UNDERSTANDING RECOVERED CARBON BLACK

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ABSTRACT

As the rubber industry turns its focus to sustainability, recovered carbon black (rCB) has emerged as a commercial candidate to replace conventional fossil-based fillers. Since rCB is a new class of rubber filler, much is still to be understood regarding which of its properties influence final applications performance. The research presented in this paper demonstrates the importance of controlling the aggregate size distribution, silica content, carbonaceous residue content, and organic residue content in producing a consistent rCB product. These parameters are also demonstrated to be the fundamental reasons behind the disparity in performance of rCB and carbon black of similar colloidal properties. The findings of this study also reveal that the properties of an rCB can be tailored for a given application with precise control of the process conditions. [doi:10.5254/rct.23.76956]

INTRODUCTION

Carbon black (CB) is an exceptionally versatile material finding use in a vast array of rubber, plastic, ink, and paint products. The bulk of global CB production finds use in tires, and due to the difficulties associated with recycling of rubber, it has historically been accepted as a single use product. Traditionally, commercial tire recycling processes have tended toward energy generation or civil engineering applications rather than focusing on recovery of the valuable materials used in their construction. More recent advances in pyrolysis technologies have led to the commercialization of recovered carbon black (rCB), finally offering a source of renewable semi-reinforcing filler to the rubber industry and beyond.

A diverse range of technologies has been developed for the production of rCB and, although these are not always referred to as pyrolysis, all involve the thermal breakdown of polymeric material into oil and/or gaseous products, normally in the absence of oxygen. Removal of organic matter leaves behind a solid mixture consisting of CB, inorganic compounding ingredients, and other pyrolysis residues, defined as "raw rCB" by ASTM committee D36.[1] The exact composition and colloidal properties of this solid mixture will be influenced by the selection of both the feedstock and process conditions.[2] Principally, the amount of CB and inorganic materials present within the feedstock will dictate the yield and composition of the "raw rCB," that is, what you put in you get out.[3,4] Note that a small amount of particulate will end up in the tire derived oil, and so recovery may not be 100%. Second, the choice of technology and processing conditions will influence the amounts of both organic and carbonaceous residues (referred to as C_{res} hereafter) formed on the surfaces of the rCB via polymer decomposition reactions.[2,3,5] All of the above factors have the potential to manipulate the form and surface chemistry of an rCB product and, therefore, the manner in which it will interact with a polymer matrix.

Further to the primary thermal process, milling and pelletization steps are normally required before the product can meet the ASTM definition of rCB, being a "solid product recovered via thermal decomposition from rubber goods which contain carbon black, which is free of wire and fabric, and when milled typically gives semi-reinforcing properties in rubber."[1] Exposure to high temperature and deposition of C_{res} during the pyrolysis step has a tendency to fuse filler

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aggregates, resulting in a raw rCB that is difficult to disperse within a polymer matrix.[2] Milling processes are necessitated to reduce the size of these fused agglomerates to improve the dispersibility of the material. Jet and impact classifier mills have been adopted within the industry to reduce particle size to d97 values of typically <10 μm. The extent of milling, and indeed the original aggregate size distribution (ASD) of the fillers within the rubber feedstock, offers a further source of variability between rCB products, and this is something that is considered in detail within this study. Finally, pelletization is normally required to reduce the bulk density of the rCB for shipping and handling purposes. Although the quality of the resultant pellets can have a significant impact on dispersion, the manufacturing processes used by the rCB industry are considered analogous to those used within the furnace CB industry, and so are not considered within this research.

Although the authors of this paper consider rCB to be a unique class of filler, furnace CB remains the closest relative, and so provides a useful point of reference. A four character classification system has been adopted for CB,[6] examples include N550 and N330. The first character is almost exclusively the letter "N," designating the material to impart a normal curing rate when used in rubber. The first digit designates the average particle size of the material, as measured by nitrogen surface area (NSA). As a rule of thumb, the smaller the final two digits, the lower the structure level of the grade; however, this is not a rule outlined by ASTM, and so there are a number of exceptions to this. Numerous studies have demonstrated that adoption of the same classification system is not a viable option for rCB, as it has consistently been demonstrated to be less reinforcing compared to a CB of similar colloidal properties.[2,7–9] Given the potential influences of feedstock selection and processing variables on the properties of the resultant rCB, it is hardly surprising that surface area and structure level measurements alone are insufficient predictors of applications performance. This is not to say that colloidal properties are irrelevant to rCB reinforcement, but rather that other characteristics must also be taken into consideration.

This paper systematically investigates how the properties of rCB, namely, colloidal, ASD, composition, organic residues, and C_{res}, influence the ability to reinforce rubber. By understanding the importance of each of these variables, more targeted testing regimes to characterize and classify rCB can be developed to aid the understanding, and adoption, of this alternative class of filler in commercial applications.

EXPERIMENTAL

ASSESSING THE INFLUENCE OF COLLOIDAL PROPERTIES ON RCB REINFORCEMENT

A total of 25 different rCB products, representing both pilot and commercial-scale operations, were sourced for this study. These samples have been anonymized, and any information relating to process technology, process conditions, or feedstock has been withheld for commercial reasons; nonetheless, the sample sizes are sufficient to provide a broad overview of current rCB fillers. Also included in the study were XT1004, N772, N660, N550, N326, N330, and N234 reference CB samples. The surface area of all samples was established using a Quantachrome NOVA 4200e nitrogen surface area analyzer following the procedure prescribed in ASTM D6556.[10] The structure level of the rCB samples and a selection of the reference samples was determined by HITEC Luxembourg using a compressed volume structure tester complying to ASTM D7854.[11]

Compounds containing the rCB and CB samples were prepared following the natural rubber (NR) based recipe and procedures outlined in ASTM D3192.[12] Test sheets of 2 mm thickness were prepared using a cure time of t90 + 5 min following Moving Die Rheometer (MDR) testing

TABLE I
MODEL FEEDSTOCK FORMULATIONS (VALUES IN PHR)

Ingredient	70 phr silica	50 phr silica	30 phr silica	10 phr silica
Oil extended SBR	137.5	137.5	137.5	137.5
Carbon black (N375)	10	30	50	70
Silica (Ultrasil 7000GR)	70	50	30	10
Zinc oxide	1.3	1.3	1.3	1.3
Wax	1.5	1.5	1.5	1.5
6PPD	1.5	1.5	1.5	1.5
TMQ	1.0	1.0	1.0	1.0
PEG 4000	2.0	2.0	2.0	2.0
Stearic acid	1.0	1.0	1.0	1.0
Si-69 silane	6.0	6.0	6.0	6.0
TBBS	1.5	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5	1.5

complying to ASTM D5289.[13] Hardness and tensile properties of each compound were determined, following ASTM procedures D2240[14] and D412,[15] respectively.

