Graphene as an additive to rubber compounds and products

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Graphene, which was invented in 2004, is a single layer of carbon atoms (C-C distance of 0.142 nm) with a hexagonal closed packed structure.1 It is an ultrathin, mechanically strong, transparent and flexible conducting material.

The hexagonal lattice structure of isolated, single-layer plates of graphene can be seen directly with transmission electron microscopy (TEM) of sheets of graphene suspended between bars of a metallic grid.2 Some of these images showed a “rippling” of the flat sheet, with amplitude of about one to three nanometers. Graphene has a theoretical specific surface area (SSA) of 2,500 to 2,700 m²/g. This is much larger than for carbon black (typically smaller than 900 m²/g) or for carbon nanotubes (CNTs). With sheet thickness of less than one nanometer, diameters can be over one micron, graphene is thus much greater than that observed with other rubber nanocomposites, such as those containing clays. There are essentially three forms of graphene: 1) graphene oxide (GO); 2) reduced graphene oxide; and 3) pure graphene (Fig. 1).

Pure graphene, or as sometimes referred to as pristine graphene, when exfoliated into monolayer sheets will be of an inert condition. For example there is no chemical functionality, such as carboxylic acid, ketone, aldehyde or hydroxyl groups on the graphene plate surface or plate edges observed in other graphene oxide derivatives (Fig. 1).

Graphene also may have defects that might disrupt some properties, and examples of such defects have been illustrated in Fig. 2. Graphene in polymer or rubber nanocomposites has been reported to have many unique properties such as antioxidant characteristics, reductions in permeability, thermal conductivity, electrical conductivity and reduction in permeability.1,3 Abrasion resistance of rubber nanocomposites also is noted, suggesting better tire wear.4 In addition, improvement in hysteresis as measured by the loss modulus divided by the storage modulus or tangent delta also has been reported. In this instance such improvements can be all improvements or reductions in whole tire rolling resistance with no loss in traction qualities.4 Many of the reported properties of graphene in rubber nanocomposites have immediate relevance in improving the performance of truck tires. The tread compound of commercial truck tires—those with a steel cord ply, typically found on heavy-duty trucks of gross vehicle weights greater than 30 tons—have an on-going need for improvements in:

• Tread wear and resistance to irregular wear;
• Tread damage resistance or chip/chunk cut resistance;
• Lower hysteresis but improved compound storage modulus (G’, E’), which influences tire rolling resistance; and
• Traction.

These parameters are largely controlled by compound abrasion resistance and tensile strength, tear strength, adhesion of the tread to adjacent compounds in the tire, and hysteresis. These fundamental performance requirements have influenced both tire tread design and the selection of rubber polymers used in compounds. For example, natural rubber is largely used over all other rubbers due to its tensile strength and low hysteresis. This in turn resulted in use of solid shoulder to mitigate compound fatigue losses.8 In all natural rubber compounds, a trade-off will be contin- ed on the type of graphene, the composition and form, graphene in a natural rubber composite may have an effect on all of these fundamental compound properties. In further viewing literature reports of rubber nanocomposites applications, the modern radial tire was in many respects made possible through the introduction and use of halobutyl rubber innerliners. Use of the polymers such as bromobutyl in the innerliner compound enabled improvements in tire performance, significant improvements in liner-to-tire casing adhesion and improvements in tire durability.6

This second generation technology represented a major advance over the use of first-generation liner technologies using regular butyl rubber found in tubes and liners of bias tires and early radial tire constructions. Since the introduction of halobutyl rubber, there has been no significant advancement in the composition of innerliner formulas used in the industry. Some of this might be due to the tolerances in properties that innerliner compounds must meet. For example, small increases in liner compound 300 percent modulus could lead to reduction in fatigue resistance and cracks with consequent loss in tire durability. In this context, the industry has therefore focused on five strategic areas for development of new innerliner technologies:

1. Tire constructions: Examples would be non-pneumatic structures such as the polyurethane tire, or self-supporting structures such as the Michelin ‘Tweed’.5

2. Compounding: Use of general purpose elastomers or specific purpose elastomers in place of halobutyl rubber, combined with other types of reinforcing fillers such as medium thermal carbon blacks, have been studied.3

3. Stoving: Application of butyl rubber coating inside the tire that may serve as an air barrier has been explored.

4. Films: Dynamically vulcanized alloys (DVA) are being introduced as liners and are highly effective at maintaining air pres-
The authors

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He is the originator of a broad range of patents in tire and rubber technology and many industry publications, including editor of Rubber Compounding, Chemistry and Applications, along with Tire Engineering, both published by CRC Press.

