New approach to circular economy for tires

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Executive summary

Tire conversion technologies can be attributed to three generations.

Generation 1 mostly was extracting oil from tires. Generation 2 focuses on recovery of carbon black (rCB). And the future Generation 3 recovers and upgrades carbon black.

Multiple publications suggest that Generation 2 (i.e. pyrolysis, carbon black) at best is able to exhibit semi-reinforcing in-rubber behavior because it consists of a mix of various grades of carbon black used in different parts of tires, with inorganic impurities and carbonaceous residue, while demonstrating reinforcement level colloidal properties (i.e. "in-rubber performance shift").

G3C technology, a representative of Generation 3, is upgrading rCB and offsetting detrimental effects of "in- rubber performance shift." The G3C process can produce reinforcing rCB and reduce PAH contents to acceptable levels.

The notion of three generations of tire conversion technologies was introduced by G3CT at the First RCB Congress in Berlin in May 2019.[1]

Generation 1 includes earlier pyrolysis systems, focusing on oil extraction from scrap tires. Pyrolysis oil can be cleaned up and further refined to gasoline, diesel and other oil products

TECHNICAL NOTEBOOK
Edited by John Dick

The Generation 2 category includes pyrolysis systems, focusing on recovery of carbon black (CB). Recovered carbon black (rCB), produced by pyrolysis, consists of the CB, which was originally built into tires, inorganic impurities and a small amount of carbonaceous residue. Oil also is extracted as a byproduct. Pyrolysis rCB can be used to produce carcass components of tires, industrial rubber and plastic products, as well as some other products.

Generation 3 category includes systems that not only recover but also upgrade CB built into tires. The Generation 3 systems are capable of producing reinforced rCB from the entire tire recycled, which can be used in tire tread, as well as semi-reinforcing rCB suitable for tire carcass.

In-rubber performance shift

It is a commonly known phenomenon of "in-rubber performance shift," which manifests itself in inferior in-rubber performance of rCB, compared to the physical rubber characteristics expected based on the rCB colloidal properties values (e.g., OAN and STSA). This phenomenon was described in several publications, including slide 31 in the presentation by C.G. Jung and J. Bouysset[2] (**Fig. 1**).

As illustrated in **Fig. 1**, rCB rubber performance ranges are shifted in the chart along the surface area and structure axes toward lower grades (red arrows by author).

According to C.J. Norris at al,[3] "Colloidal properties suggest the pCB materials to have a reinforcing potential between that of N330 and N550 CBs, whereas physical property data suggest that they are more akin to the N700 series."

C. Norris and M. Bennett[4] demonstrated yet another illustration of this phenomenon, as shown in **Fig. 2**:

The implications of this phenomenon are:

- ELT-derived pyrolysis rCB can only replace semi-reinforcing vCBs; and
- Traditional in-rubber performance prediction model, which works for vCB, does not work for rCB.

Reasons behind in-rubber performance shift

Several researchers attempted to explain the reasons behind the phenomenon of in-rubber performance shift. Pieter ter Haar, the vice chair of ASTM International Committee D36, argues that additional (in comparison to vCB) rCB contents (i.e., inorganic contaminations and chemical effects) are responsible for the suboptimal rCB performance in rubber compounds (**Fig. 3**).[5]

Chris Norris suggests that rCB underperforms in-rubber compounds due to suboptimal aggregate size distribution, limited cleanliness, deteriorated surface chemistry and composition.[6]

rCB in-rubber performance prediction model

Per referenced the above research in saying that rCB in rubber performance prediction model have additional dimensions comparing to vCB in rubber performance prediction model (**Fig. 4**). This is in addition to the two fundamental dimensions responsible for binding rubber and CB molecules in rubber compound (i.e., Surface Area and Structure). The additional dimensions include Cleanliness (i.e., oily residues and PAHs), Agglomerate PSD (i.e., particle size distribution itself, as well as sieve residue), composition (i.e., inorganic impurities contents) and surface chemistry (i.e., carbonaceous residue) other.