ASSESSING THE EFFECTS OF ASD ON RCB REINFORCEMENT

So far, the in-rubber performance of rCB has been considered in relation to individual grades of CB; however, a fairer comparison would be to a blend of CB grades that represent those contained in a whole tire feedstock. To this end, a blend consisting of 6% N234, 21% N330, 6% N375, 27% N326, 5% N550, 25% N660, 3% N683, and 7% N772 was prepared using a riffle box. This sample is referred to as Blend 1. A second blend, referred to as Blend 2, was also prepared, consisting of 82% Blend 1 plus 5% zinc oxide and 13% silica (Ultrasil 7000GR), to more accurately mimic the composition of European rCB products.

The surface area of the blends was determined following the method outlined in the "Assessing the Influence of Colloidal Properties on rCB Reinforcement" section; however, in this case, structure level measurements were made using a Brabender Absorptometer C following ASTM D2414.[16] In-rubber evaluation followed the procedures outlined in the "Assessing the Influence of Colloidal Properties on rCB Reinforcement" section, but with the addition of dynamic mechanical analysis (DMA). Strain sweeps were conducted in tension at 40 °C, 10 Hz, and double strain amplitude (DSA) range of ~0.06 to 6%.

ASSESSING THE EFFECTS OF COMPOSITION ON RCB REINFORCEMENT

To mimic changes in tire feedstock composition, four SBR based compounds containing different loadings of carbon black and silica were prepared using a 1.6 L Banbury internal mixer following the recipes displayed in Table I. The compounds were then cured and cut into ≤6 mm diameter pieces for pyrolysis treatment.

A Carbolite rotary furnace, consisting of an oscillating fused silica vessel suspended over a heated box, was used to pyrolyze the rubber feedstock samples. One hundred grams of each sample was heated from ambient to 600 °C and held at this temperature for a period of 7 h. A nitrogen flow rate of 3 L/min was used throughout to ensure an inert atmosphere. On cooling, the solid raw rCB

TABLE II
SBR TEST FORMULATION

Ingredient	Loading, phr
E-SBR 1502	100
Filler	60
TDAE oil	10
Zinc oxide	5
Stearic acid	2
6PPD	1.5
TBBS	1.5
Sulfur	1.5

samples were recovered for further preparation. Following pyrolysis, each sample was milled using a SPEX laboratory freezer mill for a period of 16 min with the aim of reducing the particle size to ≤20 μm. The samples were then characterized as follows:

1. Toluene discoloration testing to verify the samples had been fully pyrolyzed, following ASTM D1618.[17]
2. Nitrogen surface area testing as described in the "Assessing the Influence of Colloidal Properties on rCB Reinforcement" section.
3. Thermogravimetric analysis (TGA) was used to determine the percentage oxidizable matter and ash content within each of the samples. Ten milligrams of divided sample was heated from 40 to 600 °C at 20 °C/min in nitrogen and then cooled to 400 °C (also at 20 °C/min). After a 5 min isotherm at this temperature, air was introduced and the sample heated to 800 °C at 5 °C/min. A final 5 min isothermal hold was applied at 800 °C.

In this study, a generic SBR formulation was used to evaluate the in-rubber properties of the filler samples, as detailed in Table II. Compounds were produced via a two-stage mixing cycle using a 60cc Brabender internal mixer set at 40 °C and 60 rpm. During the masterbatch stage, the polymer was masticated for 30 s prior to adding the filler, oil, zinc oxide, stearic acid, and N-(1,3-Dimethylbutyl-N′-phenyl-p-phenylenediamine (6PPD) antidegradant. Following a ram bump at 2 min, the masterbatch was dumped after a total mixing time of 5 min and passed through a two-roll mill eight times using a 1 mm nip. For the conversion cycle, curatives were added to the mixer following mastication of the masterbatch for 20 s. The final compound was dumped after 2 min and passed through a two-roll mill at a 1 mm nip eight times.

ASSESSING THE EFFECTS OF CARBONACEOUS RESIDUES ON RCB REINFORCEMENT

To investigate the effects of carbonaceous residues on the properties of rCB, three batches of feedstock containing SBR 1502 and 50 phr of different grades of CB (N115, N330, and N660) were prepared using a 1.5 L Banbury internal mixer. No other compounding ingredients were used in this study so as to avoid their influence on the resultant rCB.

Each of the uncured compounds was pyrolyzed using a proprietary batch process and the yield of raw rCB recorded. The samples were post-processed using a laboratory-scale jet mill, and milled down to a size of D97 <10 μm measured with wet laser diffraction (CILAS) and 5 min ultrasonic dispersion, and EIRICH laboratory-scale pelletizer in preparation for testing. Nitrogen surface area measurements of the original and recovered carbon black samples were determined following the procedure outlined in the "Assessing the Influence of Colloidal Properties on rCB Reinforcement"

section. Compounds were then prepared containing virgin and recovered variants of N115, N330, and N660 following the recipe and procedures outlined in ASTM D3191.[18] Subsequent rheology and physical properties testing was in accordance with the procedures detailed in the preceding sections.

ASSESSING THE EFFECTS OF ORGANIC RESIDUES ON RCB REINFORCEMENT

In this study, two rCB samples were prepared via a proprietary batch pyrolysis process using the same feedstock but with differing process conditions to yield samples with either virtually no, or relatively small amounts of, organic residues. The aim of this investigation was to establish the influence of organic residues on the reinforcing behavior of rCB. Toluene discoloration and nitrogen surface area tests were used to characterize the rCB samples. Compounds containing the rCB samples and an N772 control were prepared following the recipe and procedures outlined in ASTM D3191. Subsequent rheology and physical properties testing was in accordance with the procedures detailed in the preceding sections. In addition to the in-rubber tests described previously, filler dispersion assessments were also made. Sections of each compound were prepared using fresh razor blades in order for surface roughness maps (×250 magnification) to be generated using a Hitachi TM3030 SEM fitted with an annular multi-segmented back-scattered electron detector.

