Application of recovered Carbon Black (rCB) from End-of-Life (EoL) tire Pyrolysis in Butyl Rubber Compounds

Recycling · Carbon Black (CB) · recovered Carbon Black (rCB) · Pyrolysis · Sustainability · Circular Economy · End-of-Life (EoL) Tires · Butyl Rubber (IIR)

In the present study „Application of recovered Carbon Black (rCB) from End-of-Life Tire pyrolysis in butyl rubber compounds", the research on the use of rCB in new butyl compounds is presented. In general, pyrolysis of scrap tires is considered a future-oriented additional technology regarding the lack of recycling capacities. While the pyrolysis products oil and gas already find industrial application, there is still a lack of suitable applications for the solid pyrolysis residue rCB. With its reuse in butyl blends, the study investigates a potential rCB sink.

Anwendung von „recovered Carbon Black (rCB)" aus Altreifenpyrolyse in Butyl-Kautschukmischungen

Recycling-Ruß (CB) · Recycelter Ruß (rCB) · Pyrolyse · Nachhaltigkeit · Kreislaufwirtschaft · Altreifen · Butylkautschuk (IIR)

In der vorliegenden Studie „Einsatz von recyceltem Ruß (recovered Carbon Black, rCB) aus der Altreifenpyrolyse in Butyl-Gummimischungen" wird eine Untersuchung zum Einsatz von rCB in neuen Butylmischungen vorgestellt. Generell gilt die Pyrolyse von Altreifen in Anbetracht fehlender Recyclingkapazitäten als zukunftsweisende Ergänzungstechnologie. Während die Pyrolyseprodukte Öl und Gas bereits industriell Anwendung finden, fehlt es für den festen Pyrolyserückstand rCB noch an geeigneten Einsatzzwecken. Mit dem Wiedereinsatz in Butylmischungen untersucht die Studie eine potenzielle rCB-Senke.

Figures and Tables: By a kind a approval of the authors.

Introduction

End-of-Life (EoL) tire volume and recycling

Worldwide, more than 1 billion used tires reach the end of their lives every year. [1, 2] In Europe, the amount of End-of-Life (EOL) tires in 2019 was around 3.5 million tons [3, 4], with Germany alone accounting for around 600,000 tons. [5]. About 55 % of the mentioned EOL volume in Europe was materially recycled, 40 % was recovered for energy and the remaining 5 % was stored or statistically not registered. [3] The German recovery mix in 2019 saw about 44 % of the EOL tires generated being materially recycled, 31 % being co-incinerated in cement plants, 19 % being exported for reuse, retreading or energy recovery, and a total of about 6 % being retreaded and reused domestically. [5]

Based on a current extrapolation [6], the types of scrap tires generated in Germany can be classified as shown in figure 1. The type of scrap tire and thus the individual composition is essential for the recycling process and has also been considered in the context of the present study. The prevailing EOL tire management situation is currently experiencing a fundamental change. In Germany, for example, the processing routes of retreading, domestic reuse and especially co-incineration in cement plants are declining significantly. [8] Due to the increasing discussion and regulation of the content of polycyclic aromatic hydrocarbons (PAH) in regranulates from EOL tires, the growth rates of mechanical recycling are also currently being slowed down. [8, 9] As a result of the recent developments, an increasing surplus of scrap tires that can no longer be recycled domestically is forecast for Germany in the future. [6] Since exports are not a sustainable solution, it is important to find appropriate and efficient recycling alternatives for the resulting gap.

Pyrolysis as additional EoL treatment route

As a potential solution and complementary path to existing EoL tire recycling methods, the so called feedstock recycling, in particular the technology of pyrolysis, is getting more and more in the focus of science and industry. [10, 11] During pyrolysis, EOL tires are thermochemically decomposed at temperatures between 400 and 900 °C in the absence of oxygen. [12] The products, depending on the input material and the process parameterization, are a non-condensable pyrolysis gas (14 - 46 wt. %), a pyrolysis oil (25 - 45 wt. %) and a pyrolysis char (25 - 46 wt. %) [10]. A general process scheme of EOL tire pyrolysis is shown in figure 2. The dashed lines in the illustration symbolize optional paths.

While the pyrolysis gas is commonly used for electricity or heat generation [11] and the pyrolysis oil is used as fuel or, after processing, as feedstock in the chemical industry [13], suitable industrial applications for rCB are still lacking. Potential users face the challenge that rCB obtained from EOL tire pyrolysis is different from standardized Carbon Black (CB) grades [10] and thus cannot be used as a full industrial Carbon Black substitute according to the latest technological development status. [14]

Authors

Sebastian Bogdahn, Schwalbe, Reichshof,
Edwin Koch, Maria Deininger,
Prof. Dr. Danka Katrakova-Krüger, TH Köln, Gummersbach,
Dr. Andreas Kapf, Niels Ellermann, Pyrum Innovations, Dillingen/Saar, Germany

Corresponding Author
Sebastian Bogdahn
Ralf Bohle GmbH,
Otto-Hahn-Str. 1, 51580 Reichshof, Germany
E-Mail: s.bogdahn@schwalbe.com

Carbon Black

Nevertheless, development efforts regarding the production and optimization as well as the utilization of rCB appear worthwhile considering the increasing global demand for CB. While world CB production was about 8 million tons in 1996 [15], demand evolved to 8.5 million tons in 2001 [16], to over 10 million tons in 2005 [17], to about 11 million tons in 2012 [18], up to about 12.5 million tons in 2020 [19]. A further increase to over 17 million tons per year worldwide is forecast by 2030. [19] (s. figure 3)

CB is a fossil-based raw material. It is produced almost exclusively by means of the so-called furnace process, for which crude oil and natural gas are used as feedstocks. [20] About 90 % of the world's CB production is used in rubber applications [18], and about 70 % alone is used for the production of tires as well as other rubber products for the automotive industry. [21] In terms of sustainability, it therefore makes sense to further investigate the use of rCB from EOL tire pyrolysis in the rubber processing industry and evaluate it as a CB substitute. This topic is addressed in the present paper.

