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The path to a circular economy, potential market impact

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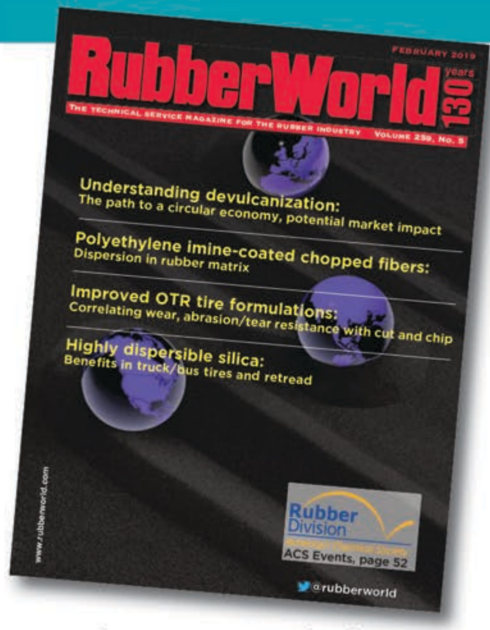

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Departments

Understanding devulcanization, the path to a circular economy and potential market impact

by Costas Tzoganakis, University of Waterloo, and Jon Visaisouk, Tyromer

Devulcanization, the process of breaking sulfur crosslinks formed in vulcanized rubber, has been considered the Holy Grail of rubber recycling for decades because it would provide the best practice in waste rubber reuse. While devulcanization technologies of the past have failed to be commercially viable or cost effective, new technology and industry adoption are proving that devulcanization deserves more attention.

There are different methods of devulcanization, and rubber reclaiming is often mistaken for, or used synonymously with devulcanization. But unlike rubber reclaiming, there is devulcanization technology available that can preferentially break sulfur links in vulcanized rubber without destroying the integrity of rubber molecules. Properly devulcanized, much of the excellent properties of rubber are retained. This devulcanized rubber can be used in meaningful amounts in a wide variety of high-end and critical applications, including new and retreaded tires.

Furthermore, incorporating devulcanization and a circular economy into current business practices does not require disruption. Through collaboration and open innovation, individual linear economies can align to form a circular solution for the industry, although it will take organization and a forward-thinking mentality. Devulcanization's potential impact on the market and industry is enormous; imagine cutting global rubber consumption by more than 10% by fully utilizing scrap tires and available technology. Devulcanization of scrap tire rubber is now feasible, and warrants more attention from the tire and rubber industry. It is also important to note that, while this article focuses on scrap tire rubber, other materials are also great candidates for devulcanization, including EPDM and butyl rubber.

Difference between devulcanization and reclaiming

Reclaimed rubber has been defined as vulcanized rubber treated by a combination of heat, chemical agents and intense kneading to give a material with essentially its pre-vulcanized plasticity, which is useful as a rubber compounding material (ref. 1). Research activities on rubber reclaiming date back to the mid 1800s, shortly after vulcanization of rubber with sulfur was patented by Charles Goodyear. Since then, various reclamation techniques have been developed, and in-depth reviews have been previously published (refs. 2 and 3). Reclaiming of rubber involves softening and swelling of rubber and the reduction of its viscosity through scission reactions induced by shear deformation and chemical action, and the role of processing conditions on reclaimed rubber properties has been reviewed early on (ref. 4). Through reclaiming, scission of several types of bonds such as carbon-carbon (C-C), carbon-sulfur (C-S) and sulfur-sulfur (S-S) is achieved. However, the reduced viscosity and recovered plasticity of reclaiming methods is primarily due to the shortening of polymer molecules by C-C scission reactions. Today, conventional reclaiming processes have been virtually eliminated in North America primarily due to concerns with the disposal of the chemical solutions used.