Rodgers has a doctorate in chemical engineering from the Queen’s University of Belfast in Northern Ireland, where he studied thermodynamics, heat transfer through large rubber sections and vulcanization kinetics. He has a master’s degree in polymer technology, also from Queen’s University, and a bachelor’s in biological chemistry from the University of Ulster.

Adal Hałasa is from Jordan and came to the U.S. to study at the University of Oklahoma, where he obtained his bachelor’s degree in chemistry. He obtained a master’s from Butler University and then earned his doctorate from Purdue University.

He joined Firestone Tire & Rubber Co. where he had roles as a group leader, research associate and senior research associate. He also played a strategic role in the development of the Duradene solution polymers, which Firestone still produces today.

Hałasa then became director of materials and petrochemicals at the Kuwait Institute of Science and Research, where he also established the polymer program at Kuwait University. On returning to the U.S., Hałasa joined Goodyear as a research and development fellow, developing new technologies in the field of anionic polymerization. Since 2009, he has been an adjunct professor at the University of Akron.

He is a contributing author to more than 150 technical publications and possesses 335 U.S. patents. He is a member of the New York Academy of Sciences, the American Association for the Advancement of Science and the American Chemical Society. He is recognized as a Purdue University Distinguished Alumni and is the recipient of the Charles Goodyear Medal, presented by the ACS Rubber Division.

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Douglas Paschall is the president of Akron Polymer Solutions. He studied at the University of Southern California and started his career in polymer science working for a small California firm that specialized in coatings and insulation materials. He returned to the University of California as a senior program manager with Lockheed Martin. His work focused on large-scale magnesium lithium-ion battery technology and energy engineering services to large industrial companies and utility companies across the country.

Paschall has assembled a very strong team of recognized subject-matter experts in the field of polymer science and tire engineering to launch Akron Polymer Solutions. The team has undertaken significant research and development and testing in the launch of APS’s proprietary graphene material, Prophene.

Experimental methods

The bromobutyl model tire innerliner compound illustrated in Table 1 was used for bench-marking purposes.4 This formulation was initially developed by ExxonMobil as a model innerliner compound, has become an industry standard for raw materials research and development.

The halobutyl polymer, ExxonBrombutyl grade 2222 (Mooney viscosity ML1+4 specification 32) was selected along with Struktol-brand 403MS, a processing resin obtained from Struktol Co. of America and commonly used in innerliners to improve factory processing, compound adhesion and fatigue resistance.

The tie-tight resin used is typically a Sencelcady International Inc. resin Si-106ST or alternatively the ExxonMobil hydrocarbon, Escozer 1102, can be substituted with no modification in the compound formula. Zinc oxide (ZnO), stearic acid, benzothiazole disulfide (MBTS) and sulfur were used as curing system. This formulation initially developed by ExxonMobil as a model innerliner compound has an industry standard for raw materials screening. The carbon black grade N660 was used as it is near universally used in tire innerliners.

Mooney viscosity and Mooney scorch times were determined. See Graphene, page 16.
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was selected for study as it represents the center point of the range of properties for the three available grades.

For the natural rubber model truck tire tread compound, the smoked sheet grade RSS2 was used though TSR 20 is equally satisfactory for laboratory work (Table 1). The carbon black grade N121 was selected as a typical tread grade material, and the remaining compounding materials again were typical of what is found in such formulations. The testing protocol was the same as what was followed for the innerliner compound study.

Results

Two studies were conducted, one in a model tire halobutyl compound and the second in a model, all-natural rubber, truck tire compound. The two studies have been considered in turn.

Tire halobutyl compound

The specific grade of graphene identified as Prophene PS150 was first blended with bromobutyl rubber using a BR-size laboratory Banbury to form a graphene-rubber masterbatch. This was then used in preparing bromobutyl compound graphene nanocomposites for testing. The graphene was added at effective PHR loadings of 0.5, 2.0, 5.0, 8.0 and 20.0 PHR to give five experimental compounds and a control (Tables 3 and 4).

To elaborate, the permeation coefficient is the transmission rate normalized for sample thickness and is expressed as volume (cc) of gas at one (mm) per unit area of sample (m²) in a discreet unit of time (24 hours). The term permeance frequently cited is the ratio of the barrier’s transmission rate to the partial vapor pressure differential across the barrier. There are three grades of Prophene available from Akron Polymer Solutions, and their general properties are shown in Table 2. Grade No. 2, or PS150,
was selected for study as it represents the center point of the range of properties for the three available grades.