Investigation of rCB application in butyl rubber compounds

It is known that gas permeation of elastomers can be reduced by using carbon blacks with a relatively low specific surface area as well as a lower structure and, as a result, a higher filling degree of the rubber compound. [22] Since rCB from EOL tire pyrolysis tends to have lower specific surface areas and structures, the feasibility of using rCB in butyl blends instead of the industrial CB N660 was investigated. The fact that butyl compounds, depending on the specific application, usually contain a relatively high proportion of CB of comparable activity favors this application as a perspective rCB sink.

Material & Methods

Material input, rCB and reference CB

Two different rubber granulate mixtures from mechanically processed EOL tires were used as input material for the study. Pure input (rubber granulate from EOL truck tires only) is referred to below as „PURE" and mixed input (rubber granulate from mixed EoL tires) as „MIX". Different batches of rCB were produced in the lab facilities of Pyrum Innovations
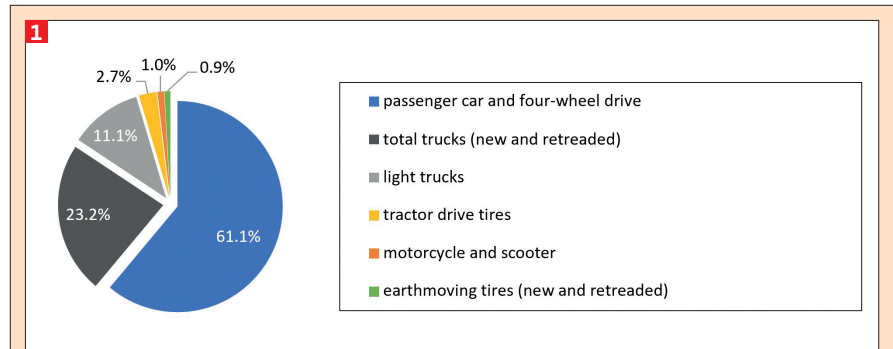
for the investigations and provided for further analysis and use. The rCB grades and their in-rubber properties were compared with a commercial industrial carbon black N660, which is commonly used as a filler in butyl compounds. Although rCB is rather a less defined mix of the different CB grades used in the pyrolyzed tires, it was compared to CB N660 as it was aimed to be substituted.

Figure 1: Weight-based distribution of EoL tire volume in Germany, mean value from 2017 and 2018, according to [6] based on data from [7].
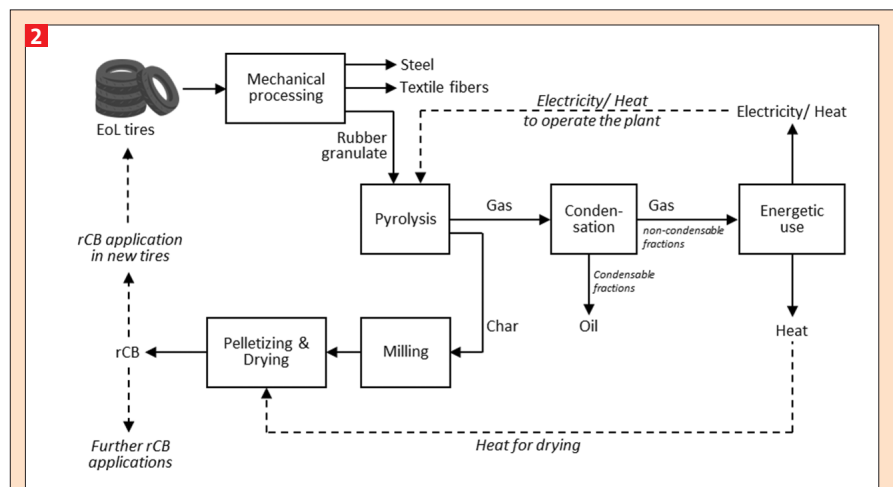

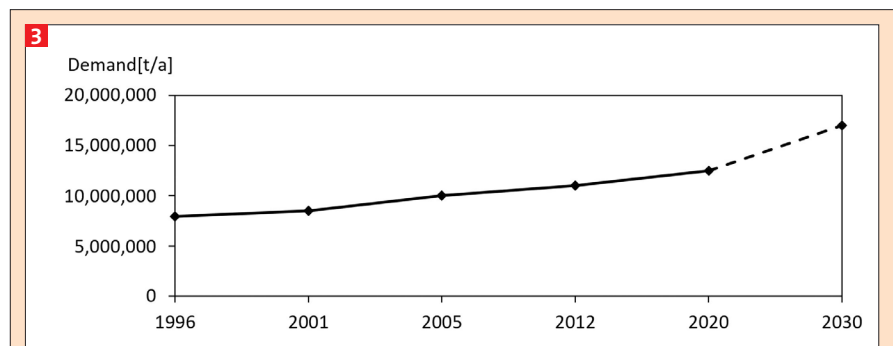**Figure 2: General process scheme of EOL tire pyrolysis.**

Figure 3: Development of global Carbon Black (CB) demand in 1996 [15], 2001 [16], 2005 [17], 2012 [18] and 2020 [19], and forecast in 2030 [19].