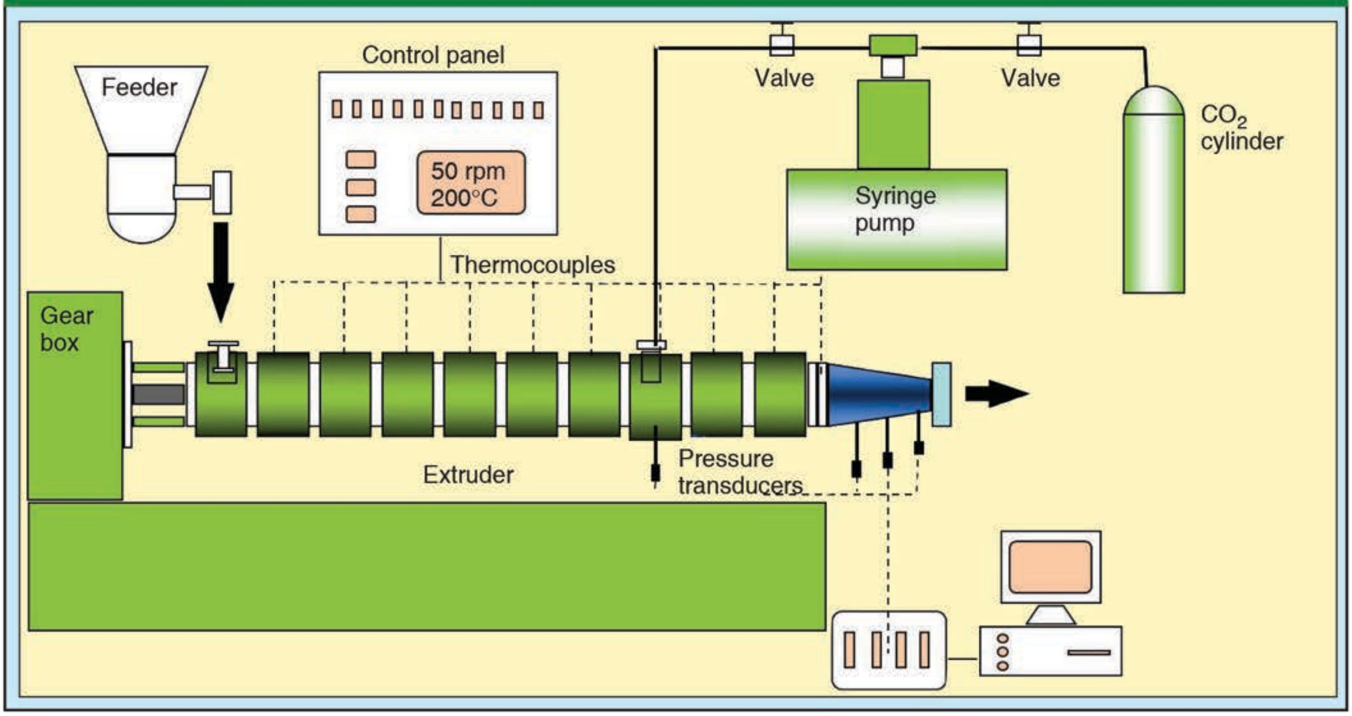
Devulcanization of rubber involves the destruction of sulfur chemical crosslinks in a vulcanized rubber (ref. 1). ASTM STP183A defines devulcanization as "a combination of depolymerization, oxidation and increased plasticity" (ref. 5). However, devulcanization is understood to be the reversal of the vulcanization process, that is the cleavage of chemical bonds formed during vulcanization. Bonds formed during sulfur vulcanization are C-S and S-S, and only such bonds should be cleaved during devulcanization. Therefore, devulcanization is the process of cleaving the mono-sulfidic (C-S-C), di-sulfidic (C-S-S-C) and poly-sulfidic (C-Sx-C) crosslinks of vulcanized rubber, while leaving intact the backbone of the rubber polymer molecules. In view of these definitions, the majority of physical and chemical methods converting waste rubber into reusable rubber should be classified as reclaiming rather than devulcanization. These methods involve random scission of chemical bonds as opposed to targeted scission of sulfur crosslinks. Table 1 shows a classification of such processes into two categories, physical and chemical, which have been previously reviewed (ref. 3). Achieving devulcanization through these various methods in research labs at low throughput has been possible, but the true test of viability is scaling to commercial output levels that match the needs of large manufacturers.