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The vulcanization rheometer results are shown in Fig. 3. Other than the sample containing 20.0 PHR of graphene, all of the profiles were equivalent, allowing two observations:

1. Since the graphene is pristine with no functional groups on the plate surfaces or edges, there is no interference with the vulcanization chemistry or the kinetics.
2. The sample, Compound 6, containing 20 PHR of graphene, showed an increase in rheometer torque, ΔT, being due to the increased total filler loading and not the state of cure or crosslink density.

Similarly with Mooney viscosity (Fig. 4), with increasing amounts of graphene there was no impact on either the peak Mooney viscosity or Mooney viscosity at ML1+4, further suggesting no chemical interactions between the graphene plates and the polymer or other compounding ingredients. And tensile strength, elongation at break and 300 percent modulus up to 8.00 PHR of graphene were similarly not affected (Table 3).

A consistent observation noted in multiple studies conducted by the authors was an increase in tear strength and peel adhesion (Figs. 5 and 6). Furthermore, the increases in adhesion and tear strength followed a near gaussian distribution with very low levels of graphene creating improvements reached a peak or plateau at between 0.5 PHR and 2.0 PHR of graphene.

The increase at low amounts of graphene would be due to the very large aspect ratios of these specific grades of graphene when compared to other large aspect ratio plate-like particles used in rubber nanocomposites.

For example, the graphene plate size can be up to 1.0 µm, which compares with kaolin clays nominally at 20 nm. The absence of organic functional groups such as carboxylic acids, aldehydes or hydride

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droplet groups would account for the absence of any shift in vulcanization kinetics unlike what would be observed with clay fillers, which have a variety of alkenes and alkanes on their surface.

Considering the large plate size, compound permeability was measured by two methods, a traditional method following ASTM D431 and an instrumented method using the Ametek Moc 222 permeability tester, which was run at the Ametek laboratories. Data has been documented on Table 4 and illustrated in Figs. 7 and 8.

Addition of 0.5 PHR of graphene resulted in a rapid drop in permeability, which continued as the graphene level increased until a near plateau is achieved.

The trend follows the typical path for rubber nanocomposites containing plate-like fillers, and has been well documented by workers such as Nielsen, who developed models relating plate aspect ratio to gas permeation through polymer systems.3-5

Truck tire tread compounds

Graphene was added to the model truck tire compound illustrated in Table 1 at levels of 0.5, 1.0, 2.0, 4.0, and 10.0 PHR to give a total of six compounds, including the control at 0.0 PHR (Table 5).

Some observations from the data were as follows:

1. Increase in graphene had no impact on Mooney viscosity (ML(1+4), peak Mooney viscosity or aged Mooney viscosity (7 days at 100°C). Peak Mooney viscosity has been related to formation of bound rubber, which in turn could be due to functional groups on the polymer or filler.6

2. There was no shift in vulcanization state of cure, AT, maximum torque or MDR at 180°C.

3. Vulcanization kinetics determined simply from the cure rate index (equation 1) similarly did not shift.

Cure Rate Index = (t90 – t10 / 100)

(1)

Fig. 14: Electrical resistivity of NR/E-SBR tread compound using N234.

Addition of 0.5 PHR of graphene resulted in a significant drop in electrical conductivity (Fig. 14). Volume conductance of the NR/E-SBR tread compound using N234 at levels of 1.0 to 4.0 PHR increased. Graphene, electrical resistivity at levels of graphene up to 4.0 PHR was found to be much lower than what would be achieved with a level of graphene used on tankers would therefore be of benefit. The electrical resistivity of the model truck tire tread compounds used in this study was therefore measured and the results shown in Fig. 15. At levels of 1.0 to 4.0 PHR of graphene, electrical resistivity showed a significant reduction even though it is well below the percolation point of graphene in the compound.

The study also was conducted on a tread compound containing natural rubber, emulsion SBR and N234 carbon black with a similar result (Fig. 14).

Discussion

Addition and study of the specific grade of graphene available as Prophene to rubber polymer nanocomposites allowed two sets of observations. First, it had no impact on a number of compound properties. For example:

1. Prophene as a drop-in compound processability and cure kinetics.

2. There is no impact on tensile strength and hardness (Shore A), though modulus increases suggest improved acrivity and cure kinetics.

3. Improved abrasion resistance. Surface profiling suggest improved quality of dispersion and strain crystallization in natural rubber compounds.

4. Improved in electrical conductivity—potential application in truck tire treads containing silica.

5. Improved barrier properties.

6. Improvements observed in adhesion and tear strength with no loss in hysteresis (i.e., increase in loss modulus). There also is peak adhesion benefits and improved chipban/knot resistance.