Pyrolysis process: parameter variations and product distribution

The pyrolysis process is primarily influenced by the composition of the input material as well as the temperature profile as a function of time, in particular the residence time and the heating rate . [23] In order to investigate the effects of the main process parameters on the mass balance yield and the quality of rCB from

EOL tires, a series of lab experiments was conducted. The tests were carried out in the laboratories of Pyrum Innovations in Dillingen (Germany). As shown in figure 4, a discontinuous batch reactor (filling volume up to 1.000 ml) and a semi-continuous moving bed reactor (filling volume up to 8.000 ml) were used.

For the screening, the batch reactor was used with variation of pyrolysis temperature (550 °C, 600 °C and 650 °C) as well as material heating rate (20 °C/min and 600 °C/min). The rubber granules were introduced into the hot reactor via the airlock after purging with nitrogen. Vapors rose due to the de-composition reactions present and were discharged via the gas path due to a minimum overpressure in the reactor. The vapors were cooled by a heat exchanger and the resulting liquid (pyrolysis oil) could be coll-

ected. The non-condensable fractions were passed through various filter systems. Finally, the rCB could be taken from the reactor after disassembly of the vessel.

The vertical moving bed reactor was used to perform the continuous pyrolysis experiments. This reactor consists of 4 separate heating zones. Heating zone 1 (550 °C) was used to heat the resulting gas phase so that it did not condense within the reactor. The material was fed via the airlock system to heating zone 2 (680 °C), where, in combination with heating zone 3 (680 °C), the main reaction of the thermal decomposition took place. Heating zone 4 (500 °C) was used for thermal post-treatment of the solid material. Before starting the experiment, the reactor was filled with raw rCB up to heating zone 2 and the system was then purged with nitrogen. The filled reactor

was then heated to the target temperature. Temperature measurements determined a heating rate of 600 °C/min. When 1 liter of granulate was added, 1 liter of rCB was discharged from the bottom of the reactor into the collecting vessel. After removal of the feed material, the target product was collected in a continuous operation with a throughput of 0,71 kg/h.

After parameter screening in the batch reactor, the most promising process parameters were scaled up to the moving bed reactor. This reactor design and mode of operation corresponds to the patented large-scale Pyrum thermolysis process and can thus be used as a basis for subsequent upscaling to industrial scale. Figure 5 shows the product yields for both conversions.

Milling process of rCB
The raw rCB was milled with a AFG 100 jet mill from Hosokawa Alpine at a pressure of 6 bar and a classifier speed of 15.000 rpm resulting in D97 percentiles of the particle sizes below 10 µm.

Compound/ Recipe
The rubber compounds were produced on a butyl rubber basis according to the recipe in table 1. The mixing was done in a Rheomix 3000 p laboratory kneader with banbury rotors from Thermo Haake (now: Merck (Germany)). The kneading chamber measures an empty volume of 379 cm³ and is electrically heated and cooled via an air pressure stream.

All compounds were produced in a two-stage mixing process. In stage 1, the base compound, containing butyl rubber, filler, plasticizer and activators were processed. The raw materials were added to the mixer following the upside-down process. Stage 2 was started with the batch from stage 1, followed by the addition of the crosslinking chemicals.

Carbon Black characterization
Industrially produced CBs are classified by the American Society for Testing and Materials (ASTM) into different classes according to the ASTM D1765-19 standard. [24] Although rCBs differ in some characteristics, CBs can be used as a helpful reference for rCB quality evaluation. Accordingly, the CB reference and rCBs in the present study were characterized as follows:

The composition (C, H, N, S) was carried out with an elemental analyzer of the type Vario Macro Cube from the compa-
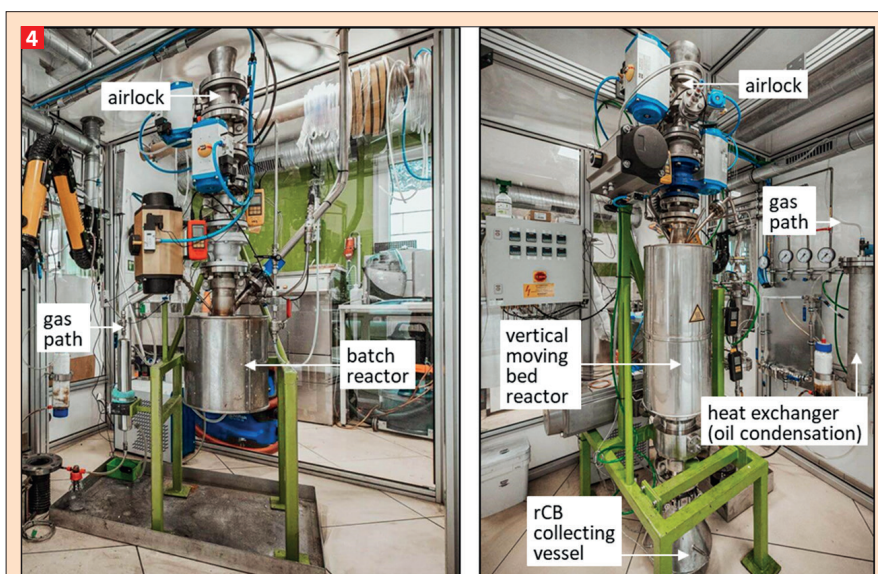