G3C approach

G3C approach is based on recognition of utmost importance of fundamental factors A and B (i.e., surface area and structure) for filler binding with rubber, leading to better performance in rubber. Therefore, the G3C approach implements a drastic increase of STSA and OAN to significantly increase filler/rubber binding and, by doing so, mitigates detrimental effects of factors E, E and F.

Factor C also is addressed by G3C process, but is not unique to it. Oily residue and PAH contents are reduced.

Factor D is addressed by thorough milling and classifying, which also is not unique to the G3C process.

Factors E and F are not specifically addressed by the G3C approach. The improvements in these areas are possible using methods complementary to G3C and would further improve rCB in-rubber performance.

Drastic increase of rCB surface area and structure can be viewed as a mitigation measure for the phenomenon of rCB in-rubber performance shift, as it provides a better starting point for this phenomenon to manifest itself as illustrated in **Fig. 5** consequently, produce better in-rubber results.

G3C intellectual property and differentiation

G3C Technologies was awarded with U.S. (9,663,662), Canadian (3 015 887) and Indian (335664) patents on the G3C process. Several national phase patent applications are filed in selected countries.

The process differentiates itself from all traditional pyrolysis processes in the following ways:

- G3C process recovers and upgrades rCB vs. traditional pyrolysis, which just recovers CB;
- The same G3C reactor can produce a variety of rCB grades with different properties from the same feedstock vs. the few grades typically produced by a conventional pyrolysis reactor;
- G3C rCB grades are replacing reinforcing vCB grades (i.e., for the entire tire, including tread) vs. pyrolysis rCB, which is replacing only semi-reinforcing vCB grades (i.e., for the tire

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The author

Vitaly Khusidman is a founder and CEO of G3C Technologies Corp. He has 35 years of innovation experience in process control for the chemical, nuclear power, pharma and material handling industries, as well as broad experience in financial services. He also is experienced in starting and growing companies, as well as in business and financial management.

Khusidman has a track record in leading multi-discipline international teams of scientists, engineers and innovation task forces. He has authored several papers and patents and is a frequent speaker on the topic of the circular economy for tires and the methods of scrap tire conversion to recovered carbon black. He is a member of ASTM International Committee D36 for recovered carbon black.

Fig. 1: rCB in-rubber performance shift.[1]

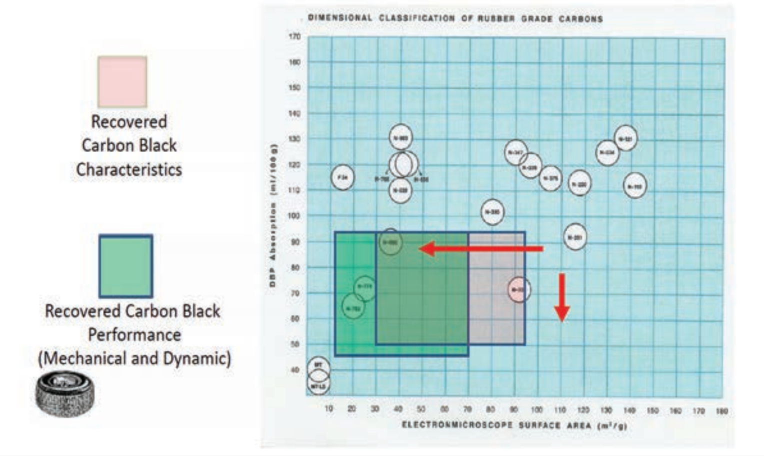
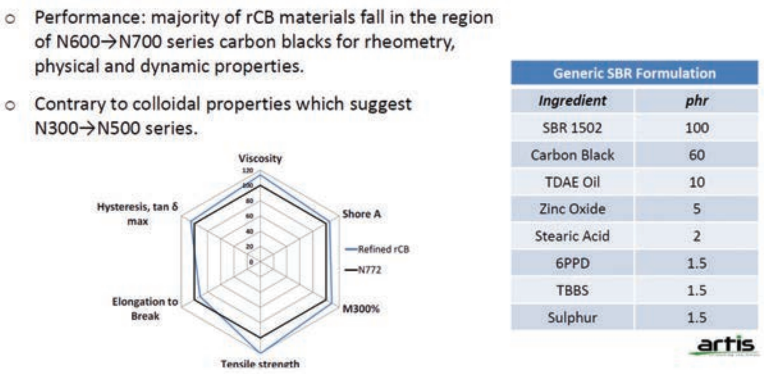