Differentiation between processes involving random or crosslink scissions can be accomplished by employing a theory previously developed to study crosslinking and scission reactions during polymer irradiation (ref. 6). This theoretical model is based on the determination of the amount of soluble polymer generated from such reactions, and it was further adopted by Horikx to model random and crosslink scissions in a vulcanized rubber (ref. 7). This theory considers the relationship between the degree of devulcanization (change in density of the crosslinked fraction) with the soluble fraction content of the rubber before and after the devulcanization process. Selective cleavage of sulfur crosslinks is expressed by equation (1), while random chain scission is expressed by equation (2). Equation (3) is used to calculate the crosslinking index γ.

Table 1 - rubber reclaiming/devulcanization processes

Physical processes	*Chemical processes*
Mechanical	Radical scavengers
Thermo-mechanical	Nucleophilic additives
Microwave	Catalyst systems
Ultrasonic	Chemical probes

Figure 1 - schematic diagram of the Tyromer devulcanization process



Selective crosslink scission

$$\text{degree of devulcanization} = 1 - \frac{\nu_{e2}}{\nu_{e1}} = 1 - \frac{\gamma_2\,(1 - s_2^{1/2})^2}{\gamma_1\,(1 - s_1^{1/2})^2} \quad (1)$$

Random scission

$$\text{degree of devulcanization} = 1 - \frac{\nu_{e2}}{\nu_{e1}} = 1 - \frac{(1 - s_2^{1/2})^2}{(1 - s_1^{1/2})^2} \quad (2)$$

where

$$s = 1/(1 + \gamma - \gamma s)^2 \quad (3)$$

and

ν_e = density of the crosslinked fraction
s = soluble fraction content
γ = crosslinking index
$_1$ = index used for the values before devulcanization
$_2$ = index used for the values after devulcanization

The predictions from these model equations can be used to assess experimental data of crosslink densities and soluble content before and after devulcanization. This is done in the form of a Horikx plot, comparing soluble content to the degree of devulcanization.

Tyromer's solution for the tire industry

Professor Tzoganakis of the University of Waterloo's Chemical Engineering department invented a supercritical CO_2-assisted twin screw extrusion process to devulcanize scrap tire rubber, which is schematically shown in figure 1. Rubber crumb is fed into the extruder, and a very small amount of supercritical CO_2 is injected into the rubber along the extruder barrel. Figure 2 highlights the role of CO_2, which is to swell the rubber and place sulfur crosslinks under tension, thus facilitating their scission and leading to production of a devulcanized rubber material. This devulcanized rubber compound is called tire-derived polymer, or TDP.

Over a decade of research and development has allowed Tyromer to commercialize this invention, and scale up production and throughput. The company has demonstrated that it is possible, without the use of chemical solvents and devulcanization chemicals, to selectively break the sulfur links to preserve the rubber network. A Horikx plot has been used (ref. 8) to evaluate results from the Tyromer devulcanization process, and figure 3 shows the Horikx plot for EPDM samples from various types of automotive seals. The soluble content is plotted against the degree of devulcanization. The dashed line represents the selective crosslink scission model according to equation (1), and the solid line represents the random scission model according to equation (2). The open

Figure 2 - role of supercritical CO_2 in swelling and devulcanization of crosslinked rubber in the Tyromer process

