Upgrading Reclaimed Carbon from Tire Pyrolysis for Tire Rubber Applications

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Abstract

Most major tire manufacturers have set a goal of using 100% sustainable materials in tire production by 2050. Carbon black (CB), which is a critical ingredient in rubber formulations and can constitute up to 30% of tire rubber by weight, is currently manufactured from fossil-based byproduct feedstocks and presents a major hurdle to this commitment. Therefore, Cabot Corporation and the tire industry are actively developing circular and sustainable alternatives to conventional CB.

Pyrolysis is a promising, emerging technology in tire recycling. This process produces tire pyrolysis oil (TPO) and reclaimed carbon (rC). Although sometimes marketed as a 1-1 replacement for carbon black, rC falls short in many important performance attributes, precluding its use in demanding "reinforcing CB" applications, and limiting concentrations to < 20% in less demanding "semi-reinforcing CB" applications.

To address some of these challenges, Cabot is developing a technology that upgrades the performance of rC and produces a product with significant rC content. The rC is upgraded to make the higher circular content possible while maintaining rubber performance similar to CB. In this paper, we first examine the performance of un-upgraded rC to illustrate the difficulties it presents with respect to meeting rigidity and other performance targets in rubber composites. We then compare a 30% rC content product made with our new technology with a conventional CB and a 30%/70% rC/CB physical blend. We show that not only can the upgraded product meet the rigidity performance of conventional reinforcing CB, but the rigidity can be tuned by the upgrading process, giving greater flexibility and increased potential to meet industry demands.

Introduction and Motivation

Approximately 20 million tons of waste tires are generated every year.[1] In the developed world, the majority of these tires are burned for energy generation, contributing significant greenhouse gas emissions, and a smaller fraction is recycled into low value rubber applications.[2] In the developing world, these tires are more likely to be discarded or landfilled.[3]

As the world moves towards a circular economy, various emerging technologies seek to address these wasteful practices. Tires may be ground to create crumb rubber which can then be incorporated into new rubber products. Unfortunately, the useable content of crumb rubber in high value applications like tires is limited to < 10% by poor performance characteristics. An alternative is to chemically recycle the rubber, breaking it down into constituent parts by pyrolysis. This approach may allow for higher levels of recycled content.

Pyrolysis is the process of heating a material in the absence of oxygen. Tire rubber is split into tire pyrolysis oil (TPO), char and syngas.[4] TPO may be used directly in the synthesis of sustainable carbon black CB (sCB) although the yield is lower than for common feedstocks. The tire char is sometimes ground, pelletized and used as a low-cost alternative to CB in tires, although, as with crumb rubber, the sustainable content achievable is low. Here we refer to ground and pelletized char as reclaimed carbon (rC) to distinguish it from carbon black (CB).

Carbon black is a highly technical material and is difficult to replace. When carbon black was first introduced in tires, the service life of a tire increased manyfold.[5] CB nanoparticles are compounded into rubber at high loadings (up to 35 wt%) to increase the rigidity, fatigue life, wear resistance, UV resistance and other performances of the tire.[6] There are over 40 standard grades of carbon black, ranging from coarse low-hysteresis grades (semi-reinforcing N772, N550 etc.) to rigidifying reinforcing grades (e.g. N330, N339) to abrasion-resistant tread grades (e.g. N234, N115 etc). Any rC produced from end-of-life tires will contain a mixture of these very different materials. In addition, the rC contains 10-30% of inorganic ash, including zinc sulfide, silica, and inorganic minerals sometimes added to tires.[7] Thus, it is inherently difficult to take a pyrolysis char that constitutes a highly modified mix of these carbons and use it to replace a single grade of carbon black in new tires in appreciable quantities.

In this paper, we focus on upgrading tire char so that it can be used as an alternative to carbon black in greater concentrations. First, we review the current approach utilized in the industry and the shortcomings of materials currently available on commercial scale. Then we present our technological approach. Finally, we present data on upgraded tire char which can be used to replace higher grades for carbon black at greater loadings.

Current State of the Technology Industry Uses

Several companies are producing rC from tire char, so that this can be considered a widely available product. The process can be summarized as follows. First, the tire char is crushed and sieved to remove rocks and other debris. Magnetic separation is then used to remove any residual steel cable. The material is then milled, using, for example a jet mill or a classifier mill, with the goal of attaining D90 < 20 µm. At best, these methods are able to reduce the tire char to a particle size distribution with a D90 < 10 µm. The material is then pelletized by adding water and agitating in an industrial pin mixer. Finally, the pellets are dried.

