Green(er) Tires

December 31, 2011

Lehigh Technologies

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Project Title: Green(er) Tires

Milestone: 100 Million Tires. In June 2011, Lehigh Technologies announced that it is Micronized Rubber Powder brand, PolyDyne™, made from end-of-life tires and other post industrial rubber, has been used as an ingredient in over 100 million tires. This is a big win for the environment and a big win for the technology and science behind the commercial use of recycled materials. It proves to industry that there are reliable, quality recycled materials available that can be made in large commercial volume, substituted for oil-derived virgin materials, used in high performance applications (tires), and made in an environmentally friendly way. However, this is just the beginning. Lehigh has recently discovered a way to increase the percent of recycled rubber in a tire from 3-7% to 10%.

Small Business Award: Lehigh Technologies meets the small business category criteria.

Focus Area: Lehigh's focus area is #1 – "the use of greener synthetic pathways."

US Component: Lehigh Technologies is a US-based company that bought the initial cryogenic turbo mill manufacturing technology from a German machinery company in 2003; all system design and process engineering and optimization work to manufacture high-quality, fine particle size in large, commercial quantities, was developed in the US (Tucker, Georgia). Lehigh developed and owns the worldwide patent rights for this cryogenic/turbo mill process (US Patents 7,445,170, 7,108,207, 7,093,781, 7,861,958, and 7,900,860).

In November 2010, Lehigh officially announced its Application & Development Center (ADC), a center adjacent to our manufacturing facility dedicated to helping customers' launch sustainable products faster and finding new uses for post-industrial rubber, including tire material.

Furthermore, all of the research and development to understand the science and chemistry behind increasing the recycled rubber (called Micronized Rubber Powder – "MRP") content has been conducted in the US: At Lehigh's Application & Development Center and The Georgia Institute of Technology (NSF SBIR sponsored).

Abstract: The nominated technology is Lehigh's PolyDyne™ 140 (105 microns/140mesh) in the production of new tires to bring recycled rubber content levels from current industry levels of 3-7% to 10%. PolyDyne™ 140 is made from a patented micronized rubber powder (MRP) derived from end-of-life tires and other post-industrial rubber produced through a cryogenic turbomill process. PolyDyne™ 140 features high surface area where 90% of the particle size is 105 micron/140 mesh, is virtually metal and fiber free, made in an environmentally friendly way, and can be produced in commercial volumes. The process used to produce PolyDyne™ 140 keeps the polymer intact, which means MRP maintains its core performance characteristics, such as durability in dynamic applications. PolyDyne 140™ is an effective, lower cost substitution material for oil-derived virgin materials, namely synthetic rubber (SBR).

This innovation is significant in that by increasing the amount of MRP in a tire further reduces the need for petroleum-based feedstock and helps eliminate the need to landfill tires. The

Rubber Manufacturers Association (RMA) estimates that there will be 287 million tire shipments in 2011. Assuming 18 pounds of rubber per tire (source: Rubber Manufacturers Association) and 287 million tire units, a seven percent increase would mean 296.5 million gallons of oil savings, 3.6 billion kWh of energy savings and 432 million pounds of CO_2 savings, annually.

Fit to Scope of Program.

Using Lehigh's PolyDyne™ 140 to increase the amount of MRP in a tire to 10% in the production of a new tire helps reduce the amount of petroleum-based feedstock; MRP is a substitute raw material for virgin materials that use oil as a building block. Every pound of MRP saves 0.8 gallons of oil and 10kWh of energy and releases nearly half the CO_2 of synthetic rubber in the manufacturing of a tire (see Figure 4). The environmental impact of this is significant when considering the number of tires produced in the US every year – 287 million.

Lehigh Technologies' Micronized Rubber Powder

Furthermore, by finding large high-volume applications for end-of-life tires and other post-industrial materials, MRP is helping eliminate environmental problems associated with land-filling tires. According to the US Environmental Protection Agency (EPA), tire piles pose two major health threats - pests and fire. Disease carrying pests, such as rodents, may live in tire piles and mosquitoes can breed in the stagnant water that collects inside tires. Fire is a second concern. Scrap tire fires are difficult to extinguish, and can burn for long periods. Tire fires release thick black smoke and can contaminate the soil with an oily residue. The oil that exudes into ground and surface water as a result of tire fires is a significant environment pollutant. For every million tires consumed by fire, about 55,000 gallons of runoff oil can pollute the environment unless contained and collected. Air pollution is also produced by tire fires. Air emissions may include polycyclic aromatic hydrocarbons (PAHs), benzene, styrene, phenols, and butadiene. (Source: www.EPA.gov).

Fit to Selection Criteria.