Fig. 2: Pyrolysis rCB with colloidal properties akin N3XX/N5XX performs in rubber as N6XX/N7XX.[4]

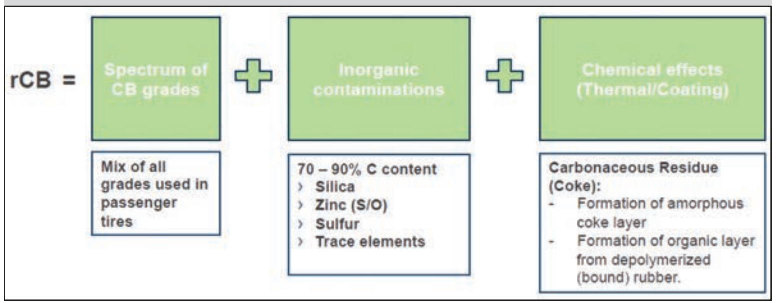


- Performance: majority of rCB materials fall in the region of N600→N700 series carbon blacks for rheometry, physical and dynamic properties.
- Contrary to colloidal properties which suggest N300→N500 series.

Generic SBR Formulation

Ingredient	phr
SBR 1502	100
Carbon Black	60
TDAE Oil	10
Zinc Oxide	5
Stearic Acid	2
6PPD	1.5
TBBS	1.5
Sulphur	1.5

Fig. 3: Reasons behind in-rubber performance shift.[5]

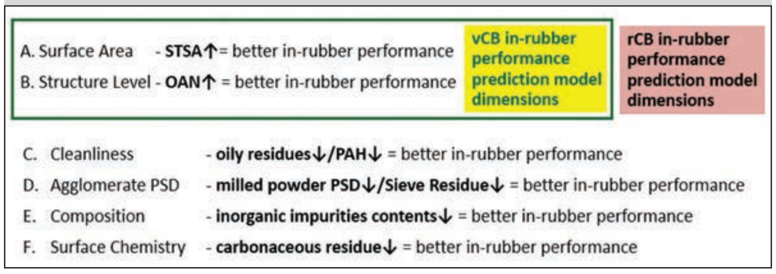


Mix of all grades used in passenger tires

70 – 90% C content
› Silica
› Zinc (S/O)
› Sulfur
› Trace elements

Carbonaceous Residue (Coke):
- Formation of amorphous coke layer
- Formation of organic layer from depolymerized (bound) rubber.

Fig. 4: vCB vs. rCB in-rubber performance prediction models.



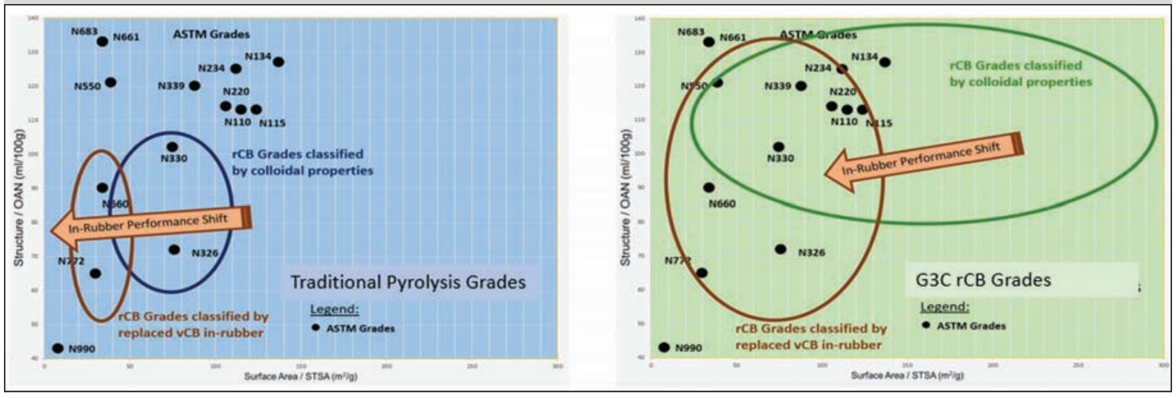
A. Surface Area - **STSA↑** = better in-rubber performance
B. Structure Level - **OAN↑** = better in-rubber performance

