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Extended Abstract of Doctoral Dissertation

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APPLICATION OF ISOTOPE METHODS FOR DETERMINATION OF BIO-BASED CONTENT IN SOLID MATERIALS

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KOMAL AZIZ

Abstract

In the rapidly developing modern world, the increasing production of waste raises concerns related to environmental pollution. Therefore, fossil-based materials are being replaced by contemporary biogenic materials. The main objective of this research is to investigate the bio-based carbon content in various materials that are directly or indirectly related to everyday use. As part of the research, I worked on tire rubber and its pyrolysis products, disposable packaging materials, and samples of technical carbon black. These materials have a significant impact on environmental pollution but are increasingly being used for recycling, energy production, and sustainable manufacturing.

The tire rubber samples and its pyrolysis products (pyrolytic oil and recovered carbon black), as well as samples of technical carbon black, were provided by Contec Inc. from Warsaw, a company specializing in tire pyrolysis. The tire rubber, pyrolytic oil, and recovered carbon black samples were sourced from both truck and car tires.

Various commercially available disposable packaging samples, made from paper, wheat bran, wood, and sugarcane, were obtained from several companies (Quick Pack, Vigo, and Bio-pack). All samples were examined for the content of the isotope ^{14}C and bio-based carbon using accelerator mass spectrometry (AMS) and liquid scintillation counting (LSC) techniques. Isotope ratio mass spectrometry (IRMS) was used to determine the isotopic fractionation correction for the LSC technique. To determine the bio-based carbon, I applied the European standard EN 16640: 2017, which relates to all bio-based products. Different atmospheric correction factor (REF) values were used depending on the sample type and the assumed year of its production.

I applied the radiocarbon method to distinguish fossil materials from modern materials. The half-life of the ^{14}C isotope is 5700 ± 30 years, meaning that fossil materials lack ^{14}C isotope, while biologically derived materials contain ^{14}C at concentrations close to atmospheric levels.

All samples were analyzed using the radiocarbon method at the ^{14}C and Mass Spectrometry Laboratory in Gliwice. The pyrolytic oil and recovered carbon black samples were graphitized at the AMS Laboratory in Gliwice, and the ^{14}C measurements were conducted at the Radiocarbon Laboratory in Poznań. Tire rubber and its pyrolysis products were further analyzed at the National Laboratory for Age Determination in Trondheim, Norway. The concentrations of the ^{14}C isotope were reported as percent modern carbon (pMC).

For the pyrolytic oil, the ^{14}C isotope concentrations varied depending on the proportion of truck to car tires in the mass subjected to pyrolysis, ranging from approximately 41 to 50 pMC, with

higher concentrations of ^{14}C observed with a higher proportion of truck tires. The same trend was observed for recovered carbon black, where concentrations ranged from about 5 to just under 7 pMC.

For the rubber samples, highly scattered ^{14}C concentration results were obtained, ranging from 12 to 42 pMC. The dispersion of results is due to the complex, layered structure of tires, which uses both natural rubber and rubber derived from fossil fuels. The ^{14}C concentration measurement in a small sample should be considered characteristic of a specific location within the tire, rather than of the batch of tires subjected to pyrolysis or even a single entire tire.

Ten different types of disposable packaging samples showed ^{14}C concentrations above 100 pMC, indicating that they were produced from modern biomass. The samples were analyzed layer-by-layer using the AMS technique. The outer (waterproof) layer exhibited relatively high ^{14}C concentrations, suggesting the use of bioplastics. Wooden cutlery samples showed high and varied ^{14}C concentrations, ranging from 114 to 136 pMC, suggesting that the samples came from trees of different ages.

In contrast, the technical carbon black samples for the four tested classes showed extremely low ^{14}C concentrations, <1 pMC, indicating the use of fossil material in their production or minimal involvement of renewable materials.

The results of this work were published in three scientific articles in JCR-listed journals and in a chapter in a scientific monograph:

1. Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N, Kłusek M, Końska K, Wróblewski K, Nadeau MJ, Seiler M. (2022). Study of bio-based carbon fractions in tires and their pyrolysis products. Radiocarbon. 64 (6): 1457-1469. DOI: 10.1017/RDC.2022.88.
2. Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N, Ustrzycka A. (2023). Technical carbon black and green technology. Geochronometria. 50 (1): 250-256. DOI: 10.2478/geochr-2023-0016.
3. Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N. (2024). Monitoring of modern carbon fraction in disposable packaging. Radiocarbon, First View DOI: 10.1017/RDC.2024.35.
4. Gill KA, Michczyńska DJ, Michczyński A. Bio-carbon content determination in disposable packaging by liquid scintillation counting. [in:] Werle S, Ferdyn-Grygierek J (eds.) POB6 Monograph “Climate and Environmental Protection, Modern Energy – Selected Issues”, Silesian University of Technology (in press).

The research allowed for the development of measurement procedures for new types of samples not previously analyzed at the ^{14}C and Mass Spectrometry Laboratory in Gliwice. It was determined that no chemical pretreatment was required, except for rinsing with demineralized water. The concentration of the ^{14}C isotope and the amount of bio-based carbon were determined in all analyzed samples. The research also enabled intra-laboratory comparisons between LSC and AMS techniques, as well as inter-laboratory comparisons.

The study demonstrated that the applied methods are appropriate and reliable for the analysis of the tested types of materials.

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List of Abbreviations

AGE	*Automated Graphitization Equipment*
AMS	*Accelerator Mass Spectrometry*
ASTM	*American Society for Testing and Materials*
CB	*Carbon Black*
DPM	*Disposable Packaging Material*
ELT	*End-of-Life Tires*
FIRI	*Fourth International Radiocarbon Intercomparison*
GC	*Gas Chromatography*
GdA	*Gliwice Laboratory code for AMS technique*
GdS	*Gliwice Laboratory code for LSC technique*
GPC	*Gas Proportional Counters*
IAEA	*International Atomic Energy Agency*
IRMS	*Isotope Ratio Mass Spectrometry*
LSC	*Liquid Scintillation Counting*
MICADAS	*Mini Carbon Dating System*
POB	*Priority Research Are*
PW	*Plastic Waste*
rCB	*Recovered Carbon Black*
TC	*Total Carbon*
TCB	*Technical Carbon Black*
TGA	*Thermogravimetric Analysis*
TRa	*Trondheim Laboratory Code for AMS Technique*
VPDB	*Vienna Peedee Belemnite*

1. Research Scope

The economies of many countries rely on fossil hydrocarbon fuels, which leads to an increase in carbon dioxide emissions. Despite the lack of precise determination of the impact of such economies on the carbon balance in the atmosphere, oceans, and land, and ultimately on humanity, much attention is currently focused on reducing carbon dioxide emissions. One approach to this is material recycling. To promote green recycling, the amount of modern biocarbon in various types of materials can be examined.

The research conducted as part of this doctoral dissertation focuses on determining the bio-based carbon content in the tested samples based on their radiocarbon (^{14}C) concentration. The ^{14}C content in the material can help determine the proportion of fossil and modern substances (referred to as biocomponents). This content depends on the origin of the materials from which the sample was made, as the contemporary biosphere contains radiocarbon, whereas fossil fuels do not.

The study covers commonly used materials such as tires (along with their pyrolysis products), disposable packaging, and technical carbon black samples.

The doctoral dissertation consists of a collection of published and thematically related articles:

- Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N, Kłusek M, Końska K, Wróblewski K, Nadeau M-J, Seiler M. (2022). Study of bio-based carbon fractions in tires and their pyrolysis products. Radiocarbon. 64(6):1457-1469. DOI: 10.1017/RDC.2022.88.
- Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N, Ustrzycka A. (2023). Technical carbon black and green technology. Geochronometria. 50(1):250-256. DOI: 10.2478/geochr-2023-0016.
- Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N. (2024). Monitoring of modern carbon fraction in disposable packaging. Radiocarbon, First View DOI: 10.1017/RDC.2024.35.
- Gill KA, Michczyńska DJ, Michczyński A. Bio-carbon content determination in disposable packaging by liquid scintillation counting. [in:] Werle S, Ferdyn-Grygierek J (Eds.) POB6 Monograph “Climate and environmental protection, modern energy - selected issues”, SUT (in press).

2. Research Objectives and Thesis

The aim of this doctoral dissertation is to develop, test, and verify a methodology for determining bio-based carbon content using isotope methods applied at the ^{14}C and Mass Spectrometry Laboratory at the Institute of Physics – Centre for Science and Education at Silesian University of Technology in Gliwice for solid samples for which there is a need to determine or verify the content of biocomponents. Such samples have not been studied in this Laboratory so far.

The basic thesis put forward is that the concentration of bio-based carbon can be determined using the ^{14}C isotope measurement method. This thesis is fully consistent with the EU and Polish standard EN16640: 'Bio-based products - bio-based carbon content - determination of the bio-based carbon content using the radiocarbon method'.