We have previously reported on the properties of this "1st generation" (Gen1) material.[8] The physical properties were similar to those expected from a blend of tire carbon blacks – with several exceptions. First, the particle size of carbon black is much finer, with D90 of ~0.5 µm, compared to 10-20 µm for Gen1 rC. Second, the structure (excluded volume in rubber) of Gen1 rC is significantly lower. Finally, the ash content is significant, in the 15-25% range, composed mainly of zinc sulfide and silica. The ZnS is derived from the curing system used in rubber, while silica is used in place of carbon black as a reinforcing filler in some applications. These differences have been reported by other groups as well.[7,9,10]

The in-rubber performance of the tested Gen1 rC materials falls short of CB grades in several respects. First, the rigidity is consistently lower than that of CB. This is likely related to the lower structure of rC.[11] Second, the dispersion is reduced, as measured by optical[8] and electronic[12] microscopy, perhaps due to the ash content or the larger particle size. Finally, the fatigue resistance of rC composites is reduced compared to CB reinforced rubber. This is likely related to the larger particle size of rC or it's reduced dispersibility in rubber.

It is difficult to compensate for the shortcomings of rC by modifying the formulation. For example, if particle loading is increased to compensate for the low rigidity, the fatigue life is reduced even further. However, it is possible to use a partial substitution of some CBs with rC without appreciable degradation of performance. For example, STERLING ™ SO RC110 reinforcing carbon, manufactured by Cabot Corp., is a physical blend containing 10% Gen1 rC, designed to replace semi-reinforcing N550. The limit increases to 20% for replacing the less reinforcing N660 grade.[13] The technological capability of Gen1 rC is summarized in Figure 1.

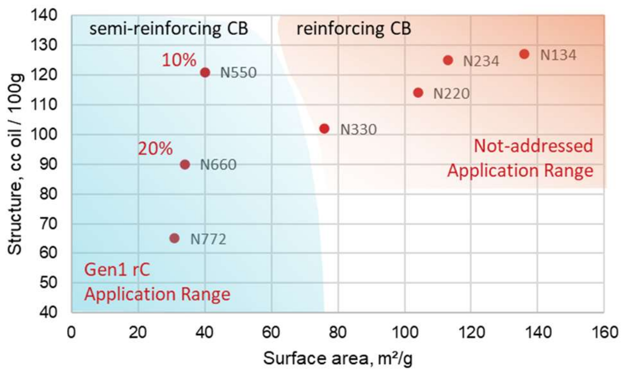

Figure 1 The automotive carbon black application space plotted as structure (composite rigidity) vs surface area (composite toughness). Commercial reclaimed carbon (Gen1 rC) can only address semi-reinforcing applications, and then only in small concentrations.

Several attempts have been made to upgrade reclaimed carbon to address these shortcomings. Most notably, aqueous chemical deashing has been used to reduce the ash content of the rC. In this approach, tire char is milled, dispersed in water and exposed to acid and or base leaching agents.[7,14] A notable study was conducted as part of the REMADE project.[15] The removal of the ash results in partial recovery of reported properties including increased tensile strength[14] and in some cases rigidity and abrasion resistance.[16] Although dispersion and fatigue performance were not mentioned, the resulting properties appeared to be close to semi-reinforcing grade CB (N772). The performance of the CB becomes more difficult to match for reinforcing grades (e.g. N330).

Despite the first patent being filed 5 years ago[17] no commercial scale production has started or is being planned, to our knowledge. This is perhaps due to the high cost and environmental concerns over acid deashing.[15] Dry phase deashing techniques, for example HCl vapor treatment, may address these concerns but they can only remove volatile contaminants such as Zn and S.[18]

As an alternative to acid leaching, etching has been used to remove part of the carbon, reducing the size, and increasing the surface area and structure of the particles. Steam,[19] CO_2[16] and air[20] have been used successfully. The performance of the product can approach that of reinforcing CB in some respects. Unfortunately, the process of etching converts a large fraction of the carbon to CO_2. Thus, these methods are not appropriate in the context of a circular economy.

In conclusion, the majority of commercially available Gen1 rC is useable only at very low concentrations in semi-reinforcing applications (e.g. STERLING™ SO RC110, 10% rC, Cabot Corp) which are far from the goals of the circular economy. Current upgrade technologies, while improving some properties, also appear to fall short of demanding rubber applications and may not be commercially viable. An acute need therefore exists for improved rC upgrading methods.

Technology Approach

The main performance drawbacks of reclaimed carbon are poor fatigue resistance and low rigidity. Fatigue performance relates to the critical flaw size of the material, and therefore to improve this performance the dispersibility of the filler, especially relating to the largest undispersed particles, should be improved. The rigidity of the material is related to the filler structure – the amount of matrix volume occupied – and the quality of filler-matrix interface. Both performances are improved when the material is upgraded using the method described in this paper.