A retrofitted MonTech D-RPA 3000 RPA was used to perform curing and dynamic property tests. Rheology measurements were performed at 180 °C, 0.5° oscillation strain angle at 1.67 Hz oscillation frequency. Dynamic test run strain sweep at 60 °C, 1–100% strain, 1 Hz frequency.

RESULTS AND DISCUSSION

INFLUENCE OF COLLOIDAL PROPERTIES ON RCB REINFORCEMENT

It is widely accepted that the greater the surface area available to interact with a rubber matrix, the more reinforcing the CB.[19,20] Similarly, higher structure levels lead to increased levels of occluded rubber, further enhancing reinforcement.[21,22] The colloidal properties of a given grade of CB are, therefore, considered to dominate its ability to reinforce rubber, hence their use in the ASTM classification system. Intuitively, it may be anticipated that the same approach could be a viable option for the recovered variant, and this has been the starting point for numerous studies into rCB. Such studies have consistently shown that the reinforcing potential of rCB is lower compared to a virgin CB of comparable colloidal properties.[2,7–19,23] Such studies have concluded that differences in surface chemistry and composition are the primary drivers for the reduced filler–filler and filler–polymer interactions exhibited by rCB. Nonetheless, if the colloidal characteristics of rCB were to provide correlation to reinforcing properties, albeit to a different level to CB, then it would provide an extremely useful tool for rCB producers and compounders alike.

To further investigate the applicability of colloidal testing to rCB, the surface area, structure level, and reinforcing properties of 25 samples was determined. The samples studied were produced using a wide range of proprietary technologies, including batch and continuous processes, also encompassing waste tire feedstocks from five continents. It is important from an end-user perspective that any rCB characterization test offers insight into product performance independent of the selected manufacturing process, hence, the array of samples included within this particular study. Although a series of in-rubber properties were determined, hardness values only are provided here, as a more detailed discussion of each individual rCB sample is beyond the scope of this paper. Furthermore, the main change in behavior of rubber due to incorporation of carbon blacks is observed with regard to stiffness,[18] of which hardness is a common measure. Shore A hardness
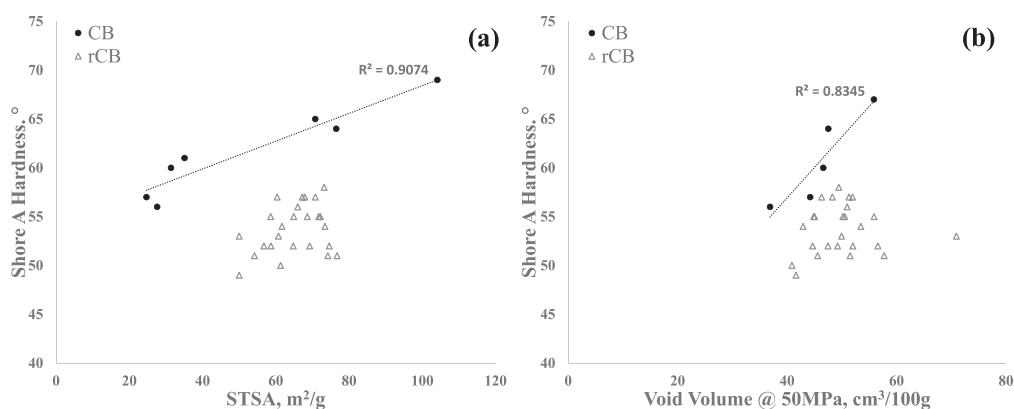
FIG. 1. — Relationships between (a) surface area and (b) structure level with Shore A hardness.

values are plotted against statistical thickness surface area (STSA) and void volume values in Figure 1.

The first thing to observe in relation to CB is the relatively good linear data fit between colloidal and hardness values, demonstrating why both are commonly adopted characterization tools. Note that a perfect R = 1 relationship is not expected, as the effects of surface area and structure level cannot be isolated from one another. Such trends cannot be established for the rCB samples, indicating that colloidal parameters alone are insufficient as rCB performance indicators. It can also be seen that all of the rCB samples impart lower hardness values compared to CB of similar colloidal properties, in good agreement with previous studies.[2,7–9,23] These observations confirm that additional rCB properties must be taken into consideration, and those identified by the authors form the basis of the discussion in the proceeding text.

INFLUENCE OF ASD ON RCB REINFORCEMENT

To date, comparisons of rCB have been made to individual grades of CB, rather than to a blend of CB grades that better represent those contained in a waste tire feedstock. To provide fairer comparison, two blends of virgin carbon black were prepared as described in the "Assessing the Influence of Colloidal Properties on rCB Reinforcement" section. Blend No. 1 being a mixture of CB grades and Blend No. 2 containing the same CB grades with the addition of 13wt% silica and 5wt% zinc oxide to better match the composition of the rCB sample included within this study. The colloidal map provided in Figure 2 confirms that the blends provide a relatively good match to the rCB sample. The inclusion of silica in Blend No. 2 had the expected result of increasing surface area. Broadly, the rCB and blend samples had surface areas toward the N300 series grades and structure levels between those of N326 and N330.

To understand how the blend samples performed in relation to the rCB, each was compounded into the NR based ASTM D3192 formulation alongside N772, N550, N326, and N330 (ASTM IRB8) control samples. Based solely on colloidal properties, one would expect the in-rubber performance of the rCB and blends to fall between that of N326 and N330; however, this was not found to be the case, with reinforcing potential found to be lower than N326 (Figure 3). Here, data are presented relative to N330 (IRB8) for ease of interpretation, as is common practice when using ASTM D3192. The physical properties of the rCB compare well with Blend No. 1, especially when taking into consideration the compositional and surface chemistry differences that exist between the two. The compound containing Blend No. 2 had slightly poorer physical properties, most likely due
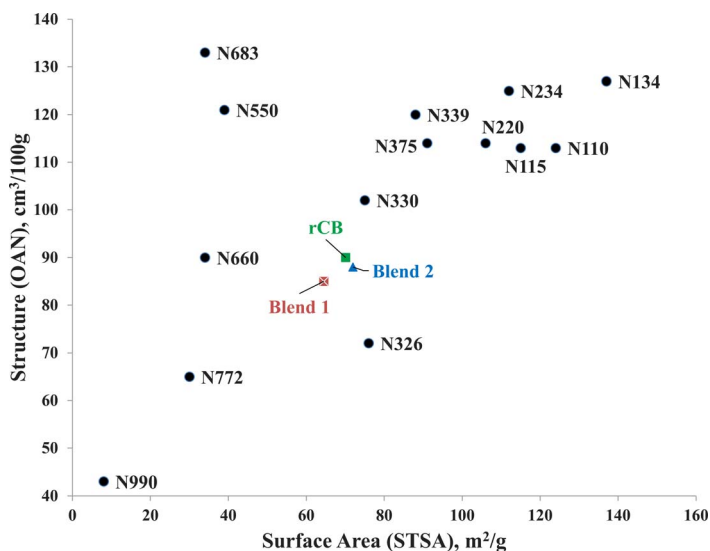
FIG. 2. — Colloidal properties of the rCB and blends in reference to virgin CB grades.