The specific objectives of this research are as follows:

i. To determine the requirements for the preliminary preparation of the materials under study.
ii. To develop an effective methodology for determining ^{14}C in various types of solid materials that have not been previously analyzed using liquid scintillation counting (LSC) and accelerator mass spectrometry (AMS) techniques.
iii. To determine the ^{14}C concentration in the solid materials under investigation.
iv. To develop efficient protocols for determining the bio-based carbon content.

This work also contributes to promoting green recycling by utilizing renewable resources in the production of all kinds of materials and controlling greenhouse gas emissions.

3. Description of Research Subject

3.1. Radiocarbon

The radioactive isotope of carbon (radiocarbon/^{14}C) is the heaviest, unstable, naturally occurring isotope of carbon. Radiocarbon is a relatively rare isotope of carbon and occurs in amount of~1×10^{-10} % compared to ~98.89% ^{12}C and ~1.11% ^{13}C (Wood 2015). It is produced naturally through the impact of cosmic rays on atmospheric nitrogen atoms, and it immediately participates in the global carbon cycle along with other carbon isotopes (Buchholz and Spalding 2010). It should be noted that a CO_2 molecule containing ^{14}C has similar chemical properties to ordinary CO_2 with stable isotopes (^{12}C and ^{13}C). Thus, $^{14}CO_2$ is transferred to plants through photosynthesis and to animals through the consumption of plants, just like any other CO_2 molecule. ^{14}C is also mixed with inorganic carbon forms, such as CO_2, HCO_3^-, and CO_3^-, in oceans through the molecular exchange process through the air-sea interface. In this way, the radiocarbon is also received by the marine biosphere. All living matter is labeled by ^{14}C atoms, which gives a very wide scope for the applicability of the radiocarbon method (Kusumgar et al. 1963; Quarta et al. 2021).

^{14}C is used as a dating tool to determine the age of carbon-containing materials and also as an environmental tracer to track carbon movement in the environment (Skinner and Bard 2022). The fundamental work on the measurement and application of ^{14}C as a radiometric dating tool is attributed to W. F. Libby (Arnold and Libby 1951; Libby et al. 1949). The half-life of the radiocarbon isotope is 5700 ± 30 years (Kutschera 2019); therefore, after about ten half-lives, the samples will be free of the radiocarbon isotope (Hajdas et al. 2021).

3.2. Radiocarbon Measurements

Radiocarbon provides an ideal tool for constructing archaeological chronologies, and in many cases can directly date the event of interest. In archaeological sites, organic materials are often abundant and provide sufficient samples for analysis. In addition to archaeological dating, radiocarbon analysis is widely used in climate, environmental, and life science research. (Szidat et al. 2014; Wood 2015).

3.3. Significance of the Radiocarbon Method in Determining Bio-Based Content

In the 20th century, the concentration of CO_2 in the atmosphere increased due to the extensive use of fossil fuels for energy production and transportation. To address this problem, the European Union has set new goals to increase the use of renewable materials (biogenic) in fuels (5.75% until 2010 in the EU Directive 2003/30/EC (Directive 2003) and at least 10% of biofuels in all liquid fuels by 2020 (Directive 2009). Due to the lower profitability of biofuel production compared to fossil fuels, the European Union's environmental policy promotes biofuels by reducing excise taxes and providing income tax credits. (Krajcar Bronić et al. 2015). Therefore, there is a need to determine the amount of biogenic material by a reliable and accurate method, not only in different types of fuels but also in all other materials of daily life, such as bioplastics, disposable packaging, wooden equipment, etc. Any material is considered bio-based if it contains a significant proportion of radiocarbon that ideally reflects the current atmospheric ^{14}C value. Radiocarbon method is a well-known and reliable method for the determination of bio-based content in different kinds of products. In the radiocarbon method, ^{14}C concentration is determined as a percent modern carbon (pMC), whereas the bio-based carbon content is determined by international standards according to the atmospheric correction factor (REF) in the determined year of 100% bio-based carbon.

In this research, I worked on tire rubber and its pyrolysis products, technical carbon black (TCB), and disposable packaging materials (DPMs), as these materials are widely used for recycling and sustainable production. The main objective of this research was to examine the modern carbon concentration in the mentioned materials to check the implementation of the laws passed by environmental protection agencies to improve green technology and control greenhouse gas emissions.

3.4. Waste Treatment

The demand for energy use and the production of waste from daily life are the two main factors considered in the developing world. Among the organic or inorganic waste produced, plastics and rubber are considered the most dangerous waste source to treat, contributing 31.2% of total waste (Hoang et al. 2020). Municipal solid waste is the important source of greenhouse gas emissions (Wang and Nakakubo 2020) and is collected from household waste, including electronic appliances, waste batteries, metals, paper and cardboard, metals, plastics, wood, furniture, etc. (Directive 2008). The recovery of energy from municipal solid waste is a great way to reduce the consumption of fossil fuels for energy production

(Ngusale et al. 2017). Landfill, incineration, and composting are roughly classified as the municipal solid waste treatment methods (Wang and Nakakubo 2020). According to the directive of the European Commission from 2008, later amended in February 2024, levels of priority order in waste prevention and management are set as follows: prevention, re-use, recycling, energy recovery and disposal. This took into account general environmental protection, sustainability, technical feasibility, protection of resources, human health, and social impacts (Directive 2008).

The rate of waste recycling has been growing in the EU-27, indicating the increased use of waste as a resource and the achievement of a circular economy. Total waste treatment increased considerably in Europe from 46% in 2004 to 60% in 2020, while total waste disposal decreased from 54% in 2004 to 45% in 2020 (Eurostate 2020). In 2021 the highest recycling rate was recorded for packaging at 64%, followed by municipal waste at 49% and electrical and electronic waste at 39%. Most of the waste was still disposed of by incineration in 2021 (European-Environmental-Agency 2023).

In Europe, from 2010-2021, paper and cardboard were the main materials generated by packaging waste (34.0 million tonnes in 2021) followed by plastic (16.1 million tonnes) and glass packaging waste (15.6 million tonnes) (Eurostate 2023). The two crucial techniques – reuse and recycling, are used for the development of a circular economy. (Di Foggia and Beccarello 2022).

Plastic pollution is being highlighted as the global crisis from its production to its disposal. Bioplastics are natural and chemically driven materials from renewable or oil-based resources and are designed to provide low carbon emissions, high recycling values, and complete biodegradability or compostability (RameshKumar et al. 2020).

Industrial plastic production was started around the 1950s and has increased exponentially. In 2016 the annual plastic production was 330 million metric tonnes (Lebreton and Andrady 2019), whereas in 2022 it reached 400.3 million metric tonnes (Statista 2023).

According to the Plastics Europe report in 2020, 24.5 million tonnes of plastic waste (PW) were generated. 14% of the PW was recycled and provided 3.5 million tonnes of recyclate products. 50% of European plastic waste is incinerated for energy recovery and 95 million tonnes of carbon dioxide gas is emitted per year. The European Commission aims to end plastic pollution by 2040 by implementing a circular economy that allows the reuse, recycling and responsible treatment of all types of plastic products, while reducing greenhouse gas emissions related to plastic management. The Commission also recommended that the transition to the EU's net zero carbon emissions and circularity targets be completed by 2050 (Plastics-Europe).

Worldwide, more than 1.7 billion tires are produced annually (Tire-Grades 2023), and around 4.2 million metric tons of rubber tires were produced in the European Union in 2020 (Statista 2021). According to (Hoang et al. 2020) two-thirds of tires are dumped in landfills or disposed of illegally, causing serious threats to the environment and human health. Waste tires are becoming the world's leading environmental problem, as waste rubber is accounted for a large percentage of solid waste.

In the case of end-of-life tires (ELTs), 80% are used as fuel or recycled material utilizing disposal and re-treading (Goksal 2022). For tire recycling, retreading, incineration, grinding, and reclaim are used as alternatives but with many drawbacks. Tires are hard to remold, in this way. Pyrolysis seems to be the most appropriate recycling method (De Marco Rodriguez et al. 2001). The effective applications of tires decrease fossil fuel and energy consumption, as tires themselves are used as fuels. As a result, there is a decrease in fossil-based CO_2 because tires already contain carbon from fossil themselves. Tires have high calorific values and also contain about 60-70% carbon and 6-7% hydrogen, so the combustion and composition properties of tires are almost equal to the coal (Rodríguez et al. 2017). In this way, the combustion of tires provides heat but reduces the additional emission of CO_2 and SO_x into the atmosphere (Krajcar Bronić et al. 2015; Rodríguez et al. 2017).