Figure 4: Pyrolysis lab reactors: Batch reactor (left) and semi-continuous vertical moving bed reactor (right).
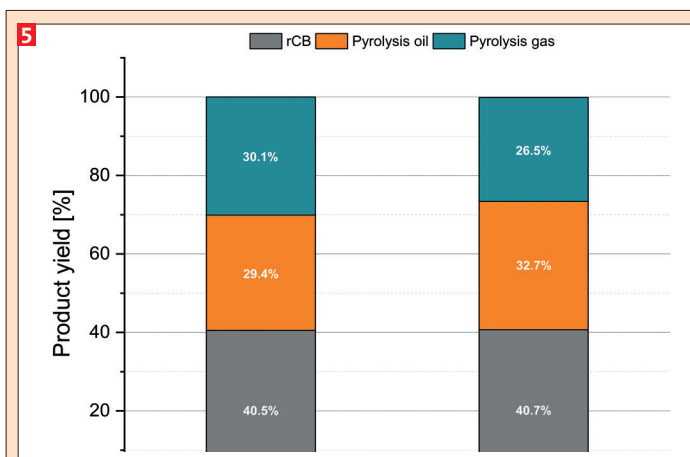

Figure 5: products yields of final pyrolysis experiments in moving bed reactor.

ny Elementar Analysensysteme (Germany). Further, the composition was analyzed using energy dispersive X-ray spectroscopy (EDX) in the scanning electron microscope (SEM) type SU5000 from Hitachi High-Technologies Corporation (Japan) and the elemental analysis software „Aztec 5.0 SP1" from Oxford Instruments (United Kingdom). The ash content was determined in a muffle furnace according to ASTM standard D1506-15 [25] and additionally to the newly published rCB standard ASTM D8474-22 [26] by thermogravimetric analysis (TGA) in an analyzer type STA 409PC/PG from the company Netzsch (Germany).

The structure was analyzed by means of the oil adsorption number (OAN) according to ASTM D2414-19 [27] and the compressed oil adsorption number (COAN) according to ASTM D3493-20 [28] using the apparatus DABS-BU01 from the manufacturer Hitec Luxembourg (Luxembourg). Void volume (VV) was determined according to ASTM D-7854 [29] using the CVST-BASU analyzer from Hitec Luxembourg (Luxembourg).

The surface area was determined according to ASTM D6556-19a [30] using the method developed by Brunauer, Emmett and Teller (BET) by means of nitrogen adsorption with the instrument Novatouch from the manufacturer Anton Paar (Austria), even though suitability of the method for rCBs has not yet been validated. At present, the industry still disagrees on the determination of the particle size of rCB, and there is no standard procedure yet. For this reason, the D90 percentile of each CB and rCB was determined using both a 24000 UHR disc centrifuge from the manufacturer CPS (USA) and D97 percentile by laser diffraction in a Mastersizer 3000 from Malvern Panalytical (United Kingdom). Surface contamination by volatile components was determined according to the German standard DIN 51720:2001-03. [31]

In addition, the concentration of polycyclic aromatic hydrocarbons (PAH) was investigated according to AfPS GS 2019:01 PAH. [32] Especially for the use of CB and rCB in products coming in contact with the human skin during use, PAH exposure is of great importance and is increasingly strictly discussed and regulated.

Compound testing

Although CB and rCB characterization gives a rough indication of the physical and chemical properties of rCB, it is the actual in-rubber performance that finally determines its usability as a filler in rubber compounds. The compounds produced were characterized as follows:

The crosslinking characteristics were determined by Rubber Process Analysers type „flex" from TA Instruments (USA) at 180 °C according to ISO 6502. [33] For the production of the sample plates, the laboratory press of Gibitre Instruments (Italy) was used. The samples were vulcanized according to t95 curing time.

The compound characteristics of the vulcanized samples were then investigated using the following parameters: The dispersion was evaluated with the DisperGrader from Alpha Technologies (USA) according to ISO 11345. [34] Tensile testing was done with Zwick Roell's Retro Line universal testing machine (10kN) according to DIN 53504 [35] on S2 samples at a testing speed of 200 mm/min. The tear resistance test was performed in accordance with DIN ISO 34-1:2015 [36] likewise on the universal testing machine at a testing speed of 500 mm/min. Shore A hardness was measured as per DIN ISO 48-4 [37] using the Bareiss U72 hardness tester. Crosslinking was investigated using a TSSR from Brabender (Germany) on S2 samples isothermally (50 % pre-strain) and anisothermally at 2 K/min in the temperature range from 23 °C to 230 °C. Abrasion testing was performed with the Gibitre Instruments „Abrasion Check" device according to DIN ISO 4649 [38]. Finally, gas permeation was tested using the GDP-C unit from Brugger Feinmechanik (Germany) on a 1 mm test plate at 23 °C according to Method D.

Results and discussion

Carbon Black characterization

The reference CB as well as the two rCB grades PURE and MIX were characterized according to the methodology described above. The results of the analysis are shown in table 2.