to scavenging of cure chemicals by the silica and the silica itself behaving as an active-filler load in the absence of a coupling agent.

In the case of Blend No. 1, which contains CB only, the reduction in reinforcing potential must be an artefact of its very wide ASD. It has been reported that the packing density of CB is increased with very broad ASD, as the small aggregates can pack between the larger ones.[24] This has been demonstrated with a blend of small and large particle size grades that was shown to only occupy 89% of the combined volumes of each individual CB when measured alone.[25] A more recent study by Diehl, Niedermeier, and Bradley demonstrated that greater reinforcement lies on the side of
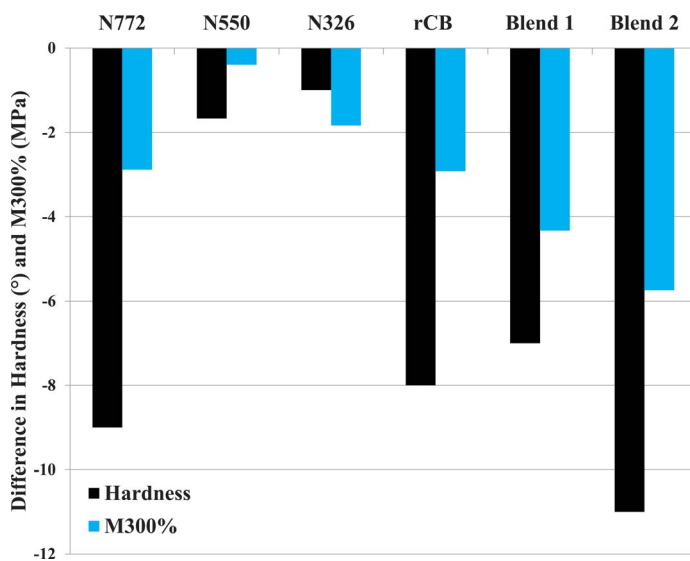
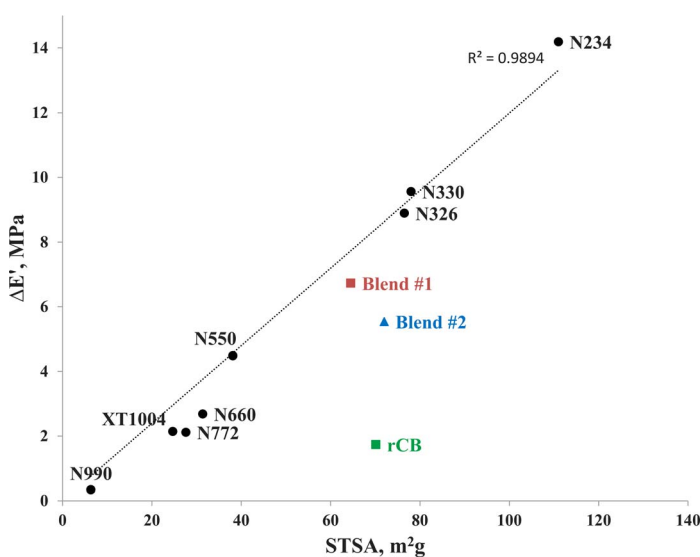FIG. 3. — Physical properties relative to the IRB8 (N330) standard.

FIG. 4. — Networking efficiency ($\Delta E'$) as a function of filler surface area.

narrower ASD.[26] This phenomena may go some way to explaining the reduction in the reinforcing potential of rCB compared to a grade of CB with the same apparent colloidal properties.

Under cyclic loading conditions, a difference exists between the elastic modulus response at low (E'_0) and high (E'_∞) strains, known as the Payne effect, which can be used as a measure of filler–filler interactions.[27–30] Since CB grades all exhibit similar surface chemistry, a linear relationship can be drawn between the level of filler–filler interactions ($\Delta E' = E'_0 - E'_\infty$) and surface area (Figure 4). Blend No. 1 falls slightly below the line of best fit for the CB samples, indicating that broadening the ASD slightly reduces filler–filler interactions, although the difference is not large enough to consider this result significant. The addition of silica and zinc oxide, Blend No. 2, reduces the actual loading of CB, resulting in a reduction in the Payne effect. This reduction is not significant enough to match the $\Delta E'$ value of the compositionally similar rCB, considered the result of deposition of C_{res} during the pyrolysis process, which masks the graphitic crystallite ends at the surface of the CB.[2,31–35] The influence of C_{res} is discussed in more detail in the "Influence of Organic Residues on rCB Reinforcement" section.

The data presented in this section suggest that a very broad ASD, such as that comprising an rCB product, leads to a substantial reduction in quasi-static properties when compared to a single grade of CB with similar colloidal properties. Each individual grade of CB will have a finite primary particle and aggregate size distribution, allowing them to be represented by a dot on colloidal maps, such as the example in Figure 2. This study has shown that representing rCB in the same manner is not representative of its true colloidal nature. The TEM image shown in Figure 5 further ratifies this observation, where the non-homogenous nature of rCB is revealed via the broad range of primary particle sizes present. For these reasons, ASD testing is considered one of the primary characterization tools required for rCB.