4. Samples for Analysis

In this project, several types of samples of daily-use goods were investigated. The first type of samples included tire rubber and pyrolysis products, such as recovered carbon black and pyrolytic oil samples. These samples were provided by Contec Inc., a Warsaw, Poland-based company that uses tire pyrolysis technology to produce an environmentally friendly substitute for virgin carbon black and petrochemical feedstock, as well as to address the global ELT waste problem. Contec Inc. provided samples in three batches, with each batch consisting of a mixture of shredded rubber from truck and passenger car tires in varying proportions, and the pyrolysis oil and recovered carbon black originated from the same batch as the rubber samples.

In the second series, I analyzed ten different types of disposable packaging materials (DPMs) collected from Quick Pack, Vigo, and Bio-pack companies. These samples included paper plates, boxes, paper straws, paper cups, baking paper, sugar cane plates and boxes, wheat bran plates, and wooden cutlery.

In the third series, I examined biogenic material in technical carbon black (TCB) samples obtained from Contec Inc. I examined four different graded technical carbon black samples, which were classified based on surface area, aggregate morphologies with nanostructures, ash content, and other chemicals (Contec ; Robertson and Hardman 2021). **Table 1** describes all the sample categories in detail.

Table 1. Description of the samples analyzed.

No.	Sample Name	Sample code	Description
1.	Pyrolytic oil-1	CONT-1	Unknown mixture of truck and passenger car tires.
2.	Pyrolytic oil-2	PCO-2	100% passenger car tires.
3.	Recovered carbon black-1	rCB-2	100% passenger car tires.
4.	Rubber-1	CR-2	100% passenger car tires.
5.	Pyrolytic oil-3	TCO-3	70% truck and 30% passenger car tires.
6.	Recovered carbon black-2	rCB-3	70% truck and 30% passenger car tires.
7.	Rubber-2	CR-3	70% truck and 30% passenger car tires.
8.	Disposable plates-1	QSCP-1	In white, a kind of paper disposable plates, made from sugarcane fibers.
9.	Disposable cups	QPC-2	Pale white, made with paper stuff.
10.	Baking paper	QBP-3	In brown color, also known as vegetable parchment; cellulose-based composite.
11.	Disposable straws	QPS-4	Brown on the outside and white on the inside, made of paper material.
12.	Disposable plates-2	QPP-5	In white color, made of paper material.
13.	Wooden cutlery	QWC-6	Consists of wooden spoons, wooden forks, and wooden knives.
14.	Disposable plates-3	QBPP-7	In brown color, made of paper.
15.	Disposable plates-4	VWBP-8	Brown in color made from wheat bran.
16.	Disposable boxes	BSCB-9	Pale white, made from sugarcane bagasse.
17.	Disposable plates-5	BPP-10	Pale white, made from paper.
18.	Technical carbon black-1	TCB-N330	Surface area of 76-80 m^2/g with medium-high reinforcement. Compounds used for tire tread, carcass, and sidewalls.
19.	Technical carbon black-2	TCB-N550	Surface area 39-41 m^2/g with medium-high reinforcement. It is used in the inner liners, carcasses, and sidewalls of passenger tires and rubber goods.
20.	Technical carbon black-3	TCB-N660	Surface area 34-36 m^2/g, medium reinforcement. It is used in inner liners, sidewalls, sealing rings, cable jackets, rubber molding, and extruded goods.
21.	Technical carbon black-4	TCB-N772	Surface area 31-32 m^2/g, with semi-reinforcement. They are used as inner liners in tires and rubber items.

5. Methodology

In this research, I used both conventional (liquid scintillation counting – LSC) and accelerator (AMS) radiocarbon techniques to determine the biobased carbon content in the samples. Isotope ratio mass spectrometry (IRMS) was used to determine the isotope fractionation correction for the samples examined by LSC.

According to (Rodríguez et al. 2017) pyrolysis-GC/MS, thermogravimetric analysis (TGA) and radiocarbon analysis (^{14}C methods) can be used to determine the biomass content in end-of-life tires (ELT) but only radiocarbon analysis is considered a valid technique (Haverly et al. 2019).

According to (Krajcar Bronić et al. 2015) manual sorting, chemical dissolution, and ^{14}C methods are used for the determination of biobased components in all kinds of fuels or wastes which are used in waste-to-energy plants. Manual sorting is time-consuming and labor-intensive, whereas selective dissolving requires laboratory personnel and equipment (Séverin et al. 2010). The ^{14}C method is the most reliable and can be applied to various kinds of solid communal waste, used car tires, liquids and fuels (Krajcar Bronić et al. 2015).

5.1. Radiocarbon Measurement Techniques

To count the ^{14}C decay rate, highly sensitive low-level radiometric measuring techniques have been devised, together with proper sample chemical pretreatment. The required amount of carbon (1-5g) in the sample is the main constraint of these methods. Sensitive low-level radiometric measuring techniques are required due to ^{14}C's low natural abundance (10^{-10} %), low specific activity (226 Bq/kg), and low electron energy (<156 keV) produced in the β decay process. In the early days of radiocarbon determination, gas proportional counters (GPC) were commonly utilized, but they are now almost obsolete, with liquid scintillation counting (LSC) dominating the decay-counting techniques (Krajcar Bronić et al. 2010; Wood 2015).

Around 50 years ago, accelerator mass spectrometry (AMS) technology was developed, which is unaffected by low specific activity or electron energies. AMS measures the ^{14}C/^{12}C or ^{14}C/^{13}C ratio in a sample compared to the standard. The tiny sample size (a few mg) and continuous improvement of AMS make it a more suitable method for a variety of applications (Hajdas et al. 2022; Krajcar Bronić et al. 2010).

5.2. Biocarbon Content Determination

Currently, the usage of biogenic materials in various fields is increasing rapidly on the industrial, customer, and consumer sides. Biogenic materials have replaced typical fossil carbon-containing materials (European-Union 2019; Pandey and Singhal 2023). The constant increase in demand for bio-based materials has been noticed in the recent decade (2010-2020), not only in the bioplastics field but also in biopolymers, bio-lubricants, bio-solvents, biosurfactants, enzymes, and bio-pharmaceuticals (Pandey and Singhal 2023).

The principle of determining the biogenic content in the tested material is based on the fact that organic matter with a well-defined radiocarbon fraction corresponding to the modern level of atmospheric $^{14}CO_2$, as well as fossil materials, was used for its production. Radiocarbon has a half-life of 5700 ± 30 years, making fossil materials free of it (Hua et al. 2022; Kutschera 2019).

There are international and European standards specifying how to determine biobased carbon, depending on the type of materials - details are included in the paper (Gill et al. 2022). In this research, I examined tire rubber and its pyrolysis products, disposable packaging materials, and technical carbon black samples. I determined the biocarbon content in the samples using the European standard (EN16640 2017), which applies to all biobased goods. The biobased carbon content of the samples is calculated using the formula below:

$$biobased\ carbon\ \ content = \frac{pMC}{REF}\ , \qquad \text{Eq. 1}$$

where:

pMC - ^{14}C concentration expressed in terms of modern percent carbon, obtained from radiocarbon techniques (LSC and AMS).

REF - an atmospheric correction factor in the determined year of 100% bio-based carbon, was used to calculate bio-based carbon content, according to data published by (CIO 2022; Hua et al. 2022).

5.3. Bio-Content Determination

The European standard EN-16785-1 defines how to correctly determine the biocomponent content using the radiocarbon method and elemental analysis. According to it, the amount of biomass is calculated as the amount of biological elements (C, H, N, O) in the sample, expressed as a percentage of the total sample mass:

$$bio - content = \frac{mass\ of\ bio\text{-}based\ content}{total\ mass\ of\ material} \times 100\ (\%) \qquad \text{Eq. 2}$$

My PhD research was limited to the radiocarbon method and bio-based carbon content.

5.4. Accelerator Mass Spectrometry (AMS) Measurements

The AMS radiocarbon technique is efficient, fast, and convenient for sample preparations for radiocarbon measurement (Wacker et al. 2010b). AMS measurements were performed in three laboratories. All of the samples listed in **Table 1**, except tire rubber, were prepared and analyzed at Gliwice ^{14}C and Mass Spectrometry Laboratory in the Institute of Physics – Centre for Science and Education, Division of Geochronology and Environment Isotopes. The tire rubber and its pyrolysis product were analyzed at the National Laboratory for Age Determination, Trondheim, Norway. In addition, graphite samples from tire pyrolysis products that were graphitized in the Gliwice Radiocarbon Laboratory were measured at the Poznań Radiocarbon Laboratory (Goslar et al. 2004).

5.4.1. Preparation and Analysis of Samples at Gliwice ^{14}C and Mass Spectrometry Laboratory

A well-equipped sample preparation laboratory for ^{14}C analysis has existed at the Silesian University of Technology in the Institute of Physics – Centre for Science and Education, Division of Geochronology and Environmental Isotopes since the late 1960s. As part of my doctoral thesis, I had the opportunity to learn how to use world-class equipment.