7. Improvement in electrical conductivity—potential application in truck tire treads containing silica.

Tire tread compound abrasion is a complex phenomenon but has been described by one of two mechanisms:

1. Tensile-tearing mechanism (fast wear).

2. Thermo-oxidative degradation (slow wear).

Addition of low amounts of Prophene has improved Din abrasion performance, which may represent the tearing mechanism for wear. This will be consistent with tear strength and peel adhesion observations, and also with the mechanism of wear described by Schallamach wave patterns (Fig. 15). And this is further supported by the nature of the tear mechanism observed in specimens tested under ASTM D624. The tear path is deflected along the direction of the tear propagation, turning resulting in a higher tear strength.

These improvements were achieved with a level of graphene much lower than what would be found with other nanocomposite materials such as organo-clays or talc. It is believed that the selective improvement in rubber nanocomposite properties is due to several factors:

1. The exceedingly large aspect ratio of graphene plates.

2. The pristine nature of these types of graphene under the trade name Prophene.

3. Assumed reactivity of the Prophene plates in the polymer matrix.

4. The inert surface and edges of the Prophene plates and absence of organic functional groups.

5. The potential mechanisms for graphene functionality in truck tire treads.

5 Components were selected with the intent to show the effect of adding graphene from 0.0 PHR to 4.0 PHR and Din abrasion measurement. Loss modulus, which continued as the graphene level increased. The result is consistent with the gaussian theory that rubber compounds have a large impact on reducing abrasion (Fig. 16). The logical place to begin any upgrade is at the plant with a technology that rubber. Prophene has improved Din abrasive properties.

Adding graphene into the rubber matrix can greatly increase the barrier properties and this has been well reported in the literature (Fig. 16). Fundamentally, this is due to the dispersion and exfoliation of the graphene network in rubber matrix resulting in a percolating network as described by Nielsen and co-workers.7-9 For gas molecules diffusing through the rubber, the rubber matrix is extended considerably, resulting in an effective drop in gas permeability, and this is illustrated in Fig. 17.

The result is significant improvement of the barrier properties. Since Prophene has a very high aspect ratio, small amounts have a large impact on reducing permeability, as has been observed in this study. Prophene has very large aspect ratio plate-like structures that, when oriented, are understood to arrest tear propagation; plates re-direct tear and crack propagation, increase mixing shear with this, in turn, improving dispersion and homogeneity.
Conti to focus investments on mixing capacity

By Don Detore

PLAHA DEL CAMDEN, Mexico—The rubber that meets the road these days is much bigger than it used to be. With rim diameters increasing year-by-year—17-inch and larger sizes account for seven of the 10 most popular passenger replacement tires sold in 2020, compared with just one 17-inch size among the 10 most popular in 2011—the time has come for Continental Tire the Americas to address that rubber.

Bill Caldwell, senior vice president of sales and marketing for the Charlotte-based U.S. subsidiary of Germany’s Continental AG, said the tire maker has begun to discuss capacity expansions at its North American plants—the capacity to mix more rubber that in turn will be used to manufacture tire.

“Assuming that the trend toward larger rim-diameter tires is going to stay and it seems like it will, at least in this market—we should plan for it,” Caldwell told Tire Business during the recent Conti Gold Trip in Playa Del Carmen.

“We need to start investing not necessarily in building machines, but in up-stream to be able to process more rubber.”

He said there is a need to process more rubber to manufacture more tires, but only so many units, and that “is where we are needing to invest now, based on the changes and growth we see.”

That investment, he said, should include all components that pertain to the rubber mixing process.

“Everything upstream there, you need to scale because all of those components are going up,” Caldwell said. “All of that mixing capacity needs to get bigger now for the same units. We need to catch up to demand change, and we also need to invest for growth.”

Caldwell said he believes it will be a three-year investment that will include upgrades in building, equipment and personnel.

According to data from the U.S. Tire Manufacturers Association, the percentage of 17-inch and larger tires represented in the U.S. replacement market nearly doubled over the last five years. The top size in 2020 was 225/65R17; in 2016 it was 205/50R16; and in 2011 it was P235/75R16, according to the USTMA.

The original equipment size is as alluring, but because the demand is not matching the growth in the market, Caldwell said much of what was invested in the past is being re-claimed now by the car manufacturers. “We are in a situation where we’re investing in capacity, but we’re not seeing the demand growth to keep that going.”

The logical place to begin any upgrade is at Conti’s plant in Mount Vernon, Ill., where the tire maker produces more than 14 million units annually, the bulk of which serves the light truck segment, according to a company spokesman.

Conti also has U.S. plants in Bolton, Miss. (commercial tires) and Sumter, S.C. (passenger/light truck).