INFLUENCE OF COMPOSITION ON RCB REINFORCEMENT

The advent of tire labeling regulations has driven the use of silica filler in place of carbon black in certain tire components to improve properties such as wet grip and fuel economy. To mimic the influence of changing feedstock composition, a series of rubber compounds was prepared that
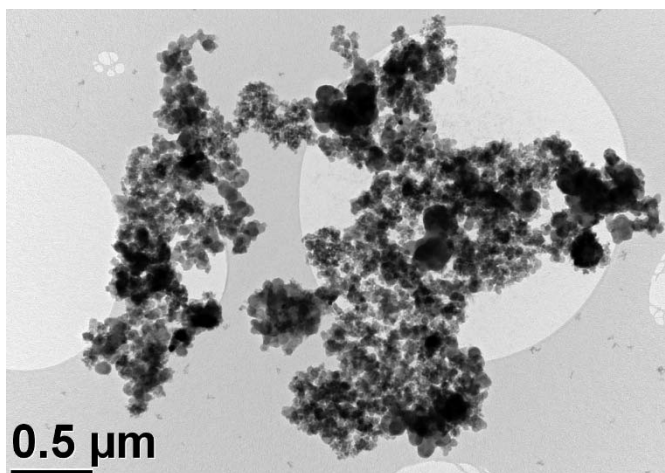
FIG. 5. — TEM image of an rCB agglomerate.

contained different loadings of carbon black and silica. These compounds were pyrolyzed to recover the fillers and subsequently milled prior to generating the test results provided in Table III.

TGA test data generated for the feedstock and resultant rCB samples (data not shown) were used to estimate the amount of C_{res} formed via polymer decomposition during pyrolysis. Calculations were based on the assumption that formation of C_{res} would increase the carbon to ash ratio in the rCB when compared to the carbon to ash ratio of the feedstock. With this approach, C_{res} contents were estimated to be in the region of 3 to 4% for all samples. These values are lower than those previously reported,[2] considered the result of efficient volatile removal during the laboratory-

TABLE III
PROPERTIES OF THE RCB SAMPLES (PHR SILICA REFERS TO THE LOADING IN THE FEEDSTOCK)

Property	70 phr silica	50 phr silica	30 phr silica	10 phr silica
Carbonaceous residue (%)	4.4	2.8	4.0	4.0
Transmission (%)	97	95	98	96
NSA (m²/g)	118.7	115.4	110.9	103.3
Ash content (TGA) (%)	77.7	55.9	33.7	11.8
MDR data				
Min. torque (*ML*) (dNm)	3.44	2.64	1.95	1.69
Max. torque (*MH*) (dNm)	18.07	14.93	13.65	13.60
Scorch time (ts2) (mm:ss)	3.46	3.56	3.69	3.86
Cure time (t90) (mm:ss)	14.90	12.17	10.80	9.58
Physical properties				
Shore A (°)	60	63	63	64
M100% (MPa)	1.39	1.62	2.05	2.19
M300% (MPa)	3.88	6.09	9.52	10.90
Tensile strength (MPa)	21.4	22.6	23.7	23.4
Elongation at break (%)	782	633	529	497
Dynamic properties				
$\Delta E'$ (MPa)	8.62	7.08	6.47	6.11

scale pyrolysis technique used for this study. The high transmission values generated from toluene discoloration testing confirm that the selected process conditions were suitable for removing the vast majority of organic matter from the rubber feedstock. These measurements confirm that pyrolysis residues were kept to a minimum, and so silica content can be considered as the dominant factor in the remainder of the results presented.

Ash contents of the rCB samples were in line with the silica content of the feedstock and ranged from 12 to 78%, with the upper end of this scale far exceeding levels expected to be present in rCB produced from waste tires. Arguably, those samples with the highest ash contents should not be referred to as rCB, as CB does not account for the bulk; however, the broad range of silica contents studied does allow for more meaningful understanding of its influence on rCB properties. It is clear that the surface area of rCB increases with increasing silica content, an expected trend given the relative surface areas of the two fillers used in the feedstock, being 93 m^2/g for the carbon black and 175 m^2/g for the silica.

Following the initial characterization tests described above, each rCB sample was compounded into Electronic (E)-SBR as detailed in the "Assessing the Influence of Colloidal Properties on rCB Reinforcement" section. It is important to note that the samples were treated as rCB regardless of their silica content, and not as silica, where the use of a coupling agent and associated reactive mixing cycle may be considered more normal practice. The in-rubber properties data summarized in Table III clearly demonstrate that rCB silica content impacts all measured parameters. First, MDR minimum (ML) and maximum (MH) torque values increase as the silica content increases, at least partially attributable to higher surface area. The stronger filler–filler interaction of silica is also proposed as a contributor to the torque values measured at the low strains tested by the MDR. This comment is augmented by the measured increase in strain dependency ($\Delta E'$) of rCB as the silica content increases.

It has been well documented that E-SBR is particularly influenced by interactions between zinc and silica, leading to removal of soluble zinc from its normal accelerator activating function and, subsequently, reducing crosslink density.[36] As well as interfering with cure reactions, filler–polymer interactions are also hampered by soluble zinc at the silica surface. These interactions between silica and zinc account for the longer cure times and significantly reduced physical properties when the silica content of the rCB is increased. When compounding silica, it is common practice to use glycols, such as PEG4000, and to delay the addition of zinc oxide during mixing to limit these effects. The results presented here would suggest that a similar approach may improve the processing and physical properties of rCB filled compounds; however, the success of this will likely be determined by the availability of silica within a given rCB. The amount of C_{res} deposited during the laboratory-scale pyrolysis process used in this study is considered low, and so the silica within the resultant rCB samples is likely to be more accessible than for an rCB exhibiting higher levels of C_{res}. Regardless, the data presented have demonstrated that the silica content of rCB can have a significant influence on its reinforcing properties and must not be ignored as part of the characterization process.

INFLUENCE OF CARBONACEOUS RESIDUES ON RCB REINFORCEMENT

The presence of C_{res} at the surface of rCB has been widely reported;[31–35] however, given the non-homogenous nature of waste tire feedstocks, quantification and isolation of their influence on the ability of rCB to reinforce rubber has proven difficult. In this study, SBR feedstocks containing different grades of CB only were prepared and then recovered following the procedure detailed in the "Assessing the Effects of Carbonaceous Residues on rCB Reinforcement" section. This approach allows for direct comparison of virgin and recovered variants of single grades of CB, namely, N660, N330, and N115.