vCB in-rubber performance prediction model dimensions

rCB in-rubber performance prediction model dimensions

C. Cleanliness - **oily residues↓/PAH↓** = better in-rubber performance
D. Agglomerate PSD - **milled powder PSD↓/Sieve Residue↓** = better in-rubber performance
E. Composition - **inorganic impurities contents↓** = better in-rubber performance
F. Surface Chemistry - **carbonaceous residue↓** = better in-rubber performance

Fig. 5: G3C approach for mitigation detrimental for in-rubber performance factors.



carcass only); and

- While pyrolysis rCB, post-treated via inorganic impurities reduction, can theoretically achieve the entry level (i.e., N330) reinforcement in rubber, the G3C rCB is capable to achieve higher reinforcement (i.e., like N339) without such post-treatment.

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G3C process upgrades rCB

The G3C process upgrades rCB recovered from scrap tires by reducing sizes of primary CB particles (aka nuclear particles or nodules). The degree of reduction of primary particle sizes is controlled by process parameters. The greater the reduction, the lower the yield of the upgraded rCB.

Automobile tires are built with different grades of CB, which are used for different tire parts. The diagram in **Fig. 6** illustrates the contents of various CB grades of a hypothetical scrap tire rubber (based on a typical 18-inch U.S. tire, as suggested by Wolfersdorff Consulting, Berlin). The average nodule size for such CB mix of grades is 35 nm, which matches grade N4XX according to ASTM D1765 - 95a Historical (the newer versions of ASTM D1765 no longer specify grades via primary particle sizes, instead nitrogen surface area is used). The same distribution of grades and the average nodule size are expected to be found in the rCB after the tire is processed with a conventional pyrolysis process.

Fig. 6: Theoretical model for nuclear particle size reduction by G3C process.

