade 3775 (A-3775) by Asbury Graphite Mills, Inc., is made by compacting fully expanded graphite, which is then ground back into a powder. The other grade, TG 679 (by GrafTech International) is made by a different method; it is based on partially expanded graphite, with lower than normal levels of initial intercalation<sup>9</sup>. TG-679 graphite is not believed to have been compacted after expansion before packaging. There are also new grades of expanded graphite that have been expanded via microwaves<sup>10</sup>

This paper compares non-compacted vermiform fully expanded graphite (derived from acid-treated Asbury Grade 3721, expanded 30 seconds at 850° C) to the two previously mentioned expanded grades. To round out the comparison, data on a micronized high surface area synthetic graphite, Asbury Grade 4827, and a typical rubber-grade synthetic graphite, Asbury Grade A99 are also given. Permeation of an aliphatic permeant (2,2,4- trimethylpentane) was significantly lower for HNBR compounds containing all grades of graphite tested compared to N-550 carbon black. The exfoliated graphite grades produced significantly lower permeation than the micronized natural graphite, and the vermiform lab expanded graphite produced the lowest permeation rate of any of the fillers tested.

Graphene (completely exfoliated graphite, comprising independent carbon sheets that are one atom thick) is a very hot research topic right now. Like nanoclay, graphene has high potential as a component of polymeric nanocomposites designed for enhanced permeation resistance. Graphene is a pure planar crystalline flake, only one atom thick (about .25 nm), whereas exfoliated organo-modified montmorillonite clay (the most common type of nanoclay) has a crystalline inorganic core that is several atoms thick (about one nanometer), but the complete platelet in the case of organo-cation substituted montmorillonite nanoclays is about twice as thick as the inorganic core if one considers the ionically bound organic cation layer (quaternary ammonium cations normally) that is attached to each side of the platelet. In the case of nanoclays, this bound cationic organic layer can greatly increase permeation of both organic molecules and water parallel to the surface of the modified clay platelet, since both water and hydrocarbons are very soluble and mobile in the organo-cationic layer. In this case, the many small clay platelets reduce permeability by creating a tortuous diffusion path as expected, but the high permeability

surface film on each platelet counteracts this effect somewhat, by forming a virtual “superhighway” for compatible permeants right at the surface of the platelets. By comparison, there is no well-defined highly permeable organic layer attached to the surface of graphene platelets to serve as a superhighway to speed diffusion of permeants around the graphene platelets. This, and the lower thickness of graphene compared to exfoliated clay imply that graphene should theoretically be much better at reducing permeability than exfoliated nanoclay.

It is interesting to note that virtually all graphene synthesis methodologies start with expanded graphite, yet there has not been much new research specifically focused on optimizing (or even studying) expanded graphite per se for polymer composite applications. I believe that incremental improvements in how expanded graphite is made and handled could result in significantly improved polymer formulations, though perhaps not achieving the phenomenal improvements in permeation and physical properties that are theoretically possible for graphene.

Rethink Technologies, Inc. (Rethink) first studied expanded graphite in elastomer composites for enhanced water permeation resistance, as one line of inquiry in a Navy SBIR (N08-042) that was aimed at developing elastomers with enhanced sea water permeation resistance. We filed a patent out of that work, which showed that expanded graphite improves water barrier performance of butyl rubber significantly more than the other platy fillers studied (Cloisite™ nanoclay, talc, and mica, including silanized grades of talc and mica). In this paper, we show that the patent pending formulations of expanded graphite and elastomers also produce lower fuel permeation, which has obvious applications

Rethink possesses proprietary equipment that is capable of applying very high shear stress and very high shear rate to polymer formulations. This process is effective for partial delamination of nanoclay, as we showed in a previous ACS Rubber Division paper<sup>6</sup>. That previous paper explored various correlations between mechanical and viscoelastic properties and exfoliation; green strength had the best correlation with the extent of exfoliation of nanoclay among the (easy to measure) properties we studied. It was decided to apply the high shear method to HNBR/graphite composites to see if we could exfoliate expanded graphite enough to see differences in green strength and/or permeability. In this case, a portion of the HNBR/graphite/antioxidant mixture prepared in the large Brabender internal mixer (not yet containing peroxide) was put through a proprietary high shear mixing process. Green strength of uncured samples of #124-6 and #124-15 was determined for these two compositionally identical samples, which differ only in terms of shear history.