TABLE IV

PROPERTIES OF THE RCB SAMPLES WITH DIFFERENT VOLATILE CONTENTS

Property	N660	rN660	N330	rN330	N115	rN115
Weight gain (%)	—	10.5	—	15.3	—	20.1
NSA (m^2/g)	33.7	42.6	77.5	75.8	130.5	93.3
STSA (m^2/g)	32.9	33.9	75.6	61.8	112.2	77.3
Ratio NSA:STSA	1.02	1.26	1.03	1.23	1.16	1.21

Mass balance data confirms that CB acts as a substrate for C_{res} deposition during pyrolysis, as shown by the increase in rCB yield as the surface area of the original CB increases (Table IV). For the pyrolysis process used, the amount of C_{res} formed was significant, leading to substantial changes in surface area properties. C_{res} appears to be porous in nature, as indicated by the increase in ratio between total surface area (NSA) and external surface area (STSA) for the recovered variants. Formation of C_{res} leads to an overall increase in surface area of the N660 after pyrolysis; however, as the amount of carbonaceous residues increase with the N330 and N115, a linear reduction in surface area was identified (Figure 6). It can be concluded that carbonaceous residues affect both the porosity and external surface area of rCB. Of particular interest to rubber reinforcement is the homogenizing effect on STSA values with the recovered samples covering a range of 43 m^2/g compared to 79 m^2/g for the virgin CB samples.

Although the data clearly demonstrate that the nature of the fillers within a rubber feedstock will influence carbonaceous residue formation, it should be acknowledged that the pyrolysis process itself will also play a major role. For example, the amounts of carbonaceous material formed here ranged from 11 to 20%, in comparison to values closer to 4% for the laboratory-scale pyrolysis process discussed in the "Influence of Composition on rCB Reinforcement" section.

Following the initial characterization, the rCB samples were jet milled and then pelletized prior to compounding, as described in the "Assessing the Effects of Carbonaceous Residues on rCB Reinforcement" section. The properties of the virgin and recovered variants of N660, N330, and
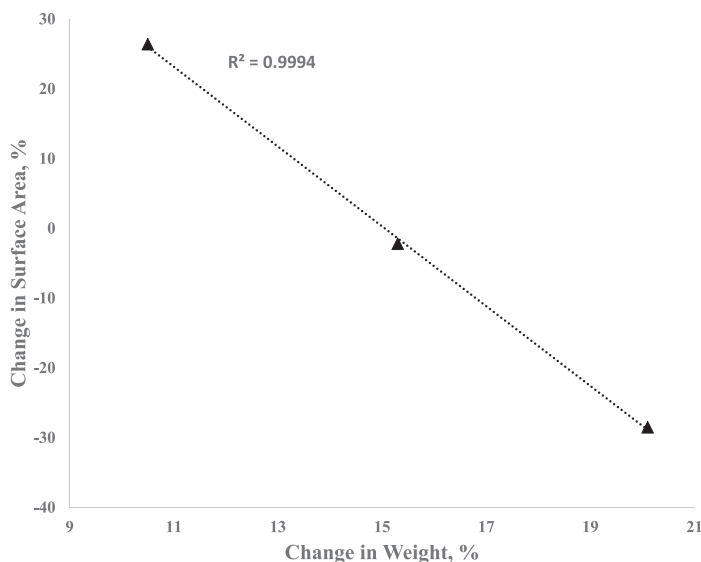

FIG. 6. — Reduction in rCB surface area as carbonaceous residues increase.

TABLE V
PROPERTIES OF THE CB AND RCB VARIANTS

Property	N660	rN660	N330	rN330	N115	rN115
MDR data						
Min. (*ML*) (dNm)	1.83	2.01	2.58	2.60	3.10	3.06
Max. (*MH*) (dNm)	18.28	17.26	20.18	19.92	21.20	20.60
Cure (t90) (mm:ss)	6.11	6.75	4.85	4.89	5.87	4.98
Physical properties						
Shore A (°)	62	62	66	65	66	68
M300% (MPa)	10.4	7.6	13.6	10.8	10.8	11.7
Tensile strength (MPa)	20.7	20.3	23.2	20.4	27.4	20.2
Elongation at break (%)	497	557	424	455	520	457

N115 when compounded into the SBR based ASTM D3191 formulation are summarized in Table V. To better demonstrate the effects of C_{res}, a plot of the percentage change in-rubber properties for the rCB samples against the amount of C_{res} deposited during pyrolysis is displayed in Figure 7. These data show that the introduction of C_{res} increased compound viscosity (*ML*) slightly for N660, but as the amount increased, the general trend was for viscosity to reduce. This observation is in line with the relative decrease in surface area as the amount of C_{res} increased. Rheology testing also indicated that cure time reduced as C_{res} increased. Further testing, such as pH determination, will be required to help understand the reasoning behind this change in cure behavior.

Considering the physical properties, hardness remained unaffected, with values for each CB and rCB variant considered to be within the range of typical experimental error. The rN660 and rN330 both exhibited significant reductions in modulus (M300%), as may be expected with reduced polymer–filler interactions resulting from masking of the original CB surface functionality; however, this was not found to be the case for the rN115, where an increase in
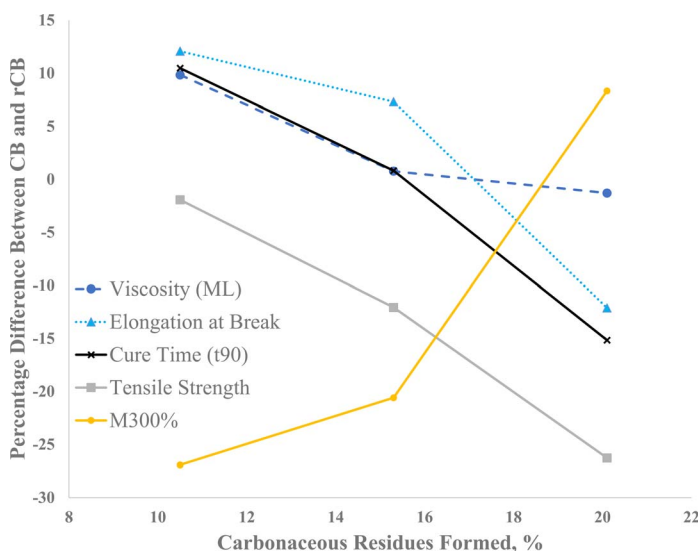

FIG. 7. — Change in-rubber properties with increasing levels of carbonaceous residues (N660 = 10.5%, N330 = 15.3% and N115 = 20.1%).

modulus was measured. Although the high surface area N115 is considered as a relatively low modulus grade, as indicated by the lower M300% compared to N330, the authors have no explanation for the increase in modulus measured for the rN115. Further testing is deemed necessary to confirm whether this result is repeatable for N115 and other high surface area grades of CB.