The light truck/SUV tire market now comprises more than half of the overall consumer (passenger/light truck) segment in North America.

Caldwell said the plan is all about broadening the capabilities of more manufacturers to make that type of product in order to keep the (light truck segment) going (in North America). “This is very different versus some other markets (globally).”

The pandemic-induced supply-chain issue that is wreaking havoc across the tire industry—really most industries, for that matter—certainly has affected Conti.

“Demand and supply are not all lined up right now,” Caldwell said. “That’s the nature of the beast.”

He called distribution/logistics “a nightmare,” with the “exorbitant” cost of shipping containers making it worse.

But, he and other executives said, the issue isn’t as severe as it might be because of Conti’s ability to source product from plants around the world, particularly in Europe, where the population is more locked down and demand remains somewhere between 70 percent to 80 percent of what it had been.

“(Europe) still remains our critical base of our manufacturing capacity,” he said. “We’ve always gotten tires there and we’ve been able to lean into that more, transferring production there. It’s been a real plus for us.”

Still, he said, that doesn’t solve the challenges of ports and containers.

“Just at the least the tires have a good distribution pipeline there,” he said. “We do think the plant challenges, the employment challenges there are as significant as they are here. So that’s helping us weather this storm, and having that flexibility kind of paid off for us.”

“It’s been a really robust year over year, month over month,” said Chris Charity, vice president of sales. “But instead of high fives, we’re worrying about how to make enough product.”

The supply issue—as well as attracting and retaining employees—were by far the two hottest topics during the five-day Gold Trip, held Sept. 20-24 at the Grand Velas Riviera Maya, near Playa Del Carmen.

It was Conti’s first Gold Trip since 2019. Around 450 people attended, including 290 dealers who qualified for the trip. On Oct. 8, Hannover, Germany-based Continental celebrated its 150th anniversary.

Joe Maher, Conti product manager, passenger and winter tires, reacquainted dealers with new products to the market, including the

• ExtremeContact DWS06 Plus, a premium performance tire released in February that covers 96 percent of the market.

• General Tire’s Altimax 365 SW, an all-weather tire released in May that is 3-Peak Mountain Snowflake certified.

• General G-Max Justice, an ultra-high-performance pursuit tire.

The G-Max Justice, an all-weather all-season product, is CATL 1922 pursuit and emergency high-speed approved and offers up to 15 percent better tread life and up to 18 percent better wet braking performance than a leading competitor, according to the company.

The pandemic caused several challenges for the marketing department, particularly since fans couldn’t attend most athletic events.

Still, Conti sponsorships remain strong, according to the spokesman. Conti’s sponsorship with Major League Soccer was renewed through 2023, with its sponsorship with the NCAA and General Tire sponsorship deals with the ARCA Menard’s Series racing and Major League Fishing having been renewed through 2024.

In addition, Conti will sponsor the Continental Tire Challenge, a college basketball game set for Nov. 26 at the Mobile Arena in Las Vegas that matches Duke University and Gonzaga University.

The company also is heavily marketing its 150th anniversary on social media, showing a commercial featuring racer Tony Stewart as a fortune teller.

General Tire has collaborated with YouTube stars Dude Perfect for an ultimate Racing Battle video series. Dude Perfect, a group of five men, has 56 million subscribers and their videos have more than 13 billion views.

The company will unveil new brand messaging soon.

“It’s all about keeping the lines of communication open,” Charity told dealers. “We are here for you.”

It won’t be long before the group gathers again. Conti is planning to hold its next Gold Trip in late March 2022, in the Dominican Republic.

Technical Graphene

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Graphene

neity, making for a potential nucleating agent for strain crystallization.

Summary

The specific Prophene grade of graphene has no impact on compound hardness, Shore TIR and modulus increase suggests improved dispersion (50 percent low strain modulus), and Prophene may also be acting as nucleating agent for strain-induced crystallization of natural rubber, resulting in improved abrasion resistance. Surface profilation suggests improved quality of dispersion.

In addition, there are improvements observed in adhesion and strength with no loss in hysteresis (i.e., increase in loss modulus), peel adhesion benefits and, by implication, improved track tire tread/compound cut resistance. There also is improvement in electrical conductivity—potentially application in truck tires treads containing silica, sometimes added for improved rolling resistance and tear strength.

And finally, an important observation is that many new technology materials, when added to rubber compound formulations, have a trade-off in other properties, in many instances negating their application. Prophene’s performance improvement due to very large aspect ratios and nature of plate surface chemistry with no loss in many other properties suggests it is a “drop-in” to existing compound formulation already in production and will not require recompounding, as is the case with many other new technology materials.

References