



TECHNICAL CARBON BLACK AND GREEN TECHNOLOGY

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Abstract

Carbon black (CB) is produced through the incomplete combustion of biomass or thermal decomposition in an oxygen-deprived environment. Technical carbon black (TCB) primarily consists of elemental carbon and comes in various grades distinguished by surface area and nanostructure morphologies. However, TCB production raises sustainability concerns due to its reliance on non-renewable feedstock, significant CO₂ emissions and high energy consumption. TCBS find extensive use as reinforcing fillers in the tire and rubber industries. Recent studies underscore the importance of eco-friendly alternatives. This research was carried out to monitor the renewability of the TCB samples by determining the ¹⁴C isotope concentration. Liquid scintillation counting (LSC) and accelerator mass spectrometry (AMS) radiocarbon techniques were employed for measuring the ¹⁴C isotope concentration, while isotope ratio mass spectrometry (IRMS) corrected standardised isotope fractionation correction. The investigation revealed that the examined TCB samples contain extremely low ¹⁴C concentrations, measuring <1 per cent modern carbon (pMC). This finding raises concerns regarding potential environmental ramifications.

Key words:

technical carbon black, ¹⁴C isotope concentration, liquid scintillation counting, accelerator mass spectrometry, isotope ratio mass spectrometry

1. Introduction

Industrial or technical carbon black (TCB) is primarily manufactured via incomplete combustion of hydrocarbons, although thermal decomposition in oxygen-deprived conditions can also yield it. The industrial-scale production of TCB involves meticulously controlled processes, employing precise techniques and measurements to ensure distinct properties that differentiate it from soot a contaminated by-product (Donnet, 2017; Khodabakhshi *et al.*, 2020).

The significance of natural rubber for humans has increased steadily over the past century (Fan *et al.*, 2020).

According to the Association of Natural Rubber Producer Countries (ANRPC), the worldwide production and consumption of natural rubber show annual increases of 0.3% and 3.5%, respectively ANRPC. TCB plays a crucial role as a reinforcing filler in tires and rubber goods. Additionally, it finds applications in pigmentation for plastics, printing inks, coatings and other applications aimed at modifying their mechanical, optical and electrical properties. Its incorporation into rubber alters its behaviour, enhancing abrasion resistance, tensile strength, tear resistance and failure characteristics (Kunioka *et al.*, 2014; Donnet, 2017; Robertson and Hardman, 2021).

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Over 90% of TCB is composed of pure elemental carbon, where fine and spherical carbon atoms combine to form aggregates. To achieve various property balances, TCBs come in a variety of grades with a wide range of particle sizes, based on surface areas, aggregate morphologies with nanostructures, amount of ash and other compounds (Contec; Robertson and Hardman, 2021). The classification of rubber-grade carbon black (CB) follows the ASTM number system and the four-character nomenclature system. The first character 'N' indicates the influence of TCB on the curing rate of typical rubber. The second character indicates the average surface area of the TCB, while the last two characters are arbitrary (ASTM:D1765-17). The most typical TCB with a mean particle surface size is referenced in (Fan *et al.*, 2020).

Globally, approximately 15 million metric tonnes of TCB are produced annually, with about 93% directed to rubber industries. Of this, around 73% is used for tire production, and the remaining 20% in various other rubber appliances. The residual 7% is used for the production of coatings, inks, plastics and paints (Robertson and Hardman, 2021). According to Pehlken and Essadiqi (2005), tires are a complex mixture with a reinforcing agent of CB with silica (ca. 25%) and about 32% of CB can be recovered by tire pyrolysis.

The production of TCB is classified as unsustainable as it utilises non-renewable feedstock, also the production contributes significantly to CO₂ emission and energy consumption. As a result, research on green fillers has gained increasing attention, especially for by-products from industrial or agricultural waste and recyclable materials (Fan *et al.*, 2020).