A relative decrease in tensile strength was identified as C_{res} increased, fitting with expectations due to the accompanying decrease in filler surface area. The actual tensile strength values were similar for all three recovered variants, and it is postulated that this may be associated with each rCB sample having similar maximum particle size post-milling. The introduction of C_{res} caused a sharp increase in elongation at break for the rN660, indicating an increase in polymer chain slippage over the filler surface. As the amount of C_{res} increased, the trend was for elongation at break to decrease. It is likely that greater amounts of C_{res} will have inhibited rCB dispersion, and this would be expected to cause such reductions in elongation at break.

It is clear from the in-rubber assessment that the amount of C_{res} formed during pyrolysis has a significant impact on most properties. Detailed dispersion analysis is recommended for the next phase of testing, as this will likely help to further explain some of the trends identified. Nonetheless, the evidence strongly indicates that inhibiting the formation of C_{res} within commercial recycling processes is highly desirable in the production of rCB.

<div align="center">INFLUENCE OF ORGANIC RESIDUES ON RCB REINFORCEMENT</div>

The amount of organic matter remaining within an rCB can be controlled by careful selection of processing conditions. At excessive levels of organic matter, rCB presents itself with a characteristic strong odor and poor reinforcing properties.[2] It is, therefore, desirable to limit the amount of organic matter in the final product; however, over-processing may also pose challenges in terms of excessive C_{res} formation. It has been reported that C_{res} formation during pyrolysis of oils arises from dehydrogenation of aromatic precursors,[37,38] and so targeting a small amount of organic residues within an rCB may be desirable.

To investigate this further, two rCB samples were prepared using differing process conditions to yield samples with slightly different amounts of organic residues (Table VI). The organic content of rCB No. 1 is not considered excessive, but at 2.8%, it was approximately twice that contained within rCB No. 2. One of the trade-offs for the higher organic content was a slight increase in polyaromatic hydrocarbons (PAH) content. Minimizing PAH content is desirable, as concerns have been raised regarding the presence of these in-rubber formulations, as they may pose a risk during manufacture, handling, or disposal.[39] It should be acknowledged that both rCB samples contained an order of magnitude lower PAH content compared to the typical tire grade N772 included within this study, thus demonstrating the potential of pyrolysis to generate low PAH grades of renewable filler.

Nitrogen surface area testing indicates that the lower organic content sample (rCB No. 2) had slightly lower external surface area but contained a higher level of porosity (as indicated by NSA-STSA). These observations are in agreement with those expected from increased levels of C_{res}, as identified in the "Influence of Carbonaceous Residues on rCB Reinforcement" section. The data also corroborate with the rCB samples discussed in the "Assessing the Influence of Colloidal Properties on rCB Reinforcement" section, where a trend for porosity to increase as organic residues decrease is apparent across the samples produced from a range of pyrolysis processes (Figure 8).

When the jet milled and pelletized rCB samples were compounded into the SBR based ASTM D3191 formulation, the effect of slightly higher organic content on the rheology properties was shown to be reduced viscosity (ML) and cure state (MH–ML) alongside slower curing. In essence,

TABLE VI
PROPERTIES OF THE RCB SAMPLES WITH DIFFERENT VOLATILE CONTENTS

Property	rCB No. 1	rCB No. 2	N772
Organic content (TGA) (%)	2.8	1.5	1.0
Transmission (%)	64	98	65
PAH content[a] (ppm)	38	9	950
NSA (m^2/g)	73	79	30
STSA (m^2/g)	65	62	28
MDR data			
Min. torque (*ML*) (dNm)	1.80	2.16	1.61
Max. torque (*MH*) (dNm)	16.3	17.8	15.7
Cure time (t90) (mm:ss)	5.43	4.72	6.49
Physical properties			
Shore A (°)	58	61	59
M100% (MPa)	1.59	1.80	1.70
M300% (MPa)	5.4	7.8	8.6
Tensile strength (MPa)	24.6	19.6	23.2
Elongation at break (%)	676	556	568
RPA strain sweep, 60 °C, 1 Hz			
$\Delta G'$ (kPa)	774	1000	631

[a] Total of the 22 PAH compounds in the U.S. FDA list.
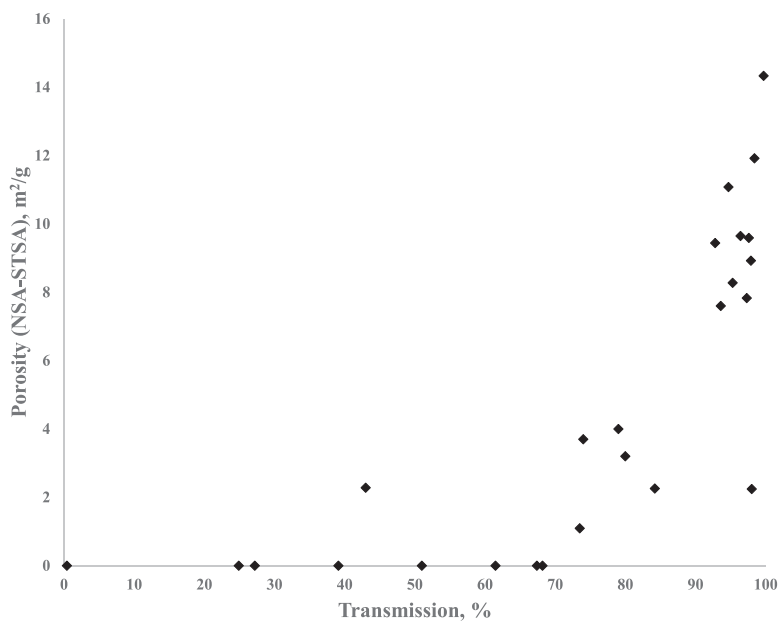