Reclaimed carbon is introduced into the Carbon Black reactor along with feedstock, Figure 2. The feedstock is converted to pyrolytic carbon which both renews the surface of the rC and creates new carbon particles. The advantage of this approach is that it requires no expensive chemicals or new process steps, as does deashing, nor does it result in significant loss of carbon, as does steam etching. Thus, we believe it to be economically viable. This concept is a new application of a proprietary Cabot process technology.[21]

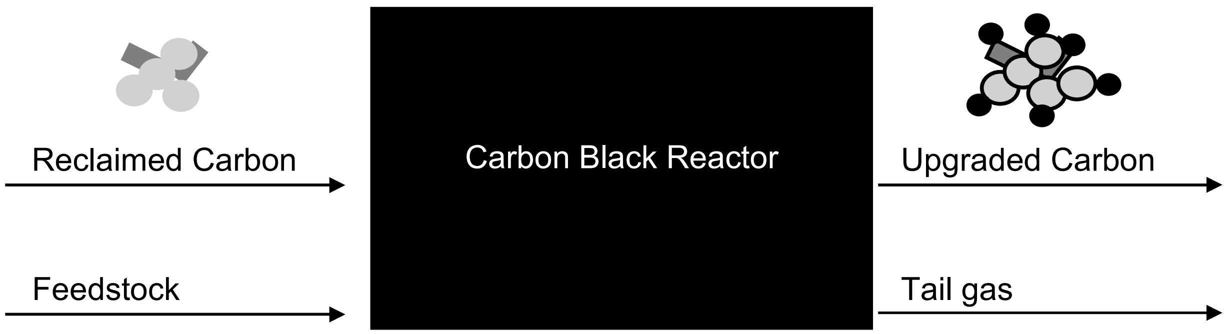

Figure 2 Reclaimed carbon is upgraded by directly feeding into the carbon black synthesis reactor. A layer of carbon is coated on the rC surface, creating a surface similar to a normal carbon black surface, and increasing particle structure.

Since Gen1 rC can already be used at low concentrations to replace semi-reinforcing CB (N700, N600, and N500 series), an interesting target becomes the N3XX and N2XX series, which are reinforcing, and are used in more demanding tire applications. Thus, to have the biggest impact, this technology should be designed to target the reinforcing carbon black space.

The properties of the synthesized carbon differ significantly from Gen1 rC[a], Table 1. The surface area is increased to match N330 specifications. The structure, as measured by OAN, is in the range of N330 and N550. Structure is important because it imparts rigidity to the rubber product, and can be controlled to some extent by reactor conditions. In this example, "Upgraded 20% rC -1" was produced with a lower structure than "Upgraded 20% rC -2", demonstrating the sort of control needed to synthesize product to customer specifications.

Table 1 Comparison of material properties for carbon black, reclaimed carbon and upgraded carbon containing 20 and 30% rC.

Property	Test	Unit	N550 CB	N330 CB	Gen 1 rC	Upgraded 20% rC -1	Upgraded 20% rC -2	Upgraded 30% rC
Surface Area	STSA (statistical external)	m^2/g	39	76	52-67	95	88	79
Structure	OAN (oil absorption)	mL/100g	121	102	79-98	112	137	118

Although the surface area is moved closer to CB, the true test is the performance in rubber. A commonly used metric is the tensile modulus – the ability of the rubber to resist deformation. We plot the true (area-corrected) secant modulus in Figure 3. In the 20% rC content experiment (left), the rigidity of the circular material can be raised to match (Upgrade 1) or even exceed (Upgrade 2) the rigidity of reinforcing N330 CB. Even in the case of 30% circular content the rigidity can be made to match N330 CB (Figure 3, right).

In addition to the "Upgraded rC" samples we also plot the modulus for "rC blend" samples. The blends are created by adding the same reclaimed carbon starting material into the rubber mixer in combination with N330 CB. Without the upgrade process, these materials cannot match the performance of CB.

[a] The ranges given are those measured by Cabot for similar commercial materials from various manufacturers.