The VarioMicroCube Elemental Analyzer coupled with an automated graphitization equipment (AGE-3) system by IonPlus AG with seven reduction reactors, was used to determine the total carbon content in samples and graphitization (**Fig. 1a**) (Němec et al. 2010; Wacker et al. 2010b). Before starting my doctoral thesis, the Gliwice AMS Radiocarbon Laboratory produced graphite targets from plant remains wood, charcoal, peat, shells, and bone samples (Piotrowska 2013). I successfully applied the previously developed methods to new types of samples, i.e. pyrolytic oil, recovered carbon black, disposable packaging samples, wooden cutlery, and technical carbon black samples (Gill et al. 2024; Gill et al. 2022; Gill et al. 2023). As part of the research conducted, it was determined that for the new types of samples mentioned above, no chemical pre-treatment is required apart from rinsing with demineralized water.

A few milligrams of sample (see **Table 2**) were used for AMS measurements. The sample was weighted in a tin capsule for liquid samples and a tin boat capsule for solid samples. The tin capsules for the liquid samples were properly sealed by a special sealing press. Due to the heterogeneity, i.e. the layered structure of disposable packaging, different subsamples were analyzed (outer layer, inner layer and their mix), as the AMS measurement results clearly indicated that the measurement result depended on the proportions of individual layers in a small (milligram) subsample. Tests were also carried out on the possibility of using sample carbonization with limited oxygen access for sample homogenization purposes, as the AMS measurement results clearly indicated that the measurement result depended on the proportions of individual layers in a small (milligram) subsample. For carbonization, a 24 g sample was placed in a metal reactor with a lid with a very small hole (to minimize oxygen access) and burned in a muffle furnace at 700 °C for about 7 to 10 minutes. The sample was then cooled and ground to a powder. In the next step, the elemental analyzer was used for sample combustion to produce CO_2 gas that was subsequently graphitized using AGE-3 in the presence of hydrogen (H_2) and Fe powder (Wacker et al. 2010b). The graphite samples were pressed using a special press into target holders (cathodes) at a pressure of 4 bar (two times for proper pressing and sealing).

Fig. 1a Elemental Analyzer coupled with automated graphitization equipment at Gliwice ^{14}C and Mass Spectrometry Laboratory.

Fig. 1b MICADAS at Gliwice ^{14}C and Mass Spectrometry Laboratory.

As the designers wrote, the small AMS system MIni CArbon DAting System (MICADAS) accelerator (**Fig. 1b**) allows ^{14}C analyses with comparable accuracy and precision as larger AMS devices. The simplified instrumental setup reduces running costs and service efforts (Synal 2013; Synal et al. 2007; Wacker et al. 2010a). The magazine holds up to 40 samples. Data reduction is performed with the BATS program (Wacker et al. 2010a).

In the measurements performed, Oxalic Acid (II) was used as the standard. Phthalic anhydride and anthracite were used to control the background of the AMS measurements. In individual cases, fossil fuel was used as an additional background control.

5.4.2. Preparation and Analysis of Samples at the National Laboratory for Age Determination, Trondheim, Norway

Tire rubber and its pyrolysis products were analyzed at the National Laboratory for Age Determination, Trondheim, Norway. Different combustion methods were used for solid and liquid samples. Solid samples of rubber and recovered carbon black were combusted and reduced in an elemental analyzer. The liquid samples of pyrolytic oil were first frozen and then sealed with copper oxide (CuO) in quartz tubes. The muffle oven was used for combustion. CO_2 produced from combustion was reduced in the Fe-Zn manual reduction system. Publication by Seiler et al. (2019) provides a detailed explanation of graphite preparation methods in this laboratory. Automated graphitization equipment was used to produce graphite targets with a mass of 1 mg. This device combines an elemental analyzer with seven reduction reactors.

Fig. 2 Accelerator mass spectrometer at the National Laboratory for Age Determination, Trondheim, Norway.

The ^{14}C measurements were performed on a 1 MV AMS system (**Fig. 2**) manufactured by High Voltage Engineering Europa B.V. (Nadeau et al. 2015; Seiler et al. 2019). A typical sample wheel holds up to 50 samples.

5.5. Liquid Scintillation Counting (LSC)

Liquid scintillation counting technique was used to determine bio-based carbon in tire rubber, tire pyrolysis products, and TCB samples at the Gliwice ^{14}C and Mass Spectrometry Laboratory at the Institute of Physics - Centre for Science and Education, Division of Geochronology and Environmental Isotopes. LSC measurements were conducted following benzene synthesis. Every used chemical was analytically pure. The detachable glassware from the benzene line **(Fig. 3)** was thoroughly cleaned with deionized water and dried at 80 °C. Benzene was synthesized from the original materials without any chemical pretreatment; only tire rubber samples were washed with hot deionized water. The Gliwice Radiocarbon Laboratory has a developed benzene synthesis line, with exhaust fume extractors ensuring safe combustion and synthesis stages, as well as fume hoods for safe benzene handling. Benzene synthesis involves the following steps:

5.5.1. Production of CO_2 and Carbide Synthesis

For carbide synthesis, a metal reactor was used, which was mechanically cleaned and rinsed with deionized water before being dried and placed in a muffle oven at 700 °C for several hours.

The analyzed solid samples, i.e., carbon black, tire rubber, and recovered carbon black, were subjected to a reaction with metallic lithium in a 1:1 ratio in a purified (as described above), hermetically sealed metal reactor at a temperature of 700°C under pressure control.

Pyrolytic oil samples undergo a two-step process. In the first step, pyrolytic oil was introduced into an internal small reactor and evaporated on heated lithium, which was placed at the bottom of the outside reactor. In the second step, after cooling, the remains from the internal reactor were transferred to the outer reactor and the same procedure as for solid samples with additional lithium metal was followed. The completion of the reaction time varied according to the type of material. For TCB samples the reaction was completed in about an hour, for pyrolytic oil it took around 40 minutes whereas for tire rubber samples it took 1 to 2 hours. The general reaction of carbide synthesis can be expressed as:

$$2CO_2 + 10Li \xrightarrow{700\ ℃} Li_2C_2 + 4Li_2O \qquad \text{Eq. 3}$$

5.5.2. Synthesis and Purification of Acetylene

Li_2C_2 is hydrolyzed in a separate line to produce acetylene (C_2H_2):

$$Li_2C_2 + H_2O \xrightarrow{\text{Room temperature}} C_2H_2 + 2LiOH \qquad \text{Eq. 4}$$

The acetylene is then purified by passing through the hygroscopic trap of potassium dichromate ($K_2Cr_2O_7$) and sulfuric acid (H_2SO_4). Pure C_2H_2 was collected in a glass cold trap cooled with liquid nitrogen.

Fig. 3 Benzene line at Gliwice ^{14}C and Mass Spectrometry Laboratory.

5.5.3. Synthesis and Purification of Benzene

Benzene is produced from acetylene by trimerization reaction which was carried out at room temperature on a preheated chromium catalyst (preactivated at 600 °C for 30 minutes):

$$3C_2H_2 \rightarrow C_6H_6 \qquad \text{Eq. 5}$$

The benzene needs to be purified from water vapors and atmospheric radon. Benzene was kept over sodium metal overnight for drying and for about a month in the freezer (at $-15\,^{\circ}$C) to make benzene radon-free. Since radon is radioactive and has a half-life of 3.8 days, after one month its amounts in the benzene sample are negligible. For radon removal, I also used the procedure of re-sublimation (Tudyka et al. 2021). A mixture of dry ice with ethanol ($-78\,^{\circ}$C) was used for re-sublimation.

When the sample was free of radon, the appropriate amount of it could be measured (a 2 ml volume was used), and after adding the scintillator in the form of butyl-PBD, the activity measurements of the sample could begin (Pawlyta et al. 1997).

^{14}C measurements were performed using Quantulus 1220^{TM} liquid scintillation β spectrometer (Pazdur et al. 2003). Commercial Polish Analar-grade benzene was used as background, ANU-Sucrose was used as standard.

5.6. Isotope Ratio Mass Spectrometry (IRMS)

The isotope ratio mass spectrometry technique was used for isotope relative abundance determination in the samples. In my research, I used spectrometer IsoPrime 100 with a continuous flow regime connected with the MultiFlow system and the Gilson GX-271 autosampler. The MultiFlow system is designed to automatically collection and transfer CO_2 from sample vessels to the mass spectrometer. The gas was sampled with an automatic needle, separated by chromatography, and passed to the IsoPrime for isotope analysis (Agnihotri et al. 2014; Multiflow 2012).

Isotope measurements were necessary to calculate the isotope fractionation correction for measurements performed using the LSC technique (Stuiver and Polach 1977).