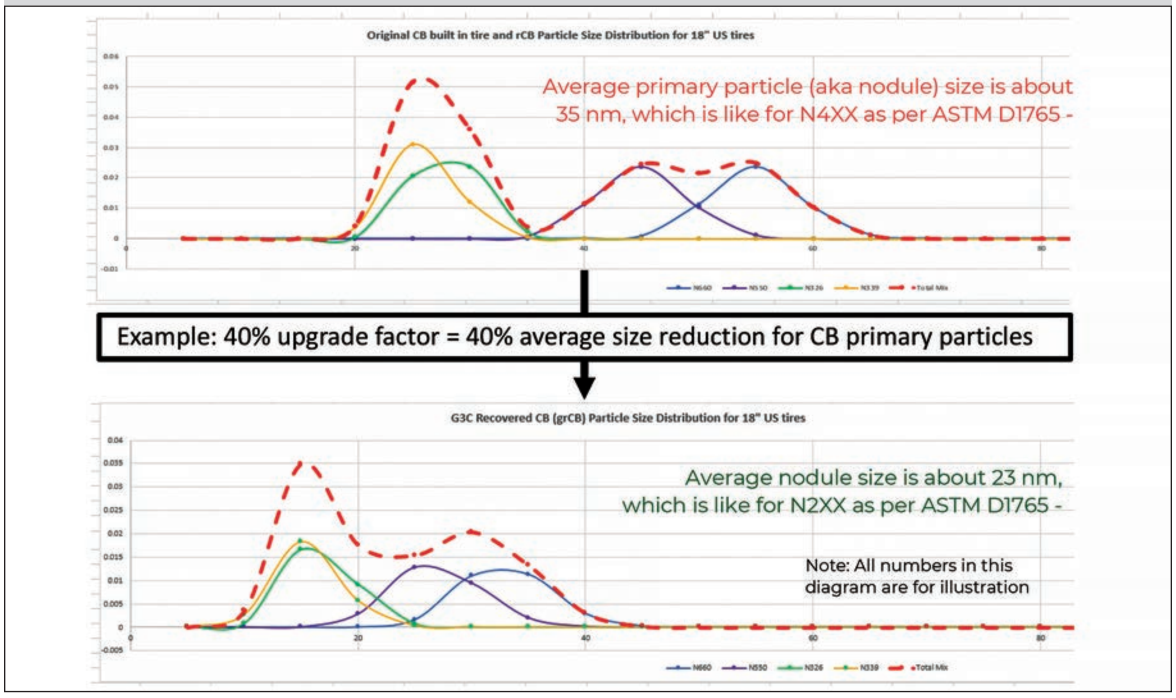
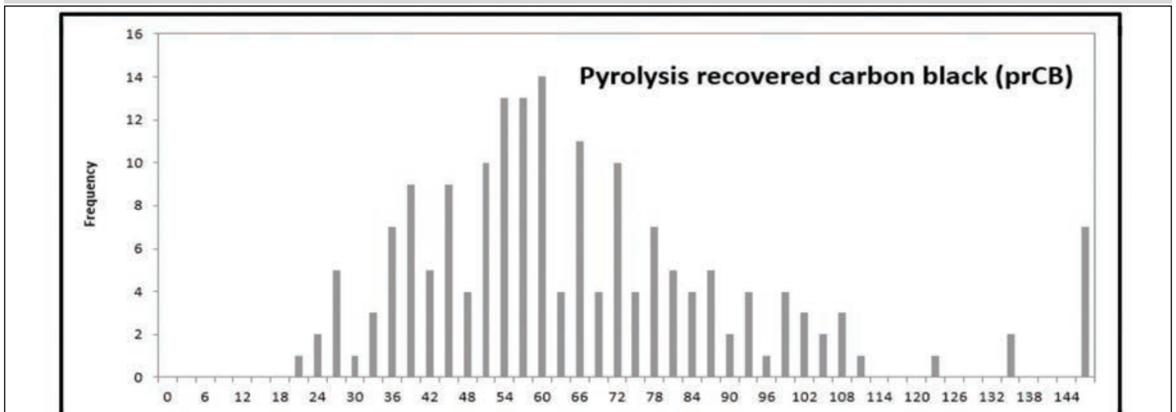


Fig. 7: Experimental results for nuclear particle size reduction by G3C process.



After G3C processing with 40 percent upgrade factor (i.e., average reduction of primary particle size) and with an assumption that all primary particles are reduced in size proportionally (which is a simplified model) the average size of a nodule was reduced to 23 nm, which matches grade N2XX according to ASTM D1765 - 95a Historical. Reduction of nuclear particle sizes effectively causes upgrade of the rCB mix of grades compared to the mix of grades that was originally built into tires or recovered using traditional pyrolysis. The diagram in **Fig. 6** also illustrates that PSD of upgraded rCB mix becomes narrower and its multi-modal shape is less apparent than in the case of original PSD.

The actual control experiment was conducted in G3CT's lab in Tbilisi, Republic of Georgia, using truck tire feedstock. The same material was separately processed with traditional pyrolysis and with G3C process. The pyrolysis produced rCB (prCB) and G3C process produced rCB (grCB). Both prCB and grCB were analyzed by Akron Rubber Development Laboratory Inc. in Akron (www.ardl.com) using ASTM D3849 method (**Fig. 7**).