FIG. 8. — Relationship between low organic content (high transmission) and higher porosity.
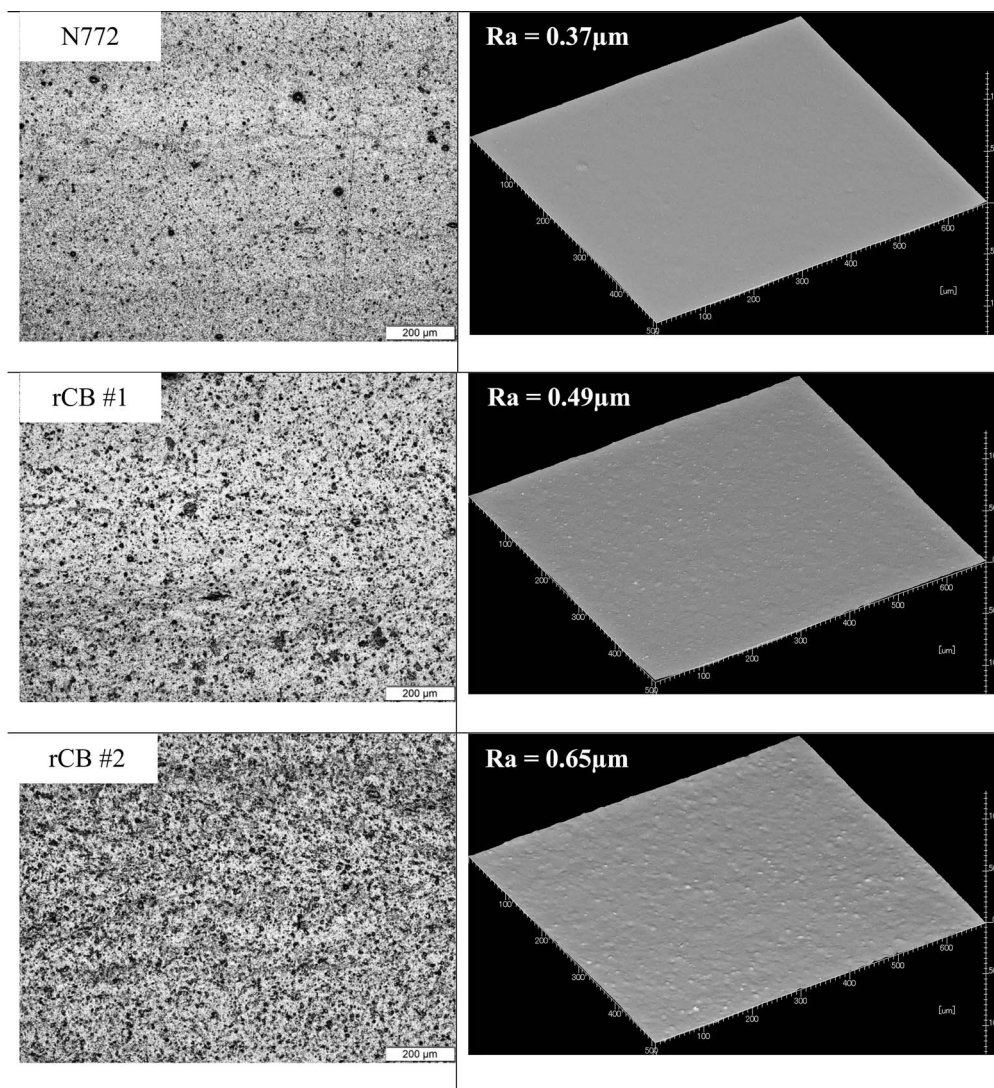
FIG. 9. — Dispersion; optical images left, SEM surface roughness maps (right). Ra = average surface roughness.

the organic residues have a slight plasticizing effect and slightly inhibit the curing reaction. Improved dispersion will also be a contributor to the lower viscosity measured for rCB No. 1 (Figure 9). The improved dispersion confirms that hindering C_{res} formation does offer a route to improved dispersibility of rCB.

The influence of higher organic content was a reduction in compound stiffness indicating that the polymer–filler interaction was slightly weakened; however, ultimate tensile properties were increased, as may be expected from the improvement in dispersion. The higher organic content was also shown to reduce the strain dependency of the filler ($\Delta G'$), indicating that the presence of organic residues also inhibits filler–filler interactions.

The above data confirm that the properties of an rCB can be tailored for a given application with careful control of the process conditions. At the lowest organic content, rCB No. 2 was shown to provide the better match to the N772 reference while offering very low PAH content. At slightly

elevated organic content, reinforcing potential was slightly reduced, but dispersion and ultimate tensile properties were enhanced.

CONCLUSIONS

The research presented in this paper has conclusively demonstrated that classification of rCB products needs to go beyond the surface area and structure measurements used for CB, with ASD, silica content, C_{res} content, and organic residue content playing significant roles in how this filler behaves when compounded into rubber. Although new test techniques need to be adopted by the rCB industry, this paper provides guidance to producers and compounders alike to which properties of rCB should be strictly controlled and monitored to guarantee consistent product performance.

First, it was shown that a very broad ASD, such as that compromising an rCB product, leads to a substantial reduction in quasi-static properties when compared to a single grade of CB with similar colloidal properties. The wide ASD arises from the range of different filler grades recovered from end-of-life tires, but it should be noted that it will also be influenced by the milling technique employed by the rCB producer. The broad ASD is considered to be one of the dominating factors for the disparity between the reinforcing potential of an rCB and CB of similar surface area and structure level, and so is recommended as one of the primary characterization tools required for rCB.

Second, the silica content of rCB can have a significant influence on its reinforcing properties and must not be ignored as part of the characterization process. The case study demonstrated a strong trend for the reinforcing behavior of an rCB to decline with increasing silica content. The silica content of an rCB will be dictated by that contained in the feedstock, which is known to vary significantly between different types of tire; therefore, strict feedstock control is a necessity in controlling this particular rCB parameter.

Finally, the amount, and type, of residues at the surface of an rCB play a significant role in filler–filler and filler–polymer interactions. The evidence presented strongly indicates that inhibiting the formation of C_{res} within commercial recycling processes is highly desirable in the production of rCB. Almost entirely eliminating organic residues demonstrated that rCB can be produced with very low PAH content and reinforcing properties similar to that of N772; however, allowing a small amount of organic residue led to improved dispersibility and ultimate tensile properties. These observations indicate that the properties of an rCB can be tailored for a given application with precise control of the process conditions.

ACKNOWLEDGEMENTS

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[*Received August 2022, Revised February 2022*]