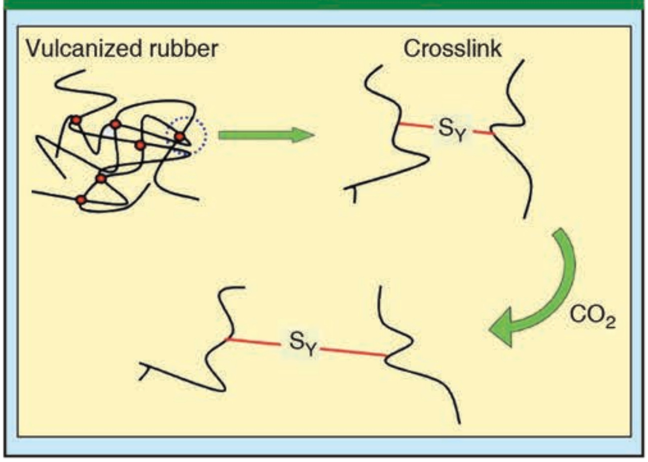


Figure 3 - Horikx plot for devulcanized EPDM samples from automotive seals

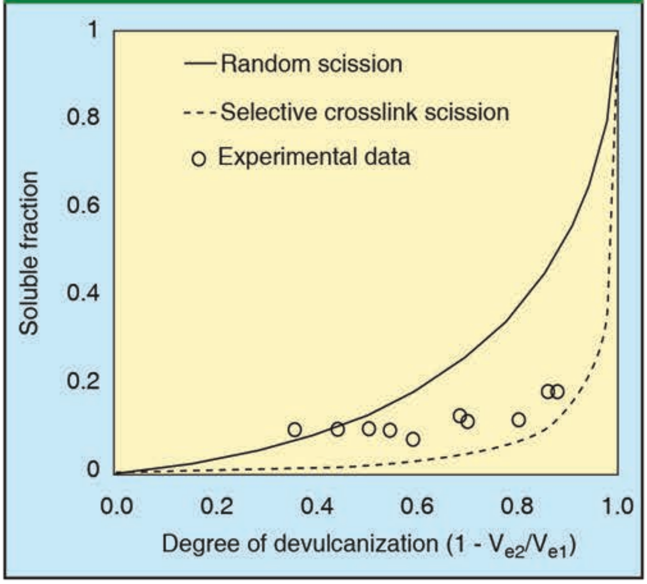
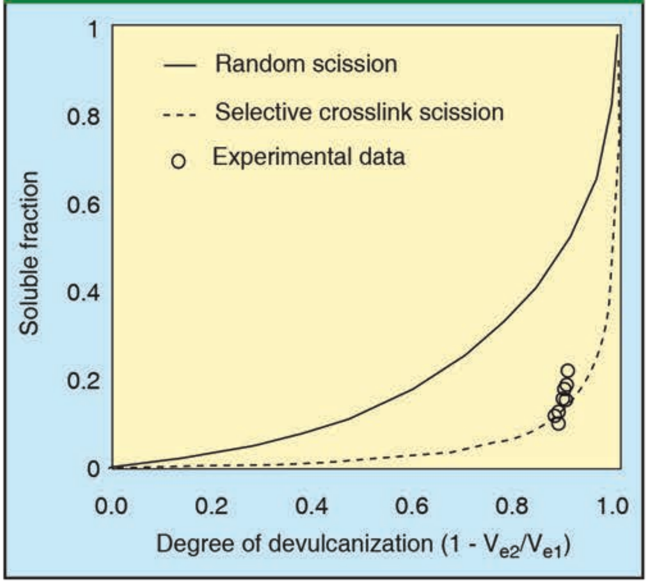


Figure 4 - Horikx plot for devulcanized tire tread crumb samples



circles represent experimental data. It can be seen that the experimental data are scattered between the two lines. This indicates that the degree of devulcanization and type of scission process depends on the EPDM material and conditions used during devulcanization.

Figure 4 shows the Horikx plot for tire tread crumb experiments. This rubber crumb is produced by grinding the tread of end-of-life (scrap) truck tires. Again, the dashed line represents the selective crosslink scission model according to equation (1), and the solid line represents the random scission model according to equation (2). The open circles represent experimental data. In this case, the experimental data are very close to the dashed line. This clearly indicates that the resulting type of scission is highly selective, and that the degree of devulcanization is relatively high.