Innovation. The innovation is the understanding of the fundamental surface chemistry of MRP and using that knowledge to develop novel formulations that enable significant increases in the recycled content of tire rubber compounds - from an industry average of three percent to ten percent. This discovery uses Lehigh Technologies PolyDyne™ Micronized Rubber Powder (MRP) type PD-140-TR.

Science/Chemistry of MRP. Micronized Rubber Powder (MRP) is classified as a dry, powdered elastomeric compound in which a significant proportion of particles are less than 100 microns. It is used as a compound extender to offset the increasing prices of natural rubber and synthetic polymers (namely SBR). It increases the sustainability and in some case the performance of the compounds in which it is used. MRP is made from cured elastomer feedstock, typically chips from end-of-life tires, via a cryogenic turbomill process at a temperature below the Tg of the polymer.

The fundamental chemistry of MRP and its behavior in tire rubber compounds must be understood in order to make (disruptive) technical advancements in the reuse of tire material. Recycled rubber has been around for years – this is not the novelty. What is novel is the ability to manufacture high technology MRP that can be used in dynamic applications (tires) at significant loading levels in commercial quantities. It is not just the manufacturing capability that is required; it is also critical that rubber compounds containing MRP be formulated in such a way to be manufacturable and to achieve target properties in the finished rubber compound. Lehigh has identified and overcome the key barriers to adoption of significant recycled rubber content in tires.

Here are three primary barriers to adoption and how Lehigh has addressed them:

1. Particle size and its effect on tensile strength

Most commercial MRP used in tires is classified as 80 mesh powder, meaning that a minimum of 90% must pass through a screen opening of 177 µm. Unfortunately, such a particle size distribution has a deleterious effect on final properties, particularly tensile strength. This effect has been noted in the literature: Kumar, et al, experimentally determined the intrinsic flaw size of carbon-filled SBR (styrene-butadiene rubber) at 130 µm[1]. In addition, researchers at Bridgestone identified the superior properties of 120 mesh (125 µm) MRP[2]. While both of these groups identified the importance of particle size on tensile strength, they did not develop compensations for the unique surface chemistry of MRP. This is discussed in parts 2 & 3 below.

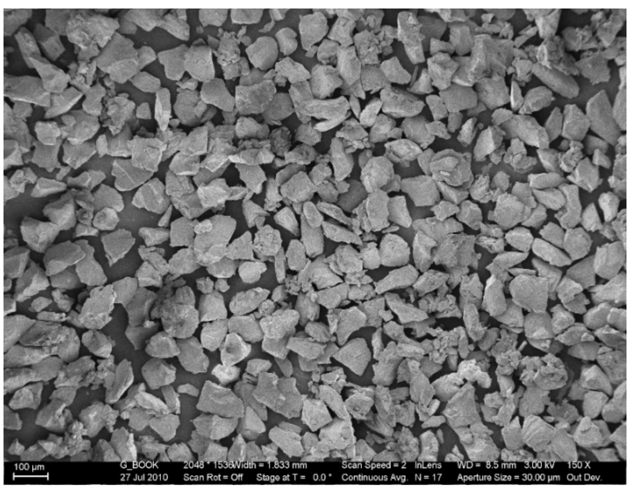

Figure 1. 140 mesh (106 µm) MRP made via a cryogenic turbo mill process. Note the 100 µm scale bar in the lower left corner.

One significant limitation to adoption of fine particle size MRP in tire rubber compounds has been availability. The throughput of conventional grinding technology is simply too low. Lehigh has addressed this through the development of high-throughput cryogenic turbo mill technology. Through continuous refinements to its state-of-the-art process technology, Lehigh is able to provide significant volumes of 140 mesh (Figure 1) and finer MRP in a capital efficient system the can easily be replicated.

2. Sulfur depletion and its effect on modulus.

[1] P. Kumar, Y. Fukahori, A. G. Thomas, J. J. C. Busfield, Rubber Chem. Technol. 80, 24(2007).

[2] Jamie J. McNutt, Michael S. James, William J. O'Briskie, William J. Corsaut, (to Bridgestone/Firestone Research, Inc.) U.S.Patent 6,265,454 (2001).

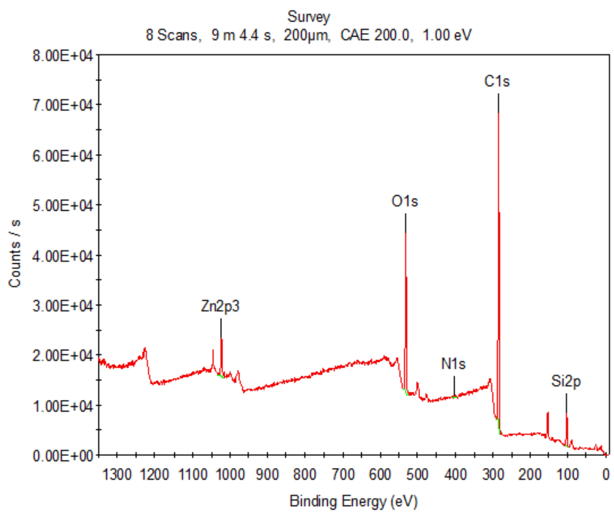

Figure 2. XPS survey scan for micronized rubber powder.