According to Intharapat *et al.* (2013) and Fan *et al.* (2020)), the non-biodegradability of petroleum-based CB feedstock can be the cause of serious environmental problems. Various research studies are being performed to transform the dependence of CB feedstock to renewable material resources over fossil fuel. Recyclability, utilisation, low cost and easy availability are the main factors when considering new feedstock. Therefore, CB industries have adopted biobased biodegradable materials as new feedstock, consisting of natural fibres (from natural resources),

sawdust and rice husk (from industrial by-products) and rice husk ash (from industrial waste material). The idea has become more tempting from an ecological or commercial point of view as the use of such kinds of materials can transform the refuse into no damage or even desirable materials.

Radiocarbon analysis can distinguish between fossil and biobased carbon by detecting the ¹⁴C/¹²C isotope ratio within the sample (Haverly *et al.*, 2019; Gill *et al.*, 2022). Fossil materials do not contain ¹⁴C isotope after about 50,000 years, as the half-life of the ¹⁴C isotope is 5700 ± 30 years (Kutschera, 2019). This research was carried out to verify the renewable material used in the production of TCB samples of different grades, by ¹⁴C determination.

There are currently no applicable standards specifying the requirements for a specific amount of biocomponents in TCB. However, the determination of the content of bio-based carbon in various materials can be carried out in accordance with the ASTM D6866 or EN 16640 standard. The EN16640 2017 standard applies in Poland and the measurements were carried out in accordance with it. The samples were analysed by two radiocarbon techniques, liquid scintillation counting (LSC) and accelerator mass spectrometry (AMS), at the Gliwice ¹⁴C and Mass Spectrometry Laboratory. Isotope ratio mass spectrometry (IRMS) measurements were used for the isotope fractionation correction.

2. Materials

In this study, four TCB samples of varying grades underwent examination. Currently, there are no existing standards specific to TCB samples. Nonetheless, the establishment of such standards is anticipated in the near future given the growing focus on environmental preservation. Manufacturers of CB typically do not disclose information regarding the presence of bioactive materials. However, exploring the viability of using the ¹⁴C method to ascertain the modern carbon content holds significance. The samples were sourced from Contec Inc. in Warsaw, Poland, and the details pertaining to each sample are outlined in **Table 1**.

Table 1. Details of the TCB samples (Contec; Fan *et al.*, 2020).

No.	Sample code	Surface area (m ² /g)	Application
1.	TCB-N330	76–80	Medium-high reinforcement. Used as tread, carcass and sidewall compounds for tires and rubber goods.
2.	TCB-N550	39–41	Medium-high reinforcement. Used in inner liners, carcass and sidewalls for passenger tires and rubber goods.
3.	TCB-N660	34–36	Medium reinforcement. Used in inner liners, sidewalls, sealing rings, cable jackets, rubber moulding and extruded items.
4.	TCB-N772	31–32	Semi-reinforcement. Used as inner liners of tires and rubber goods.

3. Methods

The samples were prepared and analysed at the Gliwice ^{14}C and Mass Spectrometry Laboratory in the frame of the Institute of Physics – Center for Science and Education, SUT, Poland (Pawlyta *et al.*, 1997; Pazdur *et al.*, 2003; Piotrowska, 2013; Gill *et al.*, 2022).

3.1. ^{14}C Analysis by LSC and $\delta^{13}\text{C}$ by IRMS

Quantulus 1220TM liquid scintillation β spectrometer, was used for LSC measurements to determine the ^{14}C isotope concentration (Pazdur *et al.*, 2003). Butyl-PBD as scintillator, ANU-Sucrose as standard and Commercial Polish Analar-grade benzene was used as a background for LSC measurements (Pawlyta *et al.*, 1997).

Liquid scintillation spectrometry is used for the β -emitting isotopes such as ^{14}C . In general, for LSC measurements, the sample preparation method passed through sample combustion (organic matter is transformed into CO_2) followed by benzene formation with the CO_2 and then mixing with a scintillation cocktail (Gill *et al.*, 2022). All chemicals were analytically pure. The samples were directly used for benzene preparation without any chemical pretreatment. The metal reactors were mechanically cleaned, rinsed with deionised water and heated at 700°C in a muffle furnace for some hours. Glassware for the benzene production line was cleaned with ethanol and then with deionised water and dried at 80°C .