The average nuclear particle size of prCB was evaluated as 66 nm, while the same of the grCB was evaluated as 36.9 nm (44.1 percent reduction). The external surface area (STSA) of prCB was measured as 48 m^2/g, while STSA of grCB was measured as 124 m^2/g. These results confirmed the fact of upgrading rCB mix by G3C process.

In-rubber testing of G3C rCB

G3CT has commissioned a project to test in-rubber several G3C rCB grades with wide range of colloidal properties. The rubber compounding and testing was conducted by the Ace Products & Consulting L.L.C. in Ohio (www.aceprodcon.com).

The project included testing of six control vCB samples (i.e., N220, N339, N330, N550, N660, and N774), and six G3C rCB samples (i.e., G3C-1, G3C-2, G3C-3, G3C-4, G3C-5, and G3C-6). All G3C rCB samples were produced from a pyrolysis char with OAN between 86 and 92 ml/100g and STSA between 53 and 72 m^2/g.

The 12 formulations included in the project are shown in **Table 1.** Each formulation contained 100 percent of the filler (i.e., 55 phr) from the respective sample.

Table 2 provides MDR, physical and dispersion testing results for the 12 formulations.

The colloidal properties of the control samples are quoted from ASTM D1765 standard and the properties of the G3C rCB samples are measured using ASTM D2414, D3493 and D6556 methods.

Table 2 shows that selected G3C rCB samples demonstrate physical in-rubber properties comparable to commonly used vCB grades, including reinforcing vCB grades N300 and N339.

For example, in-rubber performance of the following G3C grades resemble the performance of the selected vCB grades:

- G3C-1 rCB is comparable to N339 (red outline);
- G3C-2 rCB is comparable to

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Fig. 8: DMA testing results for selected G3C rCB and control vCB samples.

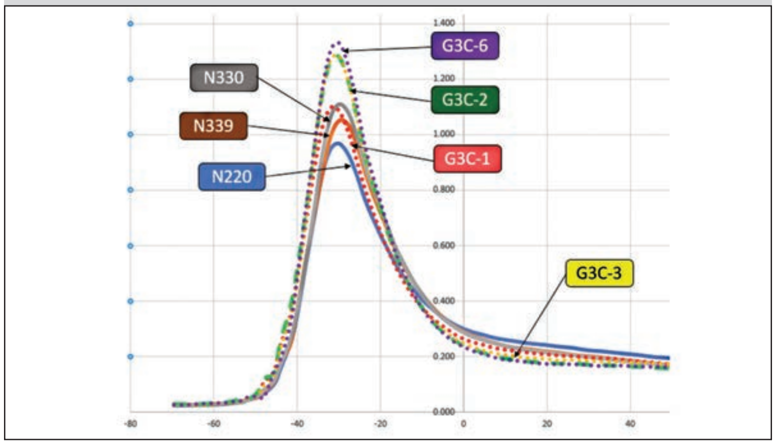

Fig. 9: G3C technology implementation models.

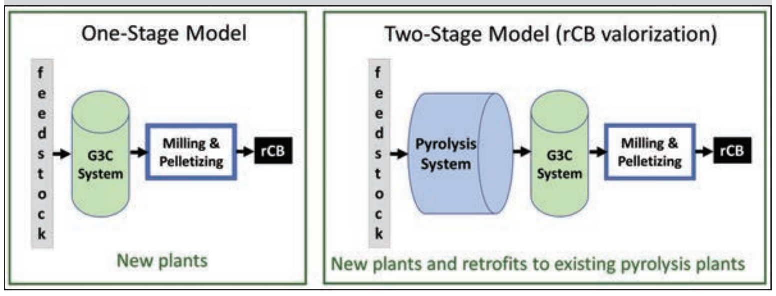

Table 1: Formulations for G3C rCB in-rubber performance testing.