It is well known that MRP additions to rubber compounds have the effect of depressing the modulus and accelerating cure[3,4,5]. What has not been understood is why. Lehigh has recently completed fundamental surface chemistry analysis that sheds light on this behavior. This is shown in the XPS survey scan in Figure 2. In this scan, there are detectable peaks for Zn, O, N, C, and Si. The predominant C peak may be attributed to the rubber polymer. The Zn to the presence of ZnO cure activator, the N to cure accelerator chemicals, and the Si to the SiO_2 flow aid that is added to prevent powder agglomeration. The O is approximately stiochiometric to the ZnO and SiO_2. Notable by its absence is any detectably trace of sulfur, which is present in all tire rubber compounds at levels of 1-2%. Sulfur is the cross-linker in vulcanized rubber compounds. The hardness, or modulus, of the cured compound is a critical target property and is dependent on the sulfur content. Lehigh believes it is the absence of sulfur at the particle surface that results in the apparent low modulus (lower than control compounds) of cured rubber compounds that contain MRP. Sulfur additions can be made to recover the modulus; this is shown in Figure 3. This figure is a plot derived from a factorial experiment. The iso lines are constant modulus. It can be seen that additional sulfur is needed to maintain constant modulus as the MRP level is increased.

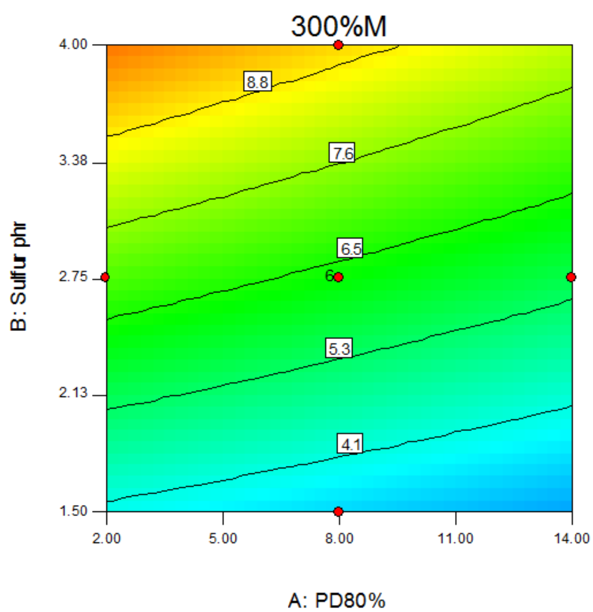

Figure 3. Plot of model that predicts the Sulfur increase required to maintain modulus (iso lines) as MRP content (PD80) is increased.

3. Accelerator contribution and its effect on cure behavior

Rubber compounds that contain MRP cure faster than compounds that do not. This is not necessarily a benefit – compounds are designed to a specific cure schedule to match the molding process. Thus, similar to the case with sulfur discussed above, accelerator adjustments must be made. However there is an additional and heretofore unknown

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[3] D. Gibala, G. R. Hamed, Rubber Chem. Technol. **67**, 636(1994).
[4] R. A. Swor, L. W. Jensen, M. Budzol, Rubber Chem. Technol. **53**, 1215(1980).
[5] Z. I. Grebenkina, N. D. Zakharov, and E. G. Volkova, International Polymer Science and Technology 5, No. 11, 2 (1978).

complicating factor: the required accelerator adjustment is dependent not only on the amount of MRP added, but also on the particle size of the MRP. For example, with a 10% addition of a 400 µm MRP, the onset of cure takes 4.17 minutes. However, if instead a 75 µm MRP is used, the time is only 3.48 minutes, which is a decrease of 17%. Lehigh believes that the reason is that a powder of smaller particle sizes has higher surface area, and it is this surface that is contributing to the active cure chemicals detected in the XPS analysis

In summary, Lehigh has identified unique attributes of the chemistry of MRP and has developed solutions that enable this vital sustainable technology to be used on a broader scale in the manufacturing of new tires. Lehigh has filed a provisional US patent application (61/420,858) comprising these innovations.

Human health and environmental benefits. According the latest numbers from Rubber Manufacturers Association (2007), approximately 300 million tires are discarded in the U.S. every year. Disposing of this highly engineered product is waste of a useful resource. By reusing this end-of-life tire material companies are reducing the need for petroleum-based feedstock and are helping solve the problem of waste in landfills. The cryogenic process is environmentally friendly; uses little water, lower energy and lower emissions (see Figure 4 below). Lehigh's plant emissions that come from the plant are nitrogen, forklifts used to move product and air compressors used. Below are results of the environmental benefits of MRP vs. synthetic rubber. This analysis takes into consideration both upstream and downstream processing (e.g., the energy required to manufacture liquid nitrogen and the average transportation distance).