For IRMS measurements, benzene produced from samples for LSC measurements was used. For this purpose, ~ 5 µl of benzene was placed in a glass capillary in Simax tubes together with ~ 300 mg of CuO. After closing the tubes with a burner, they were placed in an oven at 560 °C for approx. 12 h. Then, in a special vacuum line, each tube was broken, and carbon dioxide produced from the benzene sample was collected in a glass cold trap using liquid nitrogen after passing through a water vapor trap. After measuring the appropriate amount of CO_2 (controled by measuring the pressure in the appropriate branch of the vacuum line), three subsamples were manually collected with a special syringe into vessels for the MultiFlow system.

The standards used were materials provided by the IAEA: NBS-22 (oil; ~ 5 µl), IAEA-CH-6 (formerly ANU Sucrose; ~ 3 mg) and IAEA-C3 (~ 1 mg) and the internal standard WZS (lake sediment, ~ 2 µg) (Ustrzycka 2020). The standards were burned in Simax tubes under the same conditions as the samples and subjected to the measurement procedure as described above.

^{14}C concentrations were corrected using measured $\delta^{13}C$ value using the following equation (Eq.6) (Stuiver and Polach 1977):

$$A_{SN} = A_S \left[1 - \frac{2(25+\delta^{13}C)}{1000}\right], \qquad \text{Eq. 6}$$

where:

A_S - the measured ^{14}C concentration

A_{SN} - the corrected ^{14}C concentration

6. Summary of Main Results and Conclusions

The concentration of the ^{14}C isotope in a sample allows for distinguishing between samples made from modern materials and those produced from fossil fuels, thereby providing information about the potential use of renewable materials in their production. In my research, I determined the ^{14}C concentration (and biobased carbon) in three different categories of samples (tire rubber and its pyrolysis products, disposable packaging samples, and technical carbon black samples) by using the aforementioned radiocarbon techniques.

Below, I present the main results with conclusions, as published in the respective publications:

6.1. Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N, Kłusek M, Końska K, Wróblewski K, Nadeau M-J, Seiler M. (2022). Study of bio-based carbon fractions in tires and their pyrolysis products. Radiocarbon. 64(6):1457-1469. DOI: 10.1017/RDC.2022.88.

The article presents the results of measurements of bio-carbon concentration in tires and their pyrolysis products. Furthermore, it presents the measurement results obtained using two techniques (AMS and LSC) in three different laboratories. The study thus also served as a form of interlaboratory comparison. This research was carried out with the collaboration of Contec Inc. company in Warsaw that deals with tire pyrolysis. In this research, I worked on the products obtained from passenger car tire, truck tire samples, and their mixture. The pyrolytic oil and recovered carbon black samples were analyzed at the Gliwice ^{14}C and Mass Spectrometry Laboratory (LSC and AMS) and the National Laboratory for Age Determination, Trondheim, Norway. IRMS method was used to calculate the standardized isotope fractionation correction of LSC measurements. Rubber samples analyzed at Gliwice ^{14}C and Mass Spectrometry Laboratory by LSC technique and the National Laboratory for Age Determination, Trondheim, Norway by AMS technique.

Detailed results are summarized in **Table 2.** For pyrolysis oil, the ^{14}C isotope concentration values were dependent on the number of truck tires in the pyrolysis mass and ranged from about 41 to 50 pMC, with the larger the truck tire input, the higher the ^{14}C concentration values. The same trend was observed for the recovered carbon black. In this case, the values ranged from about 5 to less than 7 pMC. The samples were examined by two techniques, and three different laboratories showed good agreement (**Fig. 4**), and all of the methods seem to be suitable and reliable for the investigation of the pyrolysis products from tires.

Table 2. Results for the ^{14}C concentrations are reported in pMC for different categories of samples. 14C concentrations were measured by LSC (lab code-GdS) and AMS technique (lab code-GdA (Gliwice), lab code-TRa (Trondheim)). χ2 values for the samples of pyrolytic oil and recovered carbon black are also reported. The critical χ^2 values for four measurements = 11.34, and for three measurements = 9.21 (with the confidence level, α=0.01). Bio-based carbon content was calculated according to the standard (EN16640:2017) for three different REF values (CIO 2022; Hua et al. 2022). (see Table. 4 in (Gill et al. 2022)).

No.	**Sample**	**Lab code**	**^{14}C concentrate-ion (pMC)**	χ^2	**Total carbon (%)**	**Biobased carbon content (%)**		
						REF_{2011}	**REF_{2006}**	**REF_{1995}**
1	CONT-1 Pyrolytic Oil	GdS-4257	41.95 ± 0.37	*8.48*	84.8 ± 0.50	40.6 ± 0.36	39.8 ± 0.35	37.5 ± 0.33
		GdS-4258	43.43 ± 0.38			42.0 ± 0.37	41.2 ± 0.36	38.8 ± 0.34
		GdA-6611	42.64 ± 0.23			41.3 ± 0.22	40.5 ± 0.22	38.1 ± 0.21
		TRa-16675	42.86 ± 0.18			41.5 ± 0.17	40.7 ± 0.17	38.3 ± 0.16
2	PCO-2 Pyrolytic Oil	GdS-4320	41.30 ± 0.47	*20.83 without GdS-4320: 1.65*	83.5 ± 2.5	40.0 ± 0.45	39.2 ± 0.45	36.9 ± 0.42
		GdS-4365	43.90 ± 0.44			42.5 ± 0.43	41.7 ± 0.42	39.2 ± 0.39
		GdA-6612	43.49 ± 0.23			42.1 ± 0.22	41.3 ± 0.22	38.8 ± 0.21
		TRa-16676	43.35 ± 0.11			42.0 ± 0.11	41.1 ± 0.10	38.7 ± 0.10
3	TCO-3 Pyrolytic Oil	GdS-4373	50.35 ± 0.49	*7.46*	74.9 ± 7.2	48.7 ± 0.47	47.8 ± 0.46	45.0 ± 0.44
		GdA-6613	49.76 ± 0.24			48.2 ± 0.23	47.2 ± 0.23	44.4 ± 0.21
		TRa-16677	50.47 ± 0.10			48.9 ± 0.10	47.9 ± 0.09	45.1 ± 0.09
4	rCB-2 Recovered Carbon Black	GdS-4327	5.08 ± 0.18	*0.07*	71.7 ± 3.5	4.9 ± 0.17	4.8 ± 0.17	4.5 ± 0.16
		GdA-6615	5.14 ± 0.11			5.0 ± 0.11	4.9 ± 0.10	4.6 ± 0.10
		TRa-16679	5.17± 0.08			5.0 ± 0.08	4.9 ± 0.08	4.6 ± 0.07
5	rCB-3 Recovered Carbon Black	GdS-4394	6.89 ± 0.18	*19.31 without TRa-16680*	78.9 ± 1.5	6.7 ± 0.17	6.5 ± 0.17	6.2 ± 0.16
		GdA-6616	6.92 ± 0.12			6.7 ± 0.12	6.6 ± 0.11	6.2 ± 0.11

		TRa-16680	6.29 ± 0.18	*0.02*		6.1 ± 0.17	6.0 ± 0.17	5.6 ± 0.16
6	CR-2 Rubber	GdS-4337	15.54 ± 0.23	χ^2 - not applicable range: 15.54 – 34.71	83.7 ± 2.8	14.8 ± 0.22	14.5 ± 0.22	13.7 ± 0.21
		TRa-16682a	33.02 ± 0.13			32.0 ±0.13	31.3 ± 0.12	29.5 ± 0.12
		TRa-16682b	34.71 ± 0.10			33.6 ± 0.10	32.9 ± 0.09	31.0 ± 0.09
		TRa-16682c	22.21 ± 0.10			21.5 ± 0.10	21.1 ± 0.09	19.8 ± 0.09
7	CR-3 Rubber	GdS-4339	13.59 ± 0.23	χ^2 - not applicable range: 12.31 – 41.86	74.9 ± 2.3	12.9 ± 0.22	12.7 ± 0.22	11.9 ± 0.21
		GdS-4380	25.12 ± 0.22			24.2 ± 0.21	23.7 ± 0.21	22.3 ± 0.20
		GdS-4383	20.89 ± 0.32			19.9 ± 0.31	19.5 ± 0.30	18.4 ± 0.29
		GdS-4370	12.31 ± 0.21			11.7 ± 0.20	11.5 ± 0.20	10.8 ± 0.19
		GdS-4375	20.24 ± 0.31			19.4 ± 0.30	19.0 ± 0.29	17.8 ± 0.28
		GdS-4374	13.29 ± 0.25			12.6 ± 0.24	12.4 ± 0.24	11.7 ± 0.22
		TRa-16683a	18.25 ± 0.10			17.7 ± 0.10	17.3 ± 0.09	16.3 ± 0.09
		TRa-16683b	41.86 ± 0.15			40.5 ± 0.15	39.7 ± 0.14	37.4 ± 0.13
		TRa-16683c	14.57 ± 0.11			14.1 ± 0.11	13.8 ± 0.10	13.0 ± 0.10
		TRa-16683d	18.93 ± 0.07			18.3 ± 0.07	18.0 ± 0.07	16.9 ± 0.06
		TRa-16683e	22.68 ± 0.10			22.0 ± 0.10	21.5 ± 0.09	20.3 ± 0.09
		TRa-16683f	21.68 ± 0.09			21.0 ± 0.09	20.6 ± 0.09	19.4 ± 0.08
		TRa-16683g	14.85 ± 0.08			14.4 ± 0.08	14.1 ± 0.08	13.3 ± 0.07

In the case of tire rubber, the samples provided were cut into pieces of 0.5 to 1 cm in size. For the purposes of LSC measurements, several fragments with a total mass of 5-6 g were sufficient for a single measurement, while for the purposes of AMS, a sample of the order of 1 mg was cut from one piece. The results of ^{14}C concentration were widely scattered. The scatter of the received values results from the complex structure of tires, as both natural rubber (which can be treated as a biocomponent) and rubber produced from fossil fuels are used in its construction. According to tire manufacturers, these different types of rubber are used in different layers of the tire. Therefore, the result of the measurement of the ^{14}C isotope concentration in a small sample should rather be treated as characteristic for a given location in the tire, and not for the entire batch of tires subjected to pyrolysis, or even the entire single tire.