The intermediate analysis mainly shows the higher ash content in the rCB's compared to CB, which results from the mineral components of the pyrolyzed input material, resulting in a lower carbon

1 Table 1: Compound recipes: Reference, PURE and MIX

Raw materials	recipe [phr]		
	Reference	PURE	MIX
Polymer	100		
Filler „CB" (N660)	65	0	0
Filler „PURE-rCB"	0	65	0
Filler „MIX-rCB"	0	0	65
Plasticizers	10		
Chemicals	14,1		

2 Table 2: Characterization results (CB, rCB PURE und rCB MIX)X

Parameter	Unit	CB	rCB PURE	rCB MIX
Carbon	wt.%	98.6	84.1	73.1
Hydrogen	wt.%	0.2	0.8	0.9
Nitrogen	wt.%	0.2	0.4	0.2
Sulfur	wt.%	0.7	0.1	1.2
Ash content (muffle furnace) [ASTM D1506-15]	wt.%	0.3	13.0	24.6
Ash content (TGA) [ASTM D8474-22]	wt.%	1.8	15.6	29.9
Particle size D90% (Disc centrifuge)	µm	4.0	4.7	7.5
Particle size D97% (Laser diffraction)	µm	− *	9.1	9.6
BET [ASTM D-6556]	m²/g	34.0	76.0	60.0
OAN [ASTM D-2414]	cm³/100g	86.0	88.0	84.0
COAN [ASTM D-3493]	cm³/100g	73.0	77.0	75.0
VV [ASTM D-7854]	cm³/100g	49.0	48.0	46.0
Volatiles [DIN 51720]	wt.-%	0.7	1.8	1.9
Toluene transmittance [ASTM D-1618]	%	97.3	97.5	96.1
Σ15 PAH [AfPS GS 2019:01 PAH]	mg/kg	125.6	9.3	14.4

* Measurement with Mastersizer not possible because CB was in pelletized form.

content. This effect is even more significant for the MIX-rCB with a carbon content of 73.1 wt.% than for the PURE-rCB with 84.1 wt.% carbon content, which was produced from pure truck tires.

Compared to industrial carbon blacks, the reinforcement potential of rCB is limited due to its in-creased mineral content. The mineral particles also accumulated on the surface of the rCB [39], limit the surface activity of the rCB and negatively affect the filler reinforcement in the rubber product. [40] Furthermore, it can be assumed that carbonaceous residues from polymer fragments are formed during the pyrolysis process, which also accumulate on the rCB surface and negatively influence it by blocking active sites. [41]

For a more detailed description, the ash of the rCBs was examined in a scanning electron microscope with elemental analysis (EDX). Both rCBs were found to contain silicon, oxygen, zinc, sulfur, and calcium as well as small amounts of aluminum, magnesium and potassium (see figure 6). A key component is silicon, which is an alternative reinforcing filler, in the form of silicon dioxide (SiO_2), and is used, for example, in tire treads for low rolling resistance and higher fuel efficiency as well as wet braking. Zinc is used in elastomer products as an activator in the form of Zinc oxide (ZnO) and sulfur is known to be used as a crosslinking agent during vulcanization. Regarding particle size, the D90 and D97 percentiles of the rCBs milled by laboratory jet mill turn out to be slightly larger than those of the reference CB. However, both measurement methods provide comparable results.

For the application in new rubber products, the surface activity of carbon blacks is crucial, as it significantly influences the filler-filler and filler-polymer interactions, which determine the tensile strength, elongation at break and abrasion resistance of the compounds. [42] BET analysis shows that the measured surface area from the rCBs is significantly higher than that of the industrial reference CB. At 76.0 m²/g for the PURE-rCB, the value is in the range of highly reinforcing CB's from the N300 series (70 to 99 m²/g) [42] and the MIX-rCB, at 60 m²/g, is comparable to values from the CB N400 series (50 to 69 m²/g). [42]

The structure of the CB or rCB describes its primary particle arrangement and the formation of aggregates. The structure significantly influences the stress at 300% elongation and the dispersion of the material. [43] The OAN, COAN and VV used for structural characterization of the CB and rCB samples indicate a good comparability of the rCBs with the reference CB. It can therefore be assumed that similar carbon black structures are present.

Besides the chemical and physical properties, the lowest possible toxicity of the rCB is a necessary requirement for its reuse in new products. In this context, the focus in science and society is increasingly on the group of substances known as PAHs, which are harmful to humans and the environment. [44] The analyses demonstrated that the PAH content in the rCBs was over 90% lower than the concentration in CB (here: 125.6 mg/kg in the reference CB) at 14.4 mg/kg in the MIX-rCB and at 9.3 mg/kg in the PURE-rCB. This represents a key advantage of rCB compared to CB from fossil feedstocks, which are higher in pollution due to their production process.
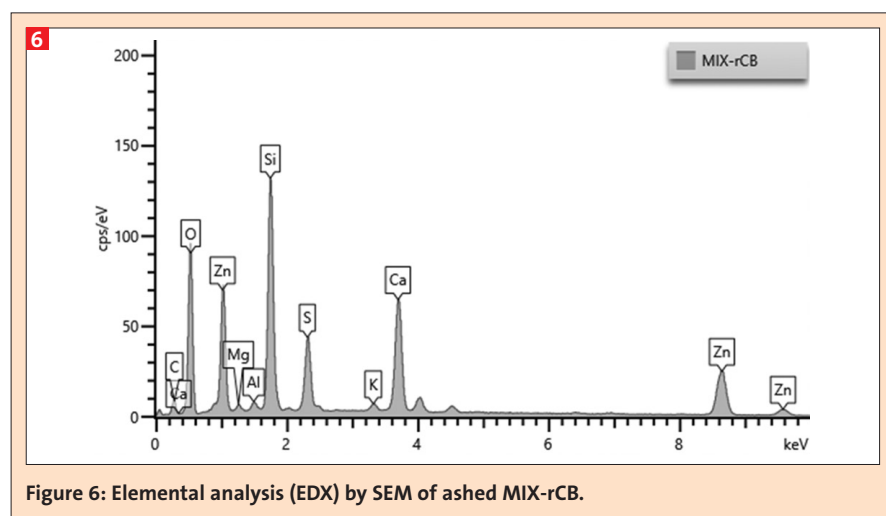