## **EXPERIMENTAL PROCEDURES**

The samples were all mixed in a Brabender internal mixer, where the non-reactive powders (antioxidant, graphite, carbon black) were added to the HNBR. The curative (DCP-40) was added on a two roll rubber mill after all other powders had been incorporated in the internal mixer. It was quite difficult to incorporate the vermiform expanded graphite; as a result this was the only sample made in the small Brabender mixer (60 cc nominal volume, roller blades were used). Two batches of the vermiform graphite/HNBR compound #124-1 were made to get enough sample to do the tests (barely), and each of these mixes took about an hour. All the other samples were mixed once in the larger Brabender mixer (the Prep Center Mixer, with Banbury blades). Temperature in the mixer was kept below 100 C during all mixes, which were done at low speeds

(26-60 RPM). Compared to shear rate and shear stress imposed on the samples during milling, the internal mixer treatment was quite mild.

High shear mixing was applied to non-curing masterbatch MB12 (see Table 1). MB12 contains one of the commercially available grades of expanded graphite (Asbury A-3775) which was first produced in the Brabender, then high shear mixed in a proprietary lab machine that is similar to that used in the previous work with nanoclay/NBR composites.

Cure testing was done in a Monsanto R100S oscillating disc rheometer (ODR) with 3 degrees of arc at 182.2° Celsius (360° F). Mechanical testing was performed by the relevant ASTM standards (these are cited in the various tables giving results herein). Green strength was also measured for two particular compounds, #124-6 and #124-15 which are identical except for their shear history. In this case, a portion of the HNBR/graphite/antioxidant mixture prepared in the large internal mixer (not yet containing peroxide) was put through a proprietary high shear mixing process. The green strength of uncured samples of #124-6 and #124-15 was determined for these two compounds after peroxide incorporation on the mill.

A tendency towards blistering has been noticed for all samples of expanded graphite studied so far. In a prior Navy SBIR research effort (N08-042), severe blistering of compounds containing high levels of expanded graphite was observed in polyisobutylene and ethylene-octene copolymer elastomers (Engage from Dow). The present study used relatively low levels of graphite to avoid this problem, which is believed to be due to adsorbed gases on the expanded graphite surfaces. There is a market need for a grade of expanded graphite that does not cause blistering, because for highly permeation resistant formulations, it is highly desired to use much higher expanded graphite loadings (25-35% volume %) than can be created using present mixing methodology and current grades of expanded graphite.

Permeability was measured by the cup method (SAE J2655, Test Procedure to Measure the Fuel Permeability of Materials by the Cup Weight Loss Method) at 40° Celsius. The permeant was 2,2,4-trimethylpentane, selected to give rapid, reproducible results. This portion of the lab work was contracted out to TRI/Environmental, Inc. of Austin Texas, and was paid for by Asbury Graphite Mills. TRI gave us excellent data that was reproducible enough to allow statistically significant differences to be detected between compounds that only varied by about 2% in permeability (see notes at the bottom of Table 2).

## **RESULTS AND DISCUSSION**

Table 1 shows the formulations and properties of the compounds prepared in this study. The focus of this study is the effect of the graphite grades on permeability, but the exceptional tear strength of the compound (#124-1) derived from vermiform expanded graphite is also noteworthy. All compounds have the same 7.6% volume fraction filler (graphite or carbon black); in realistic low permeability compounds, significantly higher graphite levels are desirable; this low level was used in the present study because of the tendency of HNBR compounds with higher expanded graphite levels to blister, and also somewhat because of the difficulty of adding the extremely fluffy vermiform graphite to compound #124-1 (it took an hour to incorporate 20.5 phr).

Two of the graphite grades tested, the vermiform graphite in compound #124-1, and the standard rubber grade synthetic graphite A-99 inhibited the peroxide cure to a significant extent. It is possible that the high tear strength of compound #124-1 could be due to lower crosslink