The content of bio-based carbon in the tested samples was calculated according to the (EN16640 2017) standard using several reference values (REF). Considering the recommended service life of tires (~5 years), the time of tire disposal (~10-15 years) and the use of natural rubber for the production of tires from tree sap (living 5-25 years), calculations were made for REF values characteristic for the years 2006, 2011 and 1995 (CIO 2022; Hua et al. 2022).

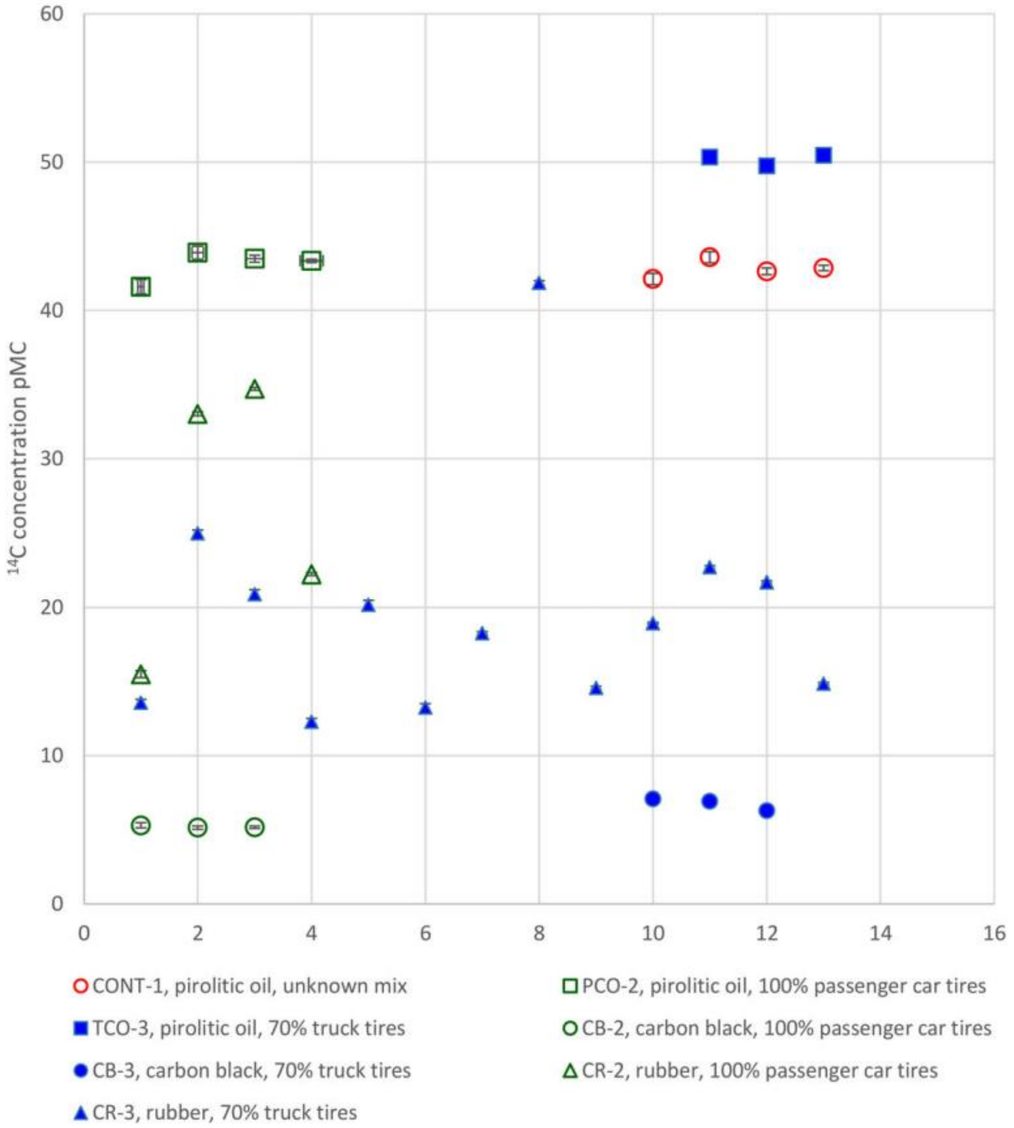

Fig. 4 Comparison of the ^{14}C isotope measurements in tire rubber and its pyrolysis products for three series of samples marked in red, green and blue and different types of samples (pyrolysis oil, recovered carbon black and rubber) marked with shapes according to the legend (see Fig. 2 in (Gill et al. 2022)).

It is worth noting that I performed part of the measurements in Norway during a 2-week research internship. The internship gave me the opportunity to learn about work in the renowned ^{14}C laboratory, as well as to ensure that the sample preparation and measurement protocols used in the Gliwice laboratory comply with global standards, as well as to familiarize myself with a different graphitization method and measurement equipment.

The research results can be useful for companies involved in tire pyrolysis, as they help determine the bio-based carbon content in pyrolysis products, which is significant both ecologically and economically.

6.2. Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N, Ustrzycka A. (2023). Technical carbon black and green technology. Geochronometria. 50(1):250-256. DOI: 10.2478/geochr-2023-0016.

The research in this article was conducted on technical carbon black samples. Four types of TCB samples with different degrees of fragmentation and specific surface area were analyzed by two radiocarbon techniques: LSC and AMS at the Gliwice ^{14}C and Mass Spectrometry Laboratory. I applied the IRMS method to calculate the standardized isotope fractionation correction of LSC results. The samples for testing were sent by Contec Inc. It was expected that the samples would contain a higher share of biocomponents, but the samples give very low value of ^{14}C concentration between 0.124 ± 0.091 pMC and 0.908 ± 0.092 pMC (<1 pMC) for both techniques. The detailed summarized results of ^{14}C concentrations and bio-based carbon content of TCB samples are mentioned in **Table 3**. Low ^{14}C concentrations of TCB samples represent their production from fossil materials. The findings suggest a need for developing eco-friendly alternatives and increasing the use of renewable materials in TCB production.

Table 3. ^{14}C concentration and bio-based carbon content in TCB samples. (see Table 2 in (Gill et al. 2023)). δ^{13}C values were obtained by IRMS (*) and AMS measurements (**).

No.	**Sample name**	**Lab code**	**Sample mass**	**Total Carbon (%)**	**$\delta^{13}C_{VPDB}$ (‰)**	**^{14}C conc. (pMC)**	**Bio-based carbon content (%)**
1.	TCB-N330	GdS-4543	6.08 g	-	−32.44 ± 0.11*	0.589 ± 0.084	0.589 ± 0.084
2.		GdA-7138.1.1	1.81 mg	99.75 ± 0.93	−29.20**	0.436 ± 0.033	0.436 ± 0.033
3.		GdA-7138.1.2	0.99 mg		−30.60**	0.410 ± 0.038	0.410 ± 0.038
4.	TCB-N550	GdS-4552	4.02 g	-	−30.417 ± 0.072*	0.189 ± 0.063	0.189 ± 0.063
5.		GdA-7137.1.2	0.98 mg	97.5 ± 2.3	−25.70**	0.508 ± 0.033	0.508 ± 0.033
6.		GdA-7137.1.3	2.05 mg		−28.80**	0.500 ± 0.035	0.500 ± 0.035

7.	TCB-N660	GdS-4554	3.91 g	-	–31.82 ± 0.44*	0.908 ± 0.092	0.908 ± 0.092
8.		GdA-7139.1.1	2.19 mg	98.1 ± 1.9	–28.80**	0.489 ± 0.033	0.489 ± 0.033
9.		GdA-7139.1.2	1.90 mg		–36.60**	0.350 ± 0.043	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	0.124 ± 0.091
12.		GdA-7140.1.2	2.03 mg	98.9 ± 1.0	–33.00**	0.380 ± 0.043	0.380 ± 0.043
13.		GdA-7140.1.3	2.03 mg		–32.90**	0.350 ± 0.043	0.350 ± 0.043
14.		GdA-7140.1.4	1.01 mg		–28.90**	0.470 ± 0.035	0.470 ± 0.035

^{14}C concentrations of all samples from LSC and AMS laboratories are presented in **Fig. 5**. The study served as an intra-laboratory comparison, demonstrating the reliability of using LSC and AMS techniques for measuring ^{14}C isotope concentrations in TCB samples. For samples TCB-N550 and TCB-N660, statistical inconsistencies were observed between the LSC and AMS results. These may be due to sample inhomogeneity (as indicated by differences in δ^{13}C values between subsamples) and ash contamination.