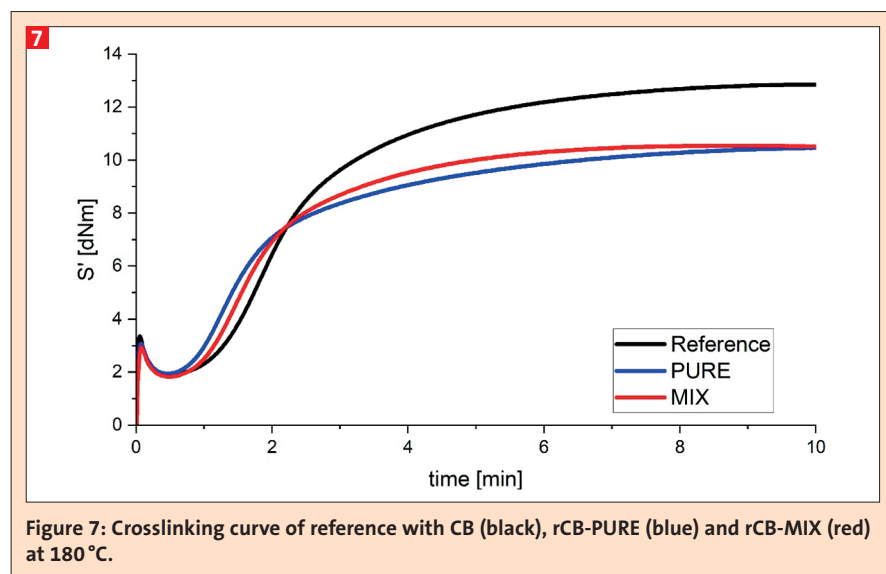**Figure 6: Elemental analysis (EDX) by SEM of ashed MIX-rCB.**

In-Rubber properties

As mentioned above, the in-rubber properties determine the usability of the rCB in new rubber compounds. In the following, the performance of the two rCB grades and the CB in the butyl rubber compound is considered using the methodology described earlier.

The crosslinking behavior of the compounds was determined at 180 °C. The result is shown in figure 7. The rCB compounds show a slightly shorter t_{90} time, which is basically positive for the later use in industrial products due to the shorter production time. Part of the reason for this is the sulfur contained in the rCBs. The mixture with the industrial CB, on the other hand, achieves a higher torque, which indicates higher crosslin-
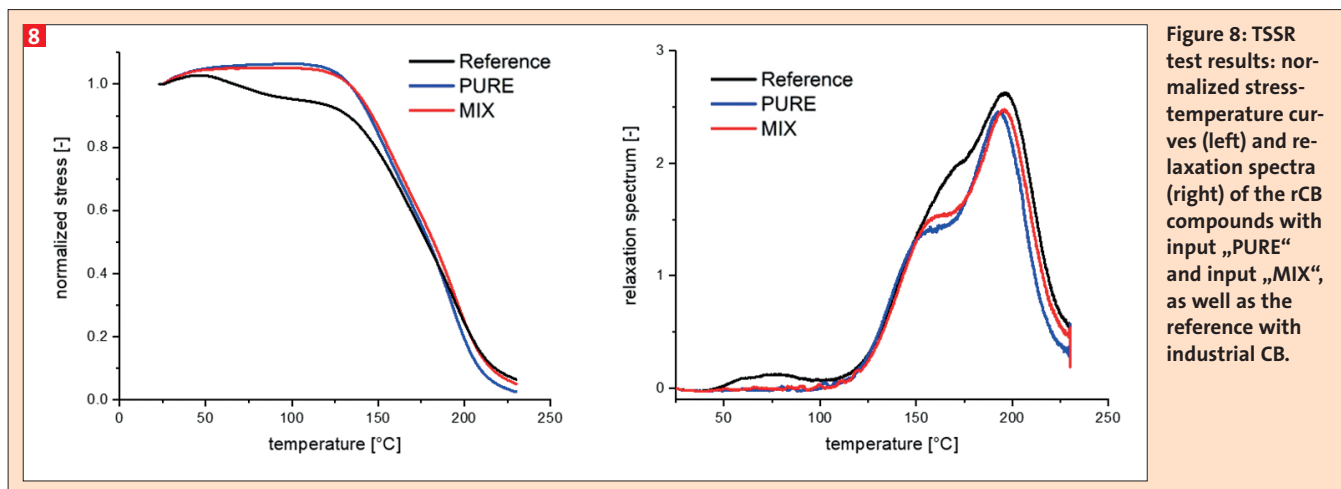

Figure 7: Crosslinking curve of reference with CB (black), rCB-PURE (blue) and rCB-MIX (red) at 180 °C.