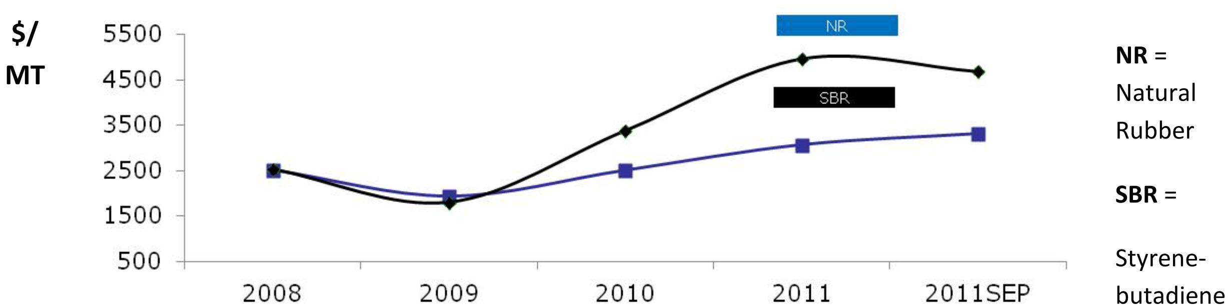
Figure 4. Lehigh Technologies' MRP Environmental Profile
Savings on a per pound basis*

	Oil Savings	Energy Savings	CO_2 Savings
Lehigh Technologies' MRP	.82 gallons	10kWh	1.17 lbs
Notes	It takes 5 gallons of oil (as feedstock) to make synthetic rubber for a tire.	It takes 11 kWh/lb to make one pound of synthetic rubber; and 1.021 kWh/lb to make one pound of MRP; this calculation includes upstream and downstream energy requirements, including energy to produce liquid nitrogen, shredding from the tire recycler as well as transportation	The GWP of synthetic rubber is 2.7. Lehigh's CO2 emissions are 1.5 lbs and includes upstream processing and transportation

Source: Sustainable Design & Manufacturing Program at Georgia Institute of Technology (12/10)
**passenger tire equivalent.*

*Applicability and Impact***.** The Rubber Manufacturers Association estimates US tire shipments to be 287 million in 2011 (a nearly 1 percent increase over 2010) and is forecasted to reach 290 million units in 2012 (an increase of more than 2%). Looked at another way, the tire industry consumes approximately six billion pounds of rubber in the US annually. There is no doubt – the tire industry is significant. Increasing the amount of MRP in a tire from three percent to ten percent has impressive environmental impact. Assuming 18 pounds of rubber per tire (source: Rubber Manufacturers Association) and 287 million units (estimated 2011 US tire shipments), this change would mean 296.5 million gallons of oil savings, 3.6 billion kWh of energy savings and 432 million pounds of CO_2 savings, annually (reference Figure 4).

Tire manufacturers are already incorporating MRP into tires – we know that they have incorporated it into over 100 million tires. Of course, tire manufacturers will need to modify their formulations and test tires to ensure safety and quality; however, incorporating a higher percent of MRP is a real and practical opportunity for tire manufacturers. Furthermore, there are incentives for tire manufacturers to increase the amount of MRP in a tire – price stability vs other materials (see chart below) and consumer interest for more environmentally friendly options.



Source: Rubber Statistics Bulletin 2011

Finally, there is the opportunity to apply these findings to other industries, namely other rubber- based goods. By expanding MRP into other segments the environmental benefits magnify, further helping reduce the need for petroleum-based feedstock and rubber waste from entering the landfill.

Potential Drawbacks. There are few, if not any, potential drawbacks to this technology, i.e., the technology is available, is lower cost (vs the alternative), can be made in commercial quantities, and is solving an environmental issue in an environmentally friendly way. One could argue that there is a technical barrier that exists of "processability;" the viscosity of the rubber changes when 10% of PolyDyne™ 140 is added and; therefore, changes to a tire manufacturer's formulation may need to be modified. However, tire manufacturers modify their formulations today when new technology becomes available so this is not new. Finally, there exists the drawback of speed of industry adoption. There are numerous environmental benefits of tire companies incorporating more MRP in the manufacturing of new tires (e.g., less dependence on petroleum-based feedstock and reducing a waste problem); however, tire companies have numerous initiatives and; therefore, modifying a formulation to incorporate more recycled content may not always fall at the top of their corporate priorities. We are seeing, however, growing evidence of tire companies putting green tires at the top of their corporate objectives - a big win for the tire industry and for the environment.