The REF value for 2022, i.e. 100%, was used to calculate the biobased carbon content (CIO 2022; EN16640 2017). Therefore, it is equal to the concentration of the ^{14}C isotope in the sample.

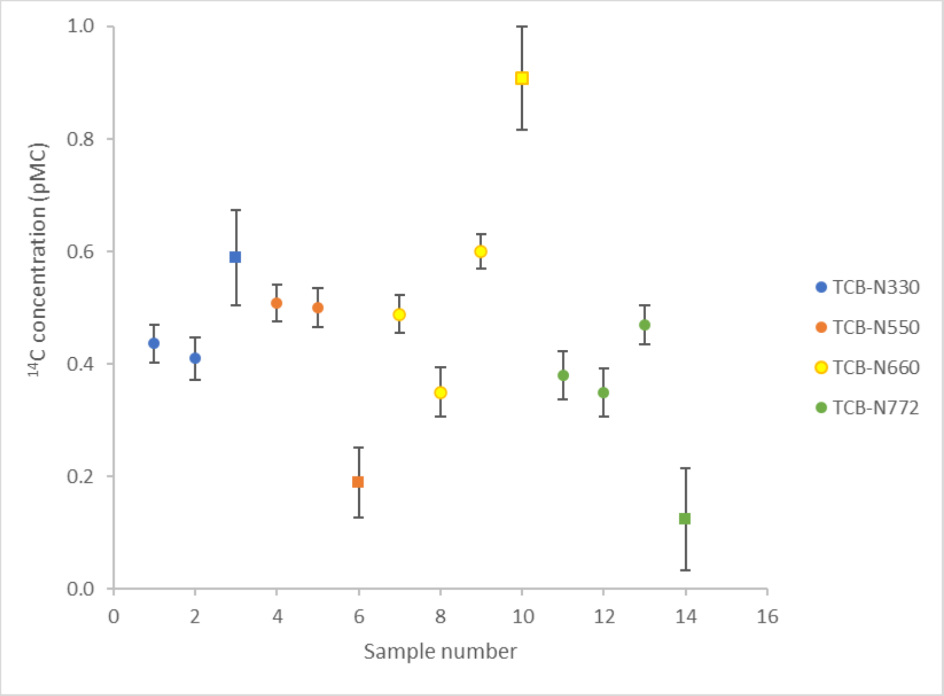

Fig. 5 Comparison between AMS and LSC ^{14}C isotope measurements in technical carbon black samples. '•' AMS measurement results, '▪' LSC measurement results. (see Fig. 1 in (Gill et al. 2023)).

The research provides valuable insights into the bio-based carbon content of TCB samples, emphasizing the importance of renewable resources and the challenges associated with current production practices.

6.3. Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N. (2024). Monitoring of modern carbon fraction in disposable packaging. Radiocarbon. First View,1-9. DOI: 10.1017/RDC.2024.35.

This research article focuses on determining the modern carbon fraction in disposable packaging samples made from four different materials: paper, wood, sugarcane, and wheat bran. The samples were received from different packaging companies. These samples included paper cups, paper plates, paper straws, brown paper plates, baking paper, wooden cutlery, sugarcane plates, wheat bran plates, sugarcane boxes, and paper boxes. I selected these samples for investigation because of their daily use and widespread recycling.

In this study, samples were analyzed samples using the AMS radiocarbon technique at the Gliwice ^{14}C and Mass Spectrometry Laboratory. The samples were analyzed in two batches. In the first batch, a small random part was analyzed, whereas, in the second batch, samples were analyzed layered-wise, except for the baking paper and wooden cutlery samples. All samples appeared to be modern as they showed a ^{14}C concentration of more than 100 pMC (see **Table** 4). Paper material samples showed ^{14}C concentration between 100 and 112 pMC. The samples of wooden cutlery had the highest concentrations of the ^{14}C isotope, ranging from just over 114 to around 136.5 pMC. The scattered results were attributed to the fact that the cutlery was not made from wood from the same tree, and the varying ages of the trees resulted in different ^{14}C values.

The samples from sugarcane and wheat bran had the lowest ^{14}C concentration values, which are almost equal to the current 14C concentration in the atmosphere, indicating that the material came from contemporary plant crops. Slightly lower ^{14}C concentrations (but still corresponding to modern ^{14}C values) were found in the outer layers compared to the inner layers of some samples, suggesting that they were coated with bioplastic to make them waterproof.

Table 4. ^{14}C concentration and bio-based carbon content in disposable packaging samples. δ^{13}C, measured by AMS - see Supplement material in (Gill et al. 2024).

No.	**Sample code**	**Material**	**Subsample**	**Lab code**	**Total Carbon (%)**	**^{14}C conc. (pMC)**	**$\delta^{13}C_{AMS}$ ‰**
1.	QSCP-1	Sugar cane plates	Random	GdA-6805.1.1	41.74 ± 0.40	100.54 ± 0.34	-18.94
			Outer layer	GdA-6805.2.1	42.47 ± 0.69	99.74 ± 0.32	-16.00
			Inner layer	GdA-6805.3.1	42.41 ± 0.64	100.11 ± 0.32	-15.80
			Mixed layers	GdA-6805.4.1	42.53 ± 0.73	99.42 ± 0.33	-17.40
			Carbonized	GdA-6805.5.1	91.25 ± 1.83	100.29 ± 0.33	-23.50
2.	QPC-2	Paper cups	Random	GdA-6806.1.1	42.30 ± 0.42	100.61 ± 0.34	-25.74
			Outer layer	GdA-6806.2.1	49.24 ± 0.93	105.46 ± 0.33	-21.10
				GdA-6806.2.2		93.95 ± 0.28	-21.5
				GdA-6806.2.4		97.72 ± 0.29	-22.0
			Inner layer	GdA-6806.3.1	44.14 ± 0.52	114.47 ± 0.36	-25.70
				GdA-6806.3.2		114.47 ± 0.31	-26.4
				GdA-6806.3.3		114.69 ± 0.33	-27.3
			Mixed layers	GdA-6806.4.1	45.31 ± 0.95	108.37 ± 0.34	-22.70
				GdA-6806.4.2		106.07 ± 0.30	-24.1
				GdA-6806.4.3		107.81 ± 0.32	-25.8
			Carbonized	GdA-6806.5.1	90.82 ± 1.08	113.7 ± 0.36	-32.10
3.	QBP-3	Baking paper	Random 1	GdA-6807.1.1	41.71 ± 0.37	107.22 ± 0.34	-25.51
			Random 2	GdA-6807.2.1	42.41 ± 0.64	106.71 ± 0.34	-26.20
			Carbonized	GdA-6807.3.1	87.38 ± 0.93	107.81 ± 0.35	-31.80
4.	QPS-4	Paper straws	Random	GdA-6808.1.1	43.55 ± 0.55	103.53 ± 0.34	-25.74
			Outer layer	GdA-6808.2.1	44.47 ± 0.73	100.04 ± 0.33	-25.90
			Inner layer	GdA-6808.3.1	44.28 ± 0.68	101.47 ± 0.33	-26.20
			Mixed layers	GdA-6808.4.1	44.95 ± 0.52	98.21 ± 0.33	-25.50
			Carbonized	GdA-6808.5.1	87.16 ± 2.65	108.46 ± 0.35	-31.40
5.	QPP-5		Random	GdA-6809.1.1	42.12 ± 0.41	112.00 ± 0.34	-25.65