TCB samples were directly reacted with lithium metal, in a proportion of 1:1, to obtain lithium carbide (Li_2C_2) at 700°C of temperature. This reaction took place in a metal reactor for about an hour under controlled pressure conditions. In the next step, Li_2C_2 is hydrolysed by deionised water to produce acetylene (C_2H_2), which is purified by a highly hygroscopic mixture of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and sulphuric acid (H_2SO_4). C_2H_2 is trimerised to benzene using a preheated chromium catalyst (at 600°C ~ 0.5 h). The water molecules from the benzene samples were removed by keeping the sample in sodium metal for 24 h, followed by sublimation. Atmospheric radon was removed by keeping the benzene samples in the refrigerator (at -15°C) for a month, since the half-life of radon is 3.8 days. The complete process for preparing benzene is detailed in (Gill *et al.*, 2022).

IRMS method is applied to calculate the standardised isotope fractionation correction (Stuiver and Polach, 1977; Multiflow, 2012; Agnihotri *et al.*, 2014). It was used for the measurements of the relative ratio of stable carbon isotopes as $\delta^{13}\text{C}$ ($^{13}\text{C}/^{12}\text{C}$). About $5\ \mu\text{L}$ benzene sample (prepared for the purpose of LSC measurement) was combusted with ~ 300 mg of CuO in Simax tubes at 560°C for ~ 12 h. CO_2 was purified using a dry ice water trap with an ethanol mixture (78°C) and the pure CO_2 gas was collected

using liquid nitrogen. NBS-22 (oil; ~ 2 mm), IAEA-CH-6 (formerly, Sucrose ANU; ~ 3 mg) and WZS (lake sediment, our internal standard; $\sim 2\ \mu\text{g}$, [Ustrzycka, 2020]) were directly combusted with CuO under same conditions. Standard $\delta^{13}\text{C}$ values of NBS-22 (oil; $\delta^{13}\text{C} = -30.03\text{‰}$ (IAEA-NBS), IAEA-CH-6 (formerly, Sucrose ANU; $\delta^{13}\text{C} = -10.45\text{‰}$; [IAEA-CH-6]) and WZS (lake sediment, $\delta^{13}\text{C} = -5.06\text{‰}$, [Ustrzycka, 2020]) were used for the correction of $\delta^{13}\text{C}$ measurements. The IsoPrime 100 spectrometer with a continuous flow regime was used for the $\delta^{13}\text{C}$ measurements. The spectrometer is connected to the MultiFlow system and the Gilson GX-271 autosampler. MultiFlow is a multipurpose-automated preparation system that is used to carry out online headspace sampling followed by isotope analysis with IsoPrime 100 spectrometer. The system is designed for high-performance analysis, allowing multiple injections of individual samples. The system extracts gas mixtures from the headspace sample vial. The MultiFlow can be used for the measurement of $\delta^{13}\text{C}$ in CO_2 . The MultiFlow system is designed to automatically extract and purify the CO_2 from a sample and then transfer it to the mass spectrometer. The gas is then sampled with the needle, separated by chromatography and passed to the IsoPrime for isotopic analysis (Multiflow, 2012; Agnihotri *et al.*, 2014). ^{14}C concentrations were corrected for isotope fractionations by using measured $\delta^{13}\text{C}$ according to Stuiver and Polach (1977) equation:

$$A_{SN} = A_S \left[1 - \frac{2(25 + \delta^{13}\text{C})}{1000} \right] \quad (1)$$

where

A_S – measured ^{14}C concentration
 A_{SN} – corrected ^{14}C concentration.

The uncertainty for $\delta^{13}\text{C}$ values were calculated as a standard deviation of the mean value of the samples multiplied by the Student-Fisher coefficient.