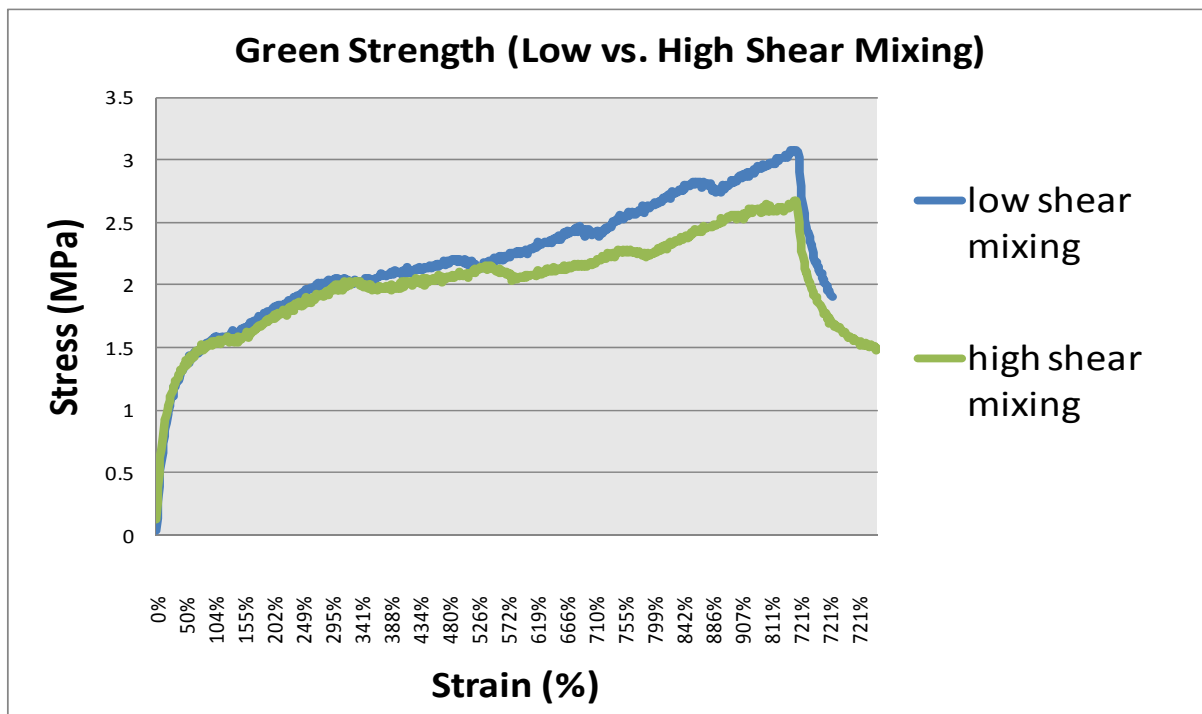
density compared to compounds 3, 4, and 5, though that fails to explain the higher durometer and low-strain modulus, and lower permeability of compound #124-1. I believe it is likely that the high modulus, high tear strength and low permeability of compound #124-1 (based on vermiform graphite) indicate that this material had the highest ration of D/t of any of the samples tested.

**Table 1: Formulations and Properties for HNBR/Graphite Compounds**

*high shear mix									
INGREDIENT:	-1	-2	-3	-4	-5	-6	-MB12	-15	-20
PHR Basis Recipes:									
Zetpol 2010 HNBR, ACN 36%, 4% unsatd.	100.00	100.00	100.00	100.00	100.00	100.00	100.00	-	100.00
RF5-124-MB12	-	-	-	-	-	-	-	122.50	-
N-550	-	-	-	-	-	-	-	-	16.73
A-99 Graphite (Asbury Graphite)	-	-	-	-	20.50	-	-	-	-
Asbury graphite 3721 (expanded graphite)	20.50	-	-	-	-	-	-	-	-
Asbury graphite 3772 (expandable; contains acid)	-	20.50	-	-	-	-	-	-	-
Asbury graphite 3775 (expanded, compacted, ground)	-	-	-	-	-	20.50	20.50	-	-
Asbury graphite 4827 (micronized natural graphite)	-	-	20.50	-	-	-	-	-	-
GrafTech TG-679, expanded and ground graphite	-	-	-	20.50	-	-	-	-	-
Naugard 445	2.00	2.00	2.00	2.00	2.00	2.00	2.00	-	2.00
TAIC, (Tri-Link 7, Lianda Corp. liquid)	-	-	-	-	-	-	-	-	-
Perkadox DCP-40-BP-pd	8.00	8.00	8.00	8.00	8.00	8.00	-	8.00	8.00
Total grams, 100 g polymer basis:	130.50	130.50	130.50	130.50	130.50	130.50	122.50	130.50	126.73
Total volume (cc), 100 g polymer basis:	121.18	121.18	121.18	121.18	121.57	121.18	116.21	121.19	121.18
Specific gravity:	1.077	1.077	1.077	1.077	1.073	1.077	1.054	1.077	1.046
ODR 182.2 °C (360 °F), 3° arc, 12 minute test	-1	-2	-3	-4	-5	-6	-MB12	-15	-20
ML (min. torque, N*m)	0.90		1.62	1.24	1.27	1.36		1.02	1.19
MH (max torque, N*m)	7.46		9.14	8.98	8.97	9.37		8.87	8.59
TS2 (minutes)			0.87	0.78	0.96	0.77		0.80	1.00
TC90 (minutes)			3.98	4.20	5.09	3.89		2.78	4.50
Physical Properties	lab book # RF5-124								
cured 10/177C + 16hour/180 C	-1	-2	-3	-4	-5	-6	-MB12	-15	-20
Shore A durometer (press cure only)	68	65	64	66	57	65			68
Average Tensile Strength ASTM D412C: (Mpa)	15.24	13.15	15.29	14.91	13.57	16.87			25.62
Average Elongation %:	649%	668%	456%	619%	650%	575%			603%
Stress at 25% elongation (MPa):	1.98	1.49	1.30	1.79	0.91	1.48			0.74
Stress at 50% elongation (MPa):	2.92	1.98	1.81	2.64	1.34	2.18			1.08
Stress at 50% elongation (MPa):	4.44	2.61	2.97	4.09	1.83	3.62			1.33
Tensile Energy to break (joule/cc) (Rethink method)	43.0	28.2	36.7	43.6	29.1	43.3			43.4
Tear Strength, (kN/m) ASTM D624C	36.4	27.1	25.4	29.1	19.8	26.3			19.4