Figure 8: TSSR test results: normalized stress-temperature curves (left) and relaxation spectra (right) of the rCB compounds with input „PURE" and input „MIX", as well as the reference with industrial CB.

king and a more viscous material. In addition, the rheometer data are listed in table 3. It can be seen that the t_{10} values are lower, which basically bears the risk of crosslinking during processing (scorch).

The results of the TSSR measurements are summarized in table 4 and figure 8. It should be mentioned that for simplification, the influence of the filler on the calculated crosslink density is not explicitly considered.

The initial stress σ_0 is lower for the compounds with rCB. The stress-temperature curves and the T50 values indicate that the rCB compounds are thermally more stable especially in the range below 170 °C. In the relaxation spectrum graph it is clearly seen that the peak observed for the reference compound between 40 and 110 °C is missing for the compounds with rCB. In this temperature range, physical effects normally occur, such as, for example, the separation of the filler from the matrix. Thus, it can be concluded that the interaction between filler and polymer is very low which is probably due to the larger particles as well as the mineral impurities and the carbonaceous residue blocking active sites at the filler surface for the rCBs. The calculated network density appears to be higher for the rCB compounds but the spread of the three measurements is also high indicating inhomogeneities in the network structure. The relaxation spectrum of the reference compound shows two peaks supposed to correspond to the breakdown of the polysulfidic links between 110 and 170 °C and to the breakdown of the mono- und disulfidic bonds around 195 °C. The mono- and disulfidic bonds predominate. It should be mentioned that the TSSR method is not well estab-

lished yet for the determination of the network architecture. Therefore it must be validated by other methods like the thiolamine method. Providing that these results are right, they indicate that the substitution of the industrial carbon black with rCB leads to reduction of the polysulfidic bonds which may connote with the calculated higher network density and the higher thermal stability expressed by t_{50} and seen in the stress-temperature curve. It is possible that the impurities of rCB containing zinc and sulfur may also play a role in the vulcanization and so change the type of crosslinks preferably built. Looking at the vulcameter results again (table 3 and figure 7) higher network density for the reference compound compared to the rCB substituted may be assumed. One possible reason may be the lower viscosity of the rCB compounds due to the lower activity and thus reinforcement effect of the rCBs leading to lower torque difference. This is supported by the fact that the rCB compounds are found to be softer as seen in the following Shore A hardness measurements. In such a case the

effect of the filler reinforcement must be seen as more significant for the torque level in the vulcameter test than the crosslinking itself. But it must be mentioned that the determination of the crosslink density via TSSR measurements is not sufficiently proved to be correct. Therefore, the results must be supported by other measurements like swelling, Horix diagramm or NMR experiments. Also for clarification further investigations on the compound viscosity, the network structure and eventually fourier trans-formed rheology are needed, which will be part of future work.

The properties of the compounds Reference, PURE (100 % CB substitute) and MIX (100 % CB substitute) are summarized in figure 9. The results of the hardness, gas permeation, abrasion, dispersion, tear resistance and tensile tests in the form of tensile strength, elongation at break and stress at 300 % elongation, are shown in percentages relative to the reference (100 %).

Overall, it can be seen that the properties of most parameters are on average about 10–20 % worse for the rCB compound

3 | Table 3: Rheometer data of the compounds Reference, PURE and MIX

Parameter		Reference	PURE	MIX
S'$_{max}$	[dNm]	13.03	10.61	10.63
S'$_{min}$	[dNm]	2.52	2.42	2.29
t_{10}	[min]	1.33	0.99	1.10
t_{90}	[min]	5.04	5.23	4.32

4 | Table 4: TSSR test results of the reference compound and the rCB compounds

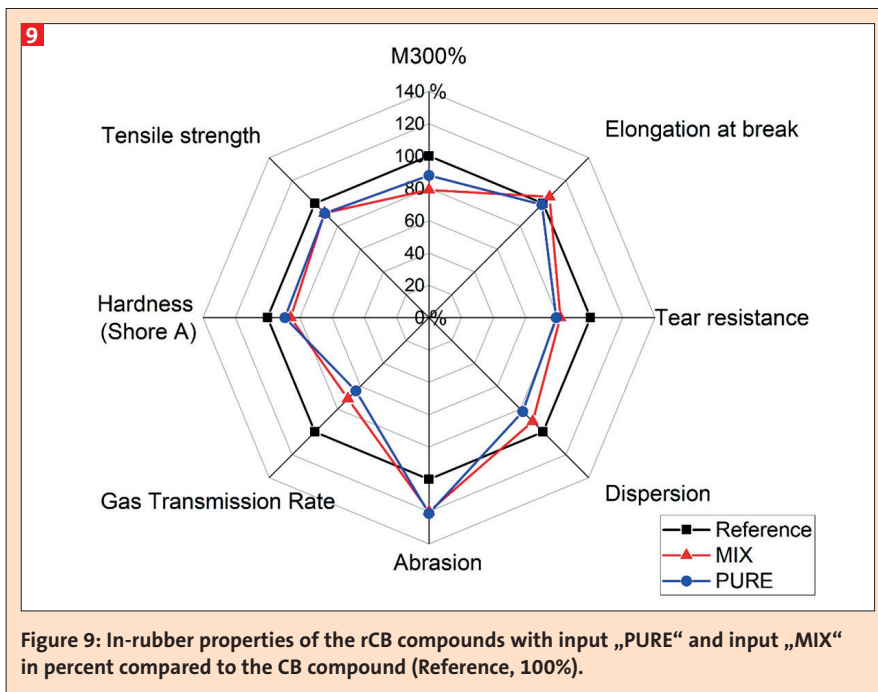| Compound	σ_0 [MPa]	T50 [°C]	Crosslink density [mol/m³]
Reference	0.62 ± 0.00	177.6 ± 1.0	127 ± 27
PURE	0.53 ± 0.02	181.0 ± 1.1	158 ± 34
MIX	0.49 ± 0.01	181.9 ± 0.3	160 ± 15