Raw Material, phr	vCB control samples						G3C rCB samples					
	N220	N339	N330	N550	N660	N774	G3C-1	G3C-2	G3C-3	G3C-4	G3C-5	G3C-6
SBR 1783	138	138	138	138	138	138	138	138	138	138	138	138
Filler (vCB)	55	55	55	55	55	55						
Filler (G3C rCB)							55	55	55	55	55	55
RAE Oil	10	10	10	10	10	10	10	10	10	10	10	10
Stearic Acid	1	1	1	1	1	1	1	1	1	1	1	1
6PPD (antioxidant)	2	2	2	2	2	2	2	2	2	2	2	2
Zink Oxide	4	4	4	4	4	4	4	4	4	4	4	4
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TBBS (accelerator)	1	1	1	1	1	1	1	1	1	1	1	1
TMTD (accelerator)	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Total	212.75	212.75	212.75	212.75	212.75	212.75	212.75	212.75	212.75	212.75	212.75	212.75

Table 2: MDR, physical and dispersion results for G3C rCB in-rubber performance testing.

		vCB control samples						G3C rCB samples					
		N220	N339	N330	N550	N660	N774	G3C-1	G3C-2	G3C-3	G3C-4	G3C-5	G3C-6
CB/rCB Properties	OAN, g/100ml	114	120	102	121	90	72	158	131	118	109	110	102
	COAN, g/100ml	98	99	88	85	74	63	113	113	91	92	84	89
	N2SA, m2/g	114	91	76	40	35	30	496	291	360	200	254	188
	STSA, m2/g	106	88	75	39	34	29	395	218	191	166	145	117
MDR (30min, 165°C)	Min (dNm)	1.63	1.67	1.58	1.27	1.04	0.98	1.73	1.34	1.15	1.12	1.17	1.23
	Max (dNm)	9.02	9.12	8.84	8.13	6.63	7.08	9.44	7.48	6.36	6.17	6.26	6.19
	Ts2	3.56	3.35	3.39	3.33	3.93	3.50	2.28	2.46	3.19	2.72	3.00	2.79
	Tc90	6.64	6.21	6.33	6.02	6.96	5.96	5.64	5.68	7.20	5.39	6.33	6.02
Physical Testing	Shore A Durometer	47.1	47.3	47.1	45.2	40.5	41.5	49.8	44.7	41.3	41.8	40.6	41.2
	Elongation, %	725	650	645	687	697	691	664	694	818	700	748	741
	Tensile Strength, MPa	19.2	15.7	13.8	14.9	12.2	12.1	17.8	15.0	14.7	12.6	12.5	13.2
	Modulus 300%, MPa	4.07	4.59	4.18	4.93	3.36	3.78	5.28	3.96	2.80	3.43	2.95	3.00
Dispersion, z-value		98.4	90.6	95.4	97.7	96.4	90.7	96.6	96.4	94.4	92.9	91.6	95.3

Table 3: Abrasion testing results for selected G3C rCB and control vCB samples.

	N220	N339	N330	G3C-1	G3C-2	G3C-6
OAN	114	120	102	158	131	102
COAN	98	99	88	113	113	89
N2SA	114	91	76	496	291	188
STSA	106	88	75	395	218	117
ARI	74.7%	49.3%	59.7%	57.7%	55.8%	51.4%

Table 4: PAH contents testing for G3C rCB samples and for feedstock low temperature pyrolysis rCB.

EU8 – REACH	Feedstock – Pyro Char (ppm)*	G3C-21 (ppm)*	G3C-22 (ppm)*	Cabot Limits (ppm) ***
Benzo[a]pyrene (BaP) (CAS No 50-32-8)	220	nd**	0.0117	0.25
Benzo[e]pyrene (BeP) (CAS No 192-97-2)	134	nd	0.0100	1.00
Benzo[a]anthracene (BaA) (CAS No 56-55-3)	151	0.0593	0.1520	1.00
Chrysen (CHR) (CAS No 218-01-9)	180	0.0722	0.1930	1.00
Benzo[b]fluoranthene (BbFA) (CAS No 205-99-2)	143	nd	0.0178	1.00
Benzo[j]fluoranthene (BjFA) (CAS No 205-82-3)	60.3	nd	nd	1.00
Benzo[k]fluoranthene (BkFA) (CAS No 207-08-9)	74.8	nd	nd	1.00
Dibenzo[a,h]anthracene (DBAhA) (CAS No 53-70-3)	30.6	nd	nd	1.00

Tires

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N330 (blue outline); and

- G3C-4 rCB is comparable to N660 (yellow outline).