Both green strength testing (Figure 1) and permeation results (Table 2) show that high shear mixing had only a small effect on delamination/exfoliation of the graphite. Apparently high shear mixing, while effective for partial delamination of nanoclay, was not effective for taking expanded graphite to graphene.

**Figure 1: Green Strength Behavior Before & After High Shear Mixing**



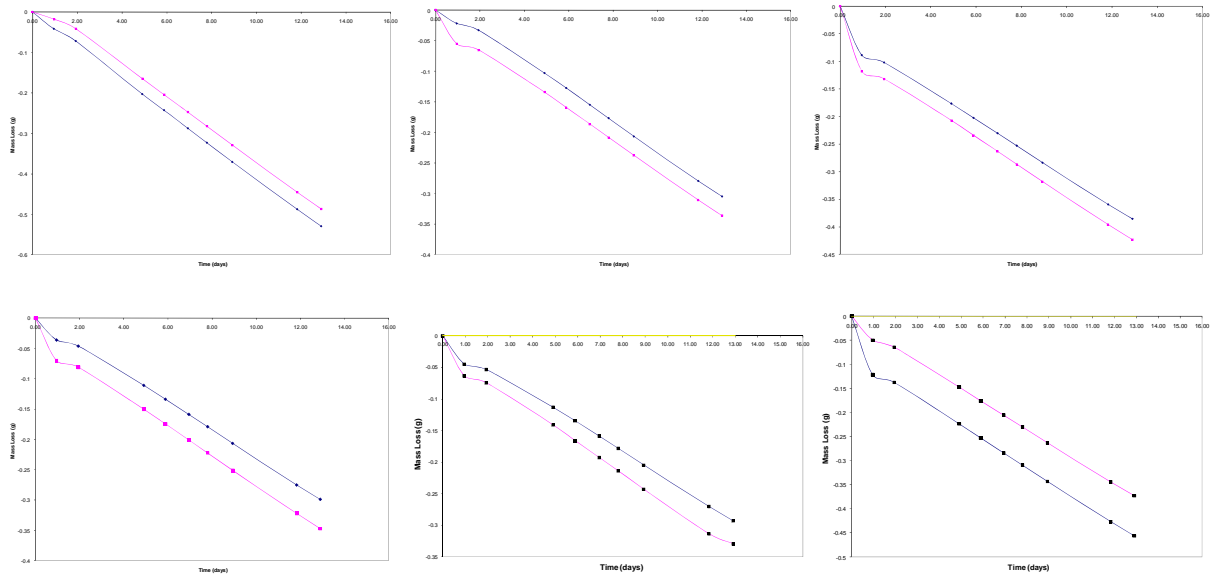
There was a small reduction in green strength due to high shear mixing, probably because the HNBR was somewhat degraded by the high shear treatment, as can also be seen from the ODR cure torques for compound #124-15 versus #124-6 (Table 1). The high-shear mixed compound #124-15 was noticeably tackier during milling than the low-shear mixed version #124-6, which was probably due to some thermo-oxidative chain cleavage of the HNBR during the high shear mixing. Permeability is not expected to be affected much by modest chain scission. The high shear-mixed sample was also tested for permeability (where it proved to have slightly less permeability than the low-shear mixed sample). The small degree of reduction of permeability seen for high shear mixed compound #124-15 is not indicative of any significant exfoliation to graphene, but may indicate some delamination has occurred.