3.2. ^{14}C Analysis by AMS

The VarioMicroCube Elemental Analyzer coupled with an automated graphitisation equipment (AGE-3) system by IonPlus AG was used for the determination of total carbon content in samples and graphitisation (Němec *et al.*, 2010; Wacker *et al.*, 2010b). Mini CARbon DAting System (MICADAS) accelerator (Synal *et al.*, 2007) and BATS software (Wacker *et al.*, 2010a) were used for the AMS measurements. Oxalic acid (II) was used as a standard, while coal and phthalic anhydride were used to control the background of AMS measurements.

AMS measures the ratios of $^{14}\text{C}/^{12}\text{C}$ and $^{13}\text{C}/^{12}\text{C}$ precisely. No chemical pretreatments were used for AMS

measurements. Approximately 1 mg of the sample was placed in tin boat capsules. The samples underwent combustion in an elemental analyser to generate CO₂ gas. This gas was subsequently graphitised using AGE in the presence of H₂ and Fe powder (Wacker *et al.*, 2010b). The graphite samples were pressed into target holders (cathodes) at a pressure of 4 bar and sealed with a Cu pin. The ¹⁴C concentrations were measured by MICADAS accelerator mass spectrometer (Synal *et al.*, 2007) and BATS software was used for the ¹⁴C concentration calculations (Wacker *et al.*, 2010a). Oxalic acid (II), coal and phthalic anhydride were used as the standard and background samples, respectively.

4. Results and discussion

The results for the ¹⁴C isotope concentration alongside bio-based carbon content according to (EN16640, 2017) from LSC (lab code GdS) and AMS (lab code GdA) laboratories are listed in **Table 2**. ¹⁴C concentrations are reported in per cent modern carbon (pMC) (Stuiver and Polach, 1977). $\delta^{13}\text{C}$ values are reported in per mil (‰) VPDB and were used for the standardised isotope fractionation correction for LSC measurements. The atmospheric correction factor (REF) in the determined year of 100% bio-based carbon

was used to calculate bio-based carbon content, based on data reported by (CIO, 2022; Hua *et al.*, 2021). Bio-based carbon content calculations for TCB samples were performed using REF values for several years and found the highest bio-based carbon fraction with 100 REF values for 2022 (CIO, 2022), listed in **Table 2**. For AMS measurements, the measured ¹⁴C content of TCB was at the same level as background graphites (0.5 pMC for coal and 0.35 pMC for phthalic anhydride), therefore the reported values for TCB were not corrected for background and the calculated bio-based carbon content for these samples would be the upper limit. However, the specificity of LSC measurements requires the subtraction of the background, which largely comes from natural radiation. The average value of background measurements for the measuring device used is 0.3587 pMC with an uncertainty of 0.0037 pMC.

The ¹⁴C isotope concentrations of TCB samples, categorised into four different grades, were measured by LSC and AMS spectrometry. **Table 2** presents the ¹⁴C concentration obtained via LSC and AMS, the corresponding $\delta^{13}\text{C}$ values, and bio-based carbon content calculated in accordance with (EN16640, 2017) for each sample. **Fig. 1** provides a graphical representation of the ¹⁴C concentration values along with their associated uncertainty.

Table 2. The ¹⁴C isotope concentrations are mentioned in pMC for the four different classification categories of TCB samples. $\delta^{13}\text{C}$ obtained by IRMS (*) and from the AMS measurements (**). The results were corrected for isotope fractionation. The critical χ^2 values for confidence level $\alpha = 0.01$ and four measurements = 11.34, for three measurements = 9.21 and for confidence level $\alpha = 0.05$ and four measurements = 7.81, for three measurements = 5.99. Bio-based carbon content was calculated according to (EN16640, 2017; CIO, 2022), 100 REF is used for the year 2022 (CIO, 2022).