Fig. 8 shows the DMA tan delta testing results for selected control and G3C rCB samples. The diagram in **Fig. 8** suggests that selected G3C rCB samples are expected to perform particularly well in tire applications in cold weather and to have good rolling resistance.

Table 3 provides results (i.e., ARI–Abrasion Resistance Index) of abrasion resistance testing for the rubber made from selected control vCB (i.e., N220, N339, and N330) and G3C rCB (i.e. G3C-1, G3C-2, and G3C-6).

G3C process reduces PAH contents

Reduction of PAH contents of rCB has at least two objectives: improvement of rCB's in-rubber performance and compliance with environmental regulations, e.g., by EPA (USA), EU-REACH (Europe), etc.

The G3C process significantly reduces PAH contents of rCB, as illustrated in **Table 4**. PAH contents testing was performed by the MAS-TP lab, Germany (www.mas-tp.com/en).

The PAH contents test was conducted for the low temperature pyrolysis char (Pyro Char), which was used as a feedstock for G3C process and for two different samples of G3C rCB, produced from this feedstock by two process instances. Cabot internal limit for EU8 set of PAHs was used as a reference.[7] The PAH contents of Pyro Char was measured as very high, while both derived G3C rCB samples had PAH contents are well below the referenced limits.

G3CT plant implementation model

The G3C process is capable of conversion of either crumbed tire rubber or pyrolysis char derived from scrap tires into rCB with high structure and high surface area. This enables two implementation models of G3C process in the tire conversion plant, as illustrated in **Fig. 9**.

In the one-stage model, the steel-free crumbed scrap tire feedstock is fed into the G3C System, which produces raw G3C rCB; the latter is milled and pelletized. In the two-stage model the scrap tire feedstock is fed into a traditional low temperature pyrolysis system, then the produced pyrolysis char is forwarded to the G3C system, which produces raw G3C rCB; the latter is milled and pelletized. Each model has pros and cons.

The one-stage model has homogeneous design and can be used in the new plants. The two-stage model can be used in the new plants, as well retrofitted into existing pyrolysis plants. Additionally, the two-stage model allows one to extract most of the high value light oil in the scrap tires in the most efficient way during the first stage pyrolysis process, while sending its solid output and excess energy to the second stage. The mass of the pyrolysis char entering the second stage represents 40-50 percent of the mass of the feedstock fed into the first stage. Therefore, the capacity of more sophisticated and more expensive second stage equipment may be cut at least in half compared to the one-stage model.

Conclusion

The rCB industry, with its reliance on traditional pyrolysis, has fundamental limitations for in-rubber performance of rCB, caused by inorganic impurities, chemical activity and other detrimental to performance factors.

Despite the colloidal properties of the best-known pyrolysis rCB products reaching the values comparable to reinforcing vCB, in-rubber performance of such rCB can only demonstrate semi-reinforcing characteristics without the additional step of removing inorganic impurities. Even with this step, only entry level reinforcing (i.e., comparable to N330) can be theoretically achieved for processing the entire tire. G3C rCB can be further improved by removing inorganic impurities from it.

The G3C process is able to produce rCB comparable to reinforcing vCB through mitigation of detrimental factors by drastically increasing structure and surface area. G3C rCB also has shown comparable to reinforcing vCB DMA and abrasion characteristics.

The G3C process produces rCB with low PAH contents, compliant with U.S. and European PAH contents regulations.

As a result, the G3C process enables a new approach to the circular economy for tires by providing filler for all parts of the tire.

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