Figure 9: In-rubber properties of the rCB compounds with input „PURE" and input „MIX" in percent compared to the CB compound (Reference, 100%).

than for the CB reference compound. On the other hand, elongation at break and, above all, gas permeability are positively influenced. The dispersion of all compounds is very good and comparable. The tensile strength of the two rCB compounds decreases by 8 % each compared to the reference. The stress at 300 % elongation (M300 %) decreases by 12 % for the PURE compound and by 20 % for the MIX compound in comparison with the reference. The elongation at break of the MIX compound is 6 % higher. In addition, the tear resistance test shows a decrease of 19−21 % compared to the reference. The hardness is also lower by 10−14 %, which matches the lower torque in the vulcanization test. Abrasion of the rCB compounds is also detrimental, being 21 % higher than the reference for both rCB compounds. The background for these property reductions is mainly the lower surface activity of the rCBs due to the mineral contents and the deposition of carbonaceous residues, resulting in a decrease of the bonds between the rubber matrix and the filler system as well as the filler-filler bonds.

It should be positively emphasized that a major advantage of the rCBs is the significantly lower gas permeability compared to CB. The PURE compound is 29 % less gas permeable than the reference compound, and the MIX compound is even 36 % less gas permeable. This is due to the larger particles of rCB's and its lower structuring compared to conventio-

nal industrial carbon black. In general, the phenomenon of lower gas permeability is very advantageous especially for the use of rCB in butyl compounds.

Conclusion

An increasing volume of EOL tires and, above all, the discontinuation of established treatment paths requires the development of innovative recycling alternatives. The mix of existing processes alone will no longer be able to process the EOL tire volume that will be generated in future.

Pyrolysis, in which the rubber granulate of the mechanically processed scrap tires is thermochemically decomposed, is considered to be a promising approach to a solution. In addition to the resulting pyrolysis products gas and oil, which are already fully utilized, there is still a need for development regarding the solid pyrolysis residue rCB.

In this study, the applicability of rCB from waste tire pyrolysis in new butyl compounds was investigated. After optimization of the pyrolysis process in the laboratory batch reactor, two rCB samples were produced and milled for this purpose in the larger moving bed laboratory reactor of Pyrum Innovations: PURE-rCB from single-variety EOL tire granulate and MIX-rCB from mixed EOL tire granulate. Analysis of the two rCBs and comparison with a commercial CB shows that the main difference between rCB and CB is the higher ash content and conse-

quently lower carbon content of the rCBs. In addition, the proportion of volatile components as well as the particle size are higher in the rCBs. In any case, the significantly lower PAH content compared to industrial CB is very positive.

In order to test the performance in the rubber compound that is crucial for industrial applications, CB and rCBs were mixed into a reference IIR compound. In each case, the total amount of carbon black was replaced by the two rCB grades PURE and MIX. The compounds were vulcanized into test samples using a laboratory heating press and then analyzed in detail. The vulcameter and TSSR tests show that the rCBs influence the crosslinking of the compound. The results show that the rCB from waste tire pyrolysis can prospectively be used as a substitute for fossil-derived CB in butyl compounds, although a complete direct substitution is not possible according to the latest technological development status and may need further recipe adjustments. While the gas impermeability of the compound, which is commonly desired for butyl compounds, is increased by up to >30 %, there is a degradation of about 10−20 % in terms of the mechanical properties.

Considering the increasing world market demand for CB and the finite nature of the fossil resources used for this purpose, pyrolysis and the partial substitution of CB by rCB in butyl compounds in particular nonetheless appear to be a worthwhile approach. Therefore, the partial substitution of CB by rCB will be tested next and the in-rubber properties of CB-rCB blends in butyl compounds will be analyzed. It is expected that the mechanical properties can be positively influenced by further adjustments of the compound recipe.

It should also be noted that there are already initial approaches to rCB posttreatment and refining. Demineralization and activation are the most important of these and can lead to an increase in quality and thus, also to improved usability of rCB in new rubber compounds. [45] In addition, it is possible to partially compensate for the quality-reducing ash content in rCB by compensation, meaning higher filling the mixture with rCB. [39] This will even further improve the gas impermeability.

In conclusion, it can be stated that rCB is currently only suitable as a partial CB substitute in new butyl compounds without further adjustments, but signifi-

cantly improves the gas tightness of the material. Taking current research and development efforts into account, especially those related to reducing the carbon footprint of products, as well as initial approaches to rCB quality improvement, the potential for its use in butyl and other rubber applications is expected to increase in the future. ∎

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