No.	Sample name	Lab code	Sample mass	Total Carbon (%)	$\delta^{13}\text{C}_{\text{VPDB}}$ (‰)	¹⁴ C conc. (pMC)	χ^2	Bio-based carbon content (%)
1.	TCB-N330	GdS-4543	6.08 g	-	-32.44 ± 0.11*	0.589 ± 0.084	6.66	0.589 ± 0.084
2.		GdA-7138.1.1	1.81 mg	99.75 ± 0.93	-29.20**	0.436 ± 0.033	Without GdS-4543	0.436 ± 0.033
3.		GdA-7138.1.2	0.99 mg		-30.60**	0.410 ± 0.038	0.28	0.410 ± 0.038
4.	TCB-N550	GdS-4552	4.02 g	-	-30.417 ± 0.072*	0.189 ± 0.063	30.76	0.189 ± 0.063
5.		GdA-7137.1.2	0.98 mg	97.5 ± 2.3	-25.70**	0.508 ± 0.033	Without GdS-4552	0.508 ± 0.033
6.		GdA-7137.1.3	2.05 mg		-28.80**	0.500 ± 0.035	0.03	0.500 ± 0.035
7.	TCB-N660	GdS-4554	3.91 g	-	-31.82 ± 0.44*	0.908 ± 0.092	51.09	0.908 ± 0.092
8.		GdA-7139.1.1	2.19 mg	98.1 ± 1.9	-28.80**	0.489 ± 0.033	Without GdS-4554	0.489 ± 0.033
9.		GdA-7139.1.2	1.90 mg		-36.60**	0.350 ± 0.043	24.17	0.350 ± 0.043
10.		GdA-7139.1.5	1.09 mg		-29.30**	0.600 ± 0.031		0.600 ± 0.031
11.	TCB-N772	GdS-4555	3.89 g	-	-31.453 ± 0.020*	0.124 ± 0.091	22.45	0.124 ± 0.091
12.		GdA-7140.1.2	2.03 mg	98.9 ± 1.0	-33.00**	0.380 ± 0.043	Without GdS-4555	0.380 ± 0.043
13.		GdA-7140.1.3	2.03 mg		-32.90**	0.350 ± 0.043	5.58	0.350 ± 0.043
14.		GdA-7140.1.4	1.01 mg		-28.90**	0.470 ± 0.035		0.470 ± 0.035

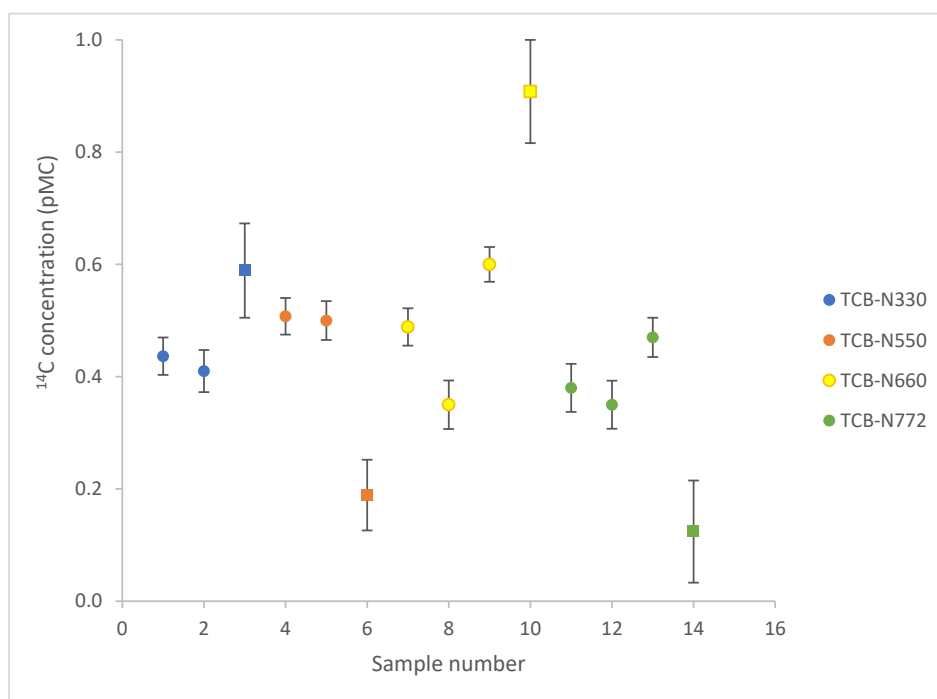


Fig 1. Comparison between AMS and LSC ^{14}C isotope measurements. ‘●’ AMS measurement results, ‘■’ LSC measurement results.