Tyromer's standard line has continuous production capacity of over 700 kg (~1,500 pounds) per hour. There are no devulcanization chemicals or chemical solvents used, there are no additives, and no waste is created during the manufacturing process. TDP currently replaces about 20% of masterbatch in tire compounds and has been used in the tire industry for the last three years. The company has a new, larger facility coming online in 2019 to supply a major tire manufacturer, has licensees in Europe and China, and looks to continue licensing its technology around the world in order to create the biggest impact on scrap tires.

Important differences between devulcanization and reclaim are the no effect level and final applications of the rubber. For example, in a tire tread compound, Tyromer devulcanized rubber can usually be added at 10-20% with excellent results, compared to 4-8% with reclaimed rubber or modified crumb rubber such as MRP. Optimization is important; however, in some cases, TDP can simply be dropped into a masterbatch compound with great results. Because of the structure of TDP compared to crumb rubber or reclaimed rubber, TDP can be used in a greater number of applications and in higher amounts. It is suitable for:

- New tires, tread and sidewall
- Retreaded tires (pre-cure, mold-cure)
- Conveyors and material handling
- Injection molding, and more

Enabling a circular economy

A circular economy is an economic model where products at end-of-life are recycled back into their originally intended purpose. The Ellen MacArthur Foundation, whose mission is to accelerate the world's transition to a circular economy, boils it down to three major points:

- Designing out waste and pollution
- Keeping products and materials in use; extending life
- Regenerating natural systems

This means identifying methods to turn scrap tires back into new tires. In the past, it has proved difficult to incorporate recycled tire rubber back into new tires because the industry has high standards and quality requirements, and recycled rubber has not met these requirements. However, by aligning and organizing individual linear economies and working together through the supply chain, quality can be controlled and the result can be a high-quality, clean, consistent recycled material readily usable by the tire industry.

Devulcanization, while promising, is not the only technology working to implement a circular economy in the tire industry. Pyrolysis, or thermal decomposition, can reduce scrap tires to their basic elements and recover recycled carbon black (rCB), oil, gas and steel. Micronized rubber powder (MRP), which is created through a cryogenic grinding process and ranges from 50-200+ mesh in size, is also growing in usage and application. Because the scrap tire problem is so immense and widespread, these other technologies will also play important roles in the greater solution.

Impact on the market

The potential market impact of devulcanization on the tire and rubber industry is enormous. There is opportunity to transform the way the industry consumes resources, and reduce the amount of chemically reclaimed rubber produced. Not only will the environment benefit, but manufacturers, dealers and ultimately consumers can realize cost savings. Devulcanized material is substantially cheaper than virgin material, and incorporating devulcanized material into operations now will insulate companies from natural rubber cost increases in the future.

The average scrap tire weighs approximately 20 pounds, and over one billion scrap tires are produced annually. Worldwide, new tire production is approaching 3 billion units annually. Utilizing scrap tires and devulcanization to replace even just 5% of virgin material would result in billions of pounds of resource conservation and meaningful greenhouse gas emission savings. The market demand for devulcanized rubber and other recycled materials is growing, but not yet the industry norm. Such as with any new product, it takes commitment to development. Each manufacturer is different, and each company will need to optimize the material based on their own recipes and needs. By incorporating devulcanized material into operations now, technical teams can gain familiarity and confidence in the product, and slowly increase usage in load levels and number of applications. When the price of natural rubber increases, those already using devulcanized material will have a large competitive advantage and added insulation from this price risk.

China is the world's major reclaimed rubber producer, and last year produced about 5,000,000 tons of reclaimed rubber. The medium and high-end reclaimed rubber can, in many cases, be substituted with devulcanized material at a similar price point, plus offers added environmental and sustainability benefits. With this volume of reclaimed rubber being produced, adding just 1% of chemicals by weight would mean over a hundred million pounds of extra chemicals used each year. Again, it will take work and experience with the product to optimize and find the best fits, but the reality is that devulcanized material is becoming much more viable.

Open innovation strategy needed

The tire and rubber industry can be secretive. Companies own patents and proprietary recipes, and operate clandestine research and development programs. Because of the sheer volume of tire manufacturing, small competitive advantages are amplified and must be protected. However, as with many new materials, including devulcanized rubber, information and technical resources should be available to spur adoption.