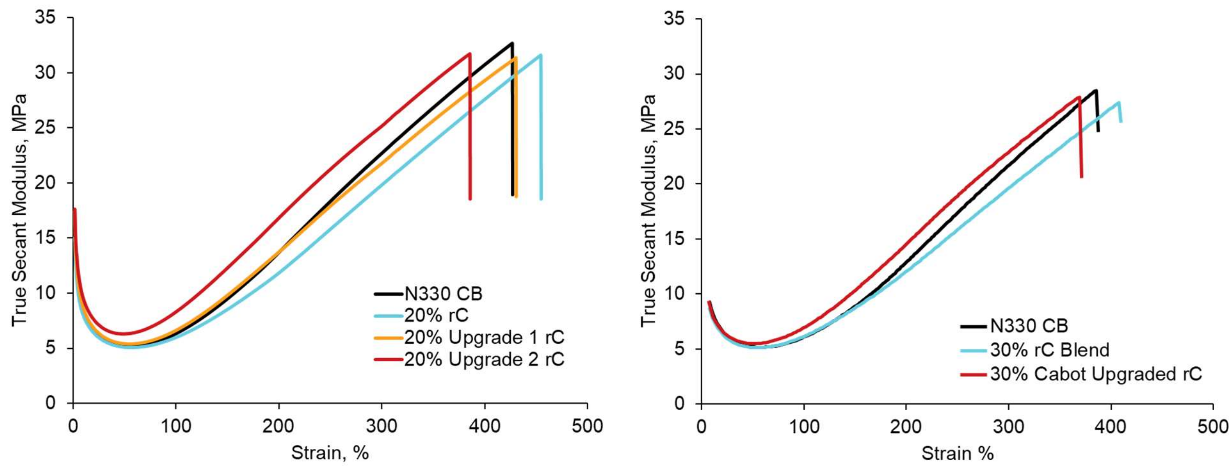

Figure 3 Tensile modulus of rubber reinforced with Upgraded rC compared to Gen1 rC at the same circular material content and to N330 CB.

In addition to rigidity, a rubber compound must possess a series of other performances and characteristics to be useful in tire technology. Table 2 summarizes the properties of rubber composites reinforced with the upgraded materials described above. The upgrade technology improves dispersion in rubber, however the dispersion does not quite match CB. Rigidity is improved across the board – tensile, indentation hardness, and shear rigidity are all improved to match N330. Hysteresis is normally lower for rC, which is good for tire performance. Importantly, the upgrade process does not degrade this benefit. This is important because as we increase circular content, we do not want to increase vehicle carbon emissions by increasing tire hysteresis. Finally, processability is not adversely affected by the upgrading process which should give confidence to tire manufacturers that the material can be successfully industrialized.

Table 2 Properties of rubber composites reinforced with rC blends as well as Upgraded rC.

Property	Test	N330 CB	20% blend	30% blend	20% rC Upgrade #1	20% rC Upgrade #2	30% rC Upgrade
Dispersion	Dispergrader, Undispersed area, %	2.1	8.2	8.8	5.4	5.2	5.6
Rigidity*	Tensile stress, 50%	100	98	94	105	120	107
	Tensile stress, 300%	100	89	86	98	112	113
	Hardness	100	99	96	101	105	98
	Dynamic G' 10%	100	97	94	115	110	100
Hysteresis**	Rebound	100	103	105	98	98	107
	Dynamic max tan delta	100	110	113	102	94	120
Processability***	Mooney ML(1+4)	100	101	98	98	92	97

*Normalized by N330 so that higher is more rigid
**Normalized by N330 so that higher is less hysteresis
*** Normalized by N330 so that higher is lower viscosity

Thus, the technical approach can be used to match the properties of N330 grade CB at 30%. We propose that the product would be delivered as pellets, similar to CB, so that it can be easily integrated into existing processes.

Discussion

It is important to consider the specific applications of a CB grade when determining whether the circular material can be useful. N330 is a reinforcing grade used to provide rigidity to parts of the tire such as the under-tread and bead. Thus, it is particularly important to match the shear rigidity of CB and not to exceed the hysteresis. The dispersion, on the other hand, is less important, so long as fatigue life is not impacted. At these low concentrations of rC (<30%) in the upgraded material fatigue life is generally not impacted. However, if the rC content were increased fatigue performance would have to be monitored.

On the whole, the tread may contain as much as half of the rubber in a tire. The tread is reinforced with more reinforcing grades such as N234 and N115. These grades provide excellent abrasion resistance which is needed in a tread compound. In order to match the performance of these grades this technology would have to be improved to also provide excellent dispersion. Higher surface area would also be necessary. If these aspects can be achieved, the improved hysteresis of rC can be of great advantage – matching the wear performance of existing tires while reducing fuel consumption would be highly attractive.

Another important avenue for exploration is the quantity of rC which is fed into the reactor compared to the quantity of feedstock. Increasing the quantity of rC would increase the circular content but would be a more radical change of the carbon black synthesis process and would require additional research.

Conclusions and Recommendations

As produced, reclaimed carbon (rC) can only be used in small amounts and in applications which require the least reinforcing grades of carbon black. To address this shortcoming, we have developed a patented process which introduces reclaimed carbon into a reactor and coats it with a layer of fresh carbon. The resulting material can be used in more demanding applications at higher concentrations without jeopardizing performance. However, tread grade carbon blacks remain out of reach. More work would be needed to further improve this process to target the most demanding applications at high loadings of circular material.

Acknowledgements

The authors would like to thank the research, marketing and management staff of the Performance Materials business unit for their support in developing this new manufacturing technique.

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