Bigger differences were seen between the three different grades of exfoliated graphite we tested compared to the effect of high shear mixing. Table 2 shows permeation results for six of the compounds of Table 1. Expanded graphite was significantly better at slowing permeation than the micronized graphite. Among the three grades of expanded graphite tested, the two grades that were not compacted after expansion produced the lowest permeability; this likely indicates that some irreversible loss of polymer-accessible surface area occurs during compaction of expanded graphite. It now appears that there is a substantial opportunity to develop special grades and/or dispersions of expanded graphite that are specifically tailored to nanocomposites, including composites in both rubber and plastics.

**Table 2: Permeation Results through HNBR/Graphite Compounds**

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:



The permeant was 2,2,4- trimethylpentane, selected to give rapid, reproducible results, because:

- it is a single pure component (except for optical isomers, which permeate at the same rate),
- it is insensitive to humidity,
- it is a weak swellant for HNBR, yet soluble & permeable enough to get good data within a week or so (~200-400 mg weight loss per day).

The calculated least significant difference at 95% confidence (Student t test) is .013 of the control compound permeability; at this confidence level each of the above six permeation results is significantly different from both neighbors. If the confidence level is increased to 99%, then the least significant difference is .022 of the control compound permeability, and the vermiform expanded graphite is not significantly better than TG-679 (shown above by shading these two results yellow). Similarly, at 99% confidence the effect of high shear mixing of the A-3775 grade of expanded graphite (#124-15 versus #124-6) on permeation is not statistically significant.

## CONCLUSIONS

- The permeability of graphite in HNBR/expanded graphite composites decreases only a little with the intensity of mixing up to 20,000 radians per second (different from the observed behavior of nanoclay in NBR).
- There is no evidence for mechanical production of graphene in situ during intensive mixing of expanded graphite with HNBR.
- All types of graphite produced much lower permeability than N-550 carbon black in HNBR.
- Expanded graphite produced consistently lower permeability than micronized synthetic graphite.
- The samples of expanded graphite which had not been compacted prior to incorporation into the elastomer produced lower permeability.
- The lowest permeability was observed for vermiform expanded graphite with bulk density of .004 g/cc.
- The expanded graphite samples all had a tendency to cause blistering.

## ACKNOWLEDGEMENT

The authors wish to thank Albert Tamashauski of Asbury Graphite mills for his help on this paper. Albert provided the sample of vermiform expanded graphite used in our study, and also much appreciated help to understand the technology of expanded graphite. We also wish to thank Asbury Graphite Mills for paying for outside permeation testing by TRI/Environmental, Inc. Rick Thomas, Principal Scientist at TRI/Environmental, Inc. went beyond the call of duty to help refine the measurements.

---

<sup>1</sup> Jonas Aylesworth, US Patent 1137373: "Expanded Graphite and Composition Thereof," April 27, 1915

<sup>2</sup> Dan Li and Marc B. Mueller et al, "Processable aqueous dispersions of graphene nanosheets," *Nature Nanotechnology* **3**, 101-105 (2008)

<sup>3</sup> Hernandez et al, "High yield production of graphene by liquid phase exfoliation of graphite," *Nature Nanotechnology* **3**, 563-568 (2008)

<sup>4</sup> Meshri, et al; US patent 3,929,918 (12/30/1975), describes synthesis of fluorographite

<sup>5</sup> Amin, et al; US patent 5,444,116 (8/22/1995), describes use of fluorographite in FFKM

<sup>6</sup> Roger Faulkner, Carl McAfee, and James Reilly, "Partially Exfoliated Nanoclay/NBR Composites," ACS Rubber Division paper #30, 170<sup>th</sup> Technical Meeting, October 10-13 2004; **ISSN: 1547-1977**

<sup>7</sup> Ray Woodhams, US patent 4,442,243 (04/10/1984), describes partially exfoliated polypropylene/mica composites

<sup>8</sup> Kim, S, Drzal, LT (2009) Multifunctional Exfoliated Graphite Nanoplatelets-LLDPE Nanocomposites Fabricated By Solution Compounding Method And Various Screw Rotating Systems, *Composites Science and Technology*

<sup>9</sup> Gilbert et al, US Patent Application 2004/0000735 (1/1/2004), by assigned to GrafTech, Inc. (now abandoned).

<sup>10</sup> Larry Drzal, United States Patent 7,550,529 (June 23, 2009) Expanded graphite and products produced therefrom