In terms of devulcanization, open innovation does not require giving away sensitive information; open innovation is more of a mindset and willingness to work together. There should be substantial dialogue between parties to develop a solution that works well for both sides. This is particularly important for testing and developing new recipes and compounds. We should consider that although each company has its own set of processes and methods of evaluation and testing, through collaboration we can generally achieve more together than the sums of individual efforts. Sharing information and knowledge is paramount to the success and more widespread adoption of recycled materials in the tire industry.

Remaining challenges for devulcanization

Although devulcanization technology has progressed significantly in recent years, a number of challenges remain, including poor public perception of recycled material, needing more development for synthetic rubber compounds, and controlling the consistency and quality of feedstock material.

Recycled material is unfortunately synonymous with second-rate or lower quality, and the general perception is that recycled material is inferior. The average scrap tire is five years old, so some degradation of the rubber is inevitable and expected over time. While devulcanized tire rubber will always be slightly lower quality than virgin rubber, under the right conditions it can perform quite similarly to virgin rubber and can be a substitute for high quality masterbatch compounds. Changing perception, however, is not a quick or easy task. Many working in the rubber industry have heard about devulcanization or tried it years ago, only to run into dead ends or reasons why it would not work. It will take education, dialogue and hands-on experience with the material to break historical thought processes.

Another challenge facing devulcanization is the processing of synthetic rubber compounds. To create world-changing impact, passenger or PLT tires must be devulcanized successfully. While devulcanizing synthetic heavy compounds does work, the quality and physical properties of these compounds are generally lower than for compounds containing higher levels of natural rubber, such as truck and OTR tires.

On that note, a determining factor in the quality of devulcanized rubber is the source and quality of feedstock. Working solely with clean factory scrap material as feedstock can provide positive results, but this has no effect on the scrap tire problem. Because of the composition of different types of tires and the varying amounts of natural and synthetic rubber, all tires are not created equal for devulcanization. Natural rubber tends to devulcanize at higher levels than synthetic rubber, meaning crumb rubber consisting mainly of passenger tires could have tensile strength and elongation 25% lower than crumb coming from truck tires, and a potentially greater gap compared to crumb from OTR/earthmover tires. However, this does not mean passenger tires cannot be devulcanized and the resulting material used in tires; it just means the load capacity will be slightly less, and like any new material, it needs to be optimized per application and quality requirements. Since devulcanized material is almost always blended into a masterbatch compound and not used at 100%, the stand-alone properties do not always provide a clear indication of final compound quality; devulcanized material must first be mixed into a masterbatch and then compared against the control.

Because different types of tires will provide different results when devulcanized, scrap tire collection and subsequent organization can beneficially impact devulcanization by helping establish standardized crumb rubber grades. Sorting and organizing scrap tires, similar to how plastics are recycled in terms of #2, #3, etc., would provide a higher level of consistency and reliability that is necessary in tire manufacturing. While some processors do this already, many treat all tires the same, since the resulting crumb rubber is used for secondary applications such as playground fill, field turf and basic molded products where performance is not as critical. By aligning individual linear economies to work together, it is possible to create a more feasible circular economy.

Conclusion and call to action

Ultimately, devulcanization technology is improving and offers the greatest opportunity to create a truly circular economy within the tire and rubber industry. Further technological and process development is needed, but potential impact should outweigh work required. While today, the largest companies in the world are spending millions on development of sustainable natural rubber and different sources such as guayule, the same attention should be given to scrap tires and developing sustainable recycling solutions. Devulcanization is about pulling more value from natural resources and reverting to the 4R strategy of reduce, reuse, recycle and renew/recover.

When purchasing rubber compounds, buyers should ask the compounder about devulcanized material and the associated cost savings. For those involved in manufacturing and mixing their own rubber, Tyromer helps customers explore the potential of devulcanization and how it can reduce costs and transform a sustainability strategy.

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