For the TCB-N330 sample, the ^{14}C concentration was measured at 0.436 ± 0.033 pMC and 0.410 ± 0.038 pMC via AMS and 0.589 ± 0.084 pMC via LSC. The AMS and LSC measurements demonstrate agreement.

In the case of the TCB-N550 sample, the ^{14}C concentrations were 0.508 ± 0.033 pMC and 0.500 ± 0.035 pMC from AMS, and 0.189 ± 0.063 pMC from LSC. These results indicate a statistical inconsistency between AMS and LSC measurements.

For the TCB-N660 sample, the ^{14}C concentrations were 0.489 ± 0.033 pMC, 0.350 ± 0.043 pMC and 0.600 ± 0.031 pMC by AMS, and 0.908 ± 0.092 pMC by LSC. The AMS and LSC measurements present statistical inconsistency. The AMS results for this sample demonstrate considerable scatter and do not pass the consistency test.

Regarding the TCB-N772 sample, the ^{14}C concentrations were determined as 0.380 ± 0.043 pMC, 0.350 ± 0.043 pMC and 0.470 ± 0.035 pMC using AMS, and 0.124 ± 0.091 pMC using LSC. Similar to previous cases, the AMS and LSC measurements are statistically inconsistent.

To explain the disparities in measurement results between LSC and AMS, the authors are inclined to support the hypothesis suggesting sample inhomogeneity, which could be because of the ash contamination, the presence of hydrogen atom (provided by the original hydrocarbon feedstock), four-general oxygen-containing chemical groups and sulphur (Contec; Fan *et al.*, 2020). The ASTM

D-1506 standard (ASTM:D1506-15, 2020) states that the ash content in TCB should not exceed 1%, but different grades of TCB can vary in ash content within the permissible 1%. Larger particles such as ash could be included more in large samples for LSC than in AMS samples, also the ash content tends to be larger for the samples with lower surface area/mass ratios. This supposition finds potential validation in the scattered AMS measurements for the TCB-N660 sample. Additionally, discrepancies in $\delta^{13}\text{C}$ values among subsamples of the same TCB, analysed via the AMS technique, lend credence to the notion of heterogeneity within the tested samples. The most notable variations are observed within the TCB-N660 sample.

The results obtained from measurements using two techniques (AMS and LSC) indicate a very low (<1 pMC) concentration of ^{14}C in the tested samples. This suggests a substantial presence of fossil components in samples, indicating their production before the use of biogenic material. The Reference Value (REF) for the year of biomass formation is required to calculate the content of bio-based carbon in the sample (EN16640, 2017). This value corresponds to the ^{14}C activity of pure biomass. The highest bio-based carbon content is determined using the REF value corresponding to the year 2022, set at 100 pMC. Therefore, the bio-based carbon content ratio corresponds to the ^{14}C concentration within the sample. In our previous research (Gill *et al.*, 2022), we measured the ^{14}C isotope

concentration in recovered CB samples obtained from the pyrolysis of truck and passenger car tires to be between 5 pMC and 7 pMC (Gill *et al.*, 2022). This variation could be attributed to the conversion of some modern carbon sourced from natural rubber into recovered CB during the pyrolysis process.

5. Conclusion

TCB samples underwent analysis in this study. The ^{14}C isotope concentrations were measured in the samples using LSC and AMS radiocarbon techniques at the Gliwice ^{14}C and Mass Spectrometry Laboratory. These TCB samples were sourced from the Contec Inc. Company. According to

previous research, the TCB samples were expected to contain a higher concentration of modern carbon. However, all samples exhibited only a minute amount of ^{14}C isotope concentration <1 pMC. The bio-based carbon content mirrors the ^{14}C isotope concentrations of each sample. This study indicates that the four differently graded TCB samples were either not produced from renewable resources or were produced with a minimal share of them.

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