		Paper plates	Outer layer	GdA-6809.2.1	40.38 ± 0.12	111.41 ± 0.36	-24.60
			Inner layer	GdA-6809.3.1	44.26 ± 0.37	111.92 ± 0.36	-25.90
			Mixed layers	GdA-6809.4.1	42.98 ± 0.42	111.64 ± 0.36	-25.00
			Carbonized	GdA-6809.5.1	69.74 ± 2.52	111.24 ± 0.36	-30.60
6.	QWC-6	Wooden cutlery	Random	GdA-6810.1.1	46.02 ± 0.43	123.44 ± 0.34	-26.49
			Fork	GdA-6810.2.1	47.05 ± 1.19	136.53 ± 0.42	-26.00
			Knife	GdA-6810.3.1	45.12 ± 3.03	114.72 ± 0.37	-26.20
			Mixed fork & knife	GdA-6810.4.1	46.70 ± 1.35	129.7 ± 0.40	-26.20
			Carbonized	GdA-6810.5.1	92.50 ± 3.43	121.77 ± 0.39	-35.20
7.	QBPP-7	Brown paper plates	Random	GdA-6811.1.1	44.11 ± 0.25	108.13 ± 0.34	-26.21
			Outer layer	GdA-6811.2.1	44.15 ± 0.64	108.11 ± 0.35	-25.80
			Inner layer	GdA-6811.3.1	45.86 ± 0.77	107.22 ± 0.36	-25.20
			Mixed layers	GdA-6811.4.1	44.67 ± 0.19	108.35 ± 0.35	-24.80
			Carbonized	GdA-6811.5.1	90.90 ± 1.65	109.63 ± 0.28	-31.30
8.	VWBP-8	Wheat bran plates	Random	GdA-6812.1.1	44.22 ± 1.02	101.35 ± 0.34	-27.84
			Outer layer	GdA-6812.2.1	43.56 ± 0.63	100.92 ± 0.29	-27.60
			Inner layer	GdA-6812.3.1	43.39 ± 0.52	100.86 ± 0.29	-27.50
			Mixed layers	GdA-6812.4.1	43.52 ± 0.56	100.81 ± 0.29	-27.00
			Carbonized	GdA-6812.5.1	65.99 ± 1.25	100.72 ± 0.29	-32.10
9.	BSCB-9	Sugar cane boxes	Random	GdA-6813.1.1	43.01 ± 1.01	100.02 ± 0.34	-14.72
			Outer layer	GdA-6813.2.1	43.26 ± 0.13	100.14 ± 0.29	-13.90
			Inner layer	GdA-6813.3.1	43.28 ± 0.15	100.54 ± 0.29	-14.50
			Mixed layers	GdA-6813.4.1	43.32 ± 0.12	100.64 ± 0.29	-14.10
			Carbonized	GdA-6813.5.1	91.31 ± 0.12	99.89 ± 0.29	-21.50
10.	BPP-10	Paper plates	Random	GdA-6814.1.1	43.14 ± 0.14	111.98 ± 0.34	-25.62
			Outer layer	GdA-6814.2.1	44.79 ± 0.30	110.98 ± 0.29	-26.00
			Inner layer	GdA-6814.3.1	45.10 ± 0.12	111.54 ± 0.29	-25.40
			Mixed layers	GdA-6814.4.1	45.09 ± 0.11	111.32 ± 0.28	-25.10
			Carbonized	GdA-6814.5.1	94.97 ± 3.77	111.71 ± 0.29	-33.30

Although the obtained ^{14}C concentration values indicated that all the samples were produced from biomass, four out of the ten tested samples showed a large variation in results. This suggests that in their case, there is a need for homogenizing a larger volume of the sample to obtain a result representative of the batch of the tested DPM.

The ^{14}C concentrations of all DPMs obtained by AMS are presented in **Fig. 6**.

The bio-based carbon content can be calculated by using Eq. 1. Since every sample gives a ^{14}C concentration higher than 100 pMC and is considered to be modern and completely biogenic, and because the specific year of the material origin was unknown, a REF value of 100 for the year 2022 (CIO 2022) was used for all samples to calculate the bio-based carbon content. Therefore, the bio-based carbon content is equal to the measured ^{14}C concentration values.

The study underscores the importance of ensuring sample homogeneity for accurate measurements. Simple carbonization was found to be insufficient for homogenization; therefore, complete combustion in a vacuum line is recommended for future studies to prevent light carbon loss and reduce isotope fractionation. The findings support the use of bio-based, recyclable packaging materials to reduce environmental impact and promote sustainable development, in accordance with the European Waste Directive (EU) 2018/852.

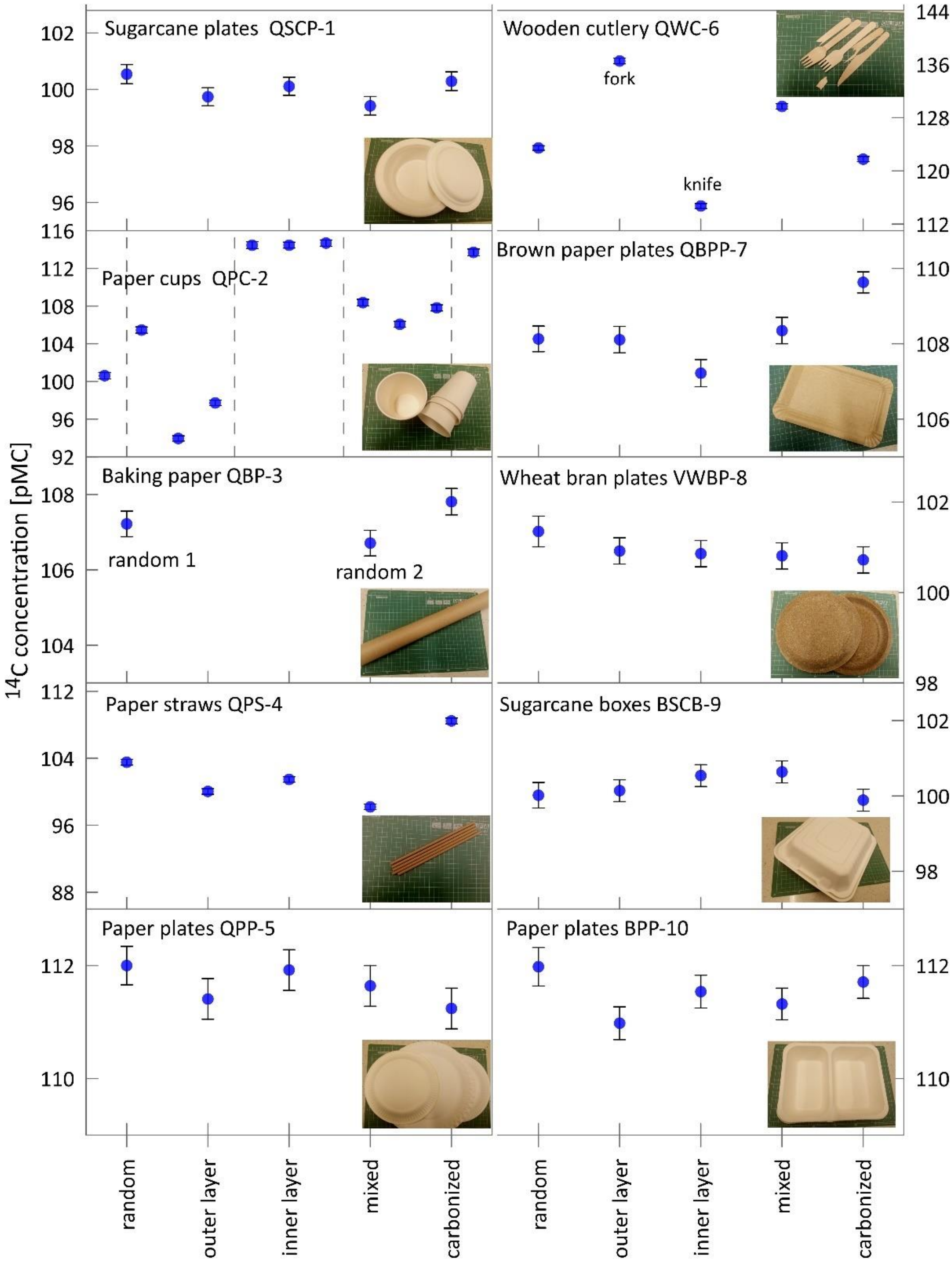

Fig. 6 Comparison of the ^{14}C isotope measurements of DPMs by AMS. (see Fig. 1 in (Gill et al. 2024)).

6.4. Gill KA, Michczyńska DJ, Michczyński A. Bio-carbon content determination in disposable packaging by liquid scintillation counting. [in:] POB6 Monograph "Climate and environmental protection, modern energy - selected issues", SUT (in press).

This research work was a continuation of previous study (Monitoring of modern carbon fraction in disposable packaging), which involved ^{14}C measurements in disposable packaging samples using the AMS technique. In this study, the ^{14}C concentration and the amount of biocarbon were determined using the LSC technique at the Gliwice ^{14}C and Mass Spectrometry Laboratory. Additionally, the IRMS method was applied to measure the relative ratio of stable carbon isotopes (^{13}C/^{12}C) in the samples, followed by the calculation of a correction for isotope fractionation.

Table 5. ^{14}C concentration and bio-based carbon content in disposable packaging samples. δ^{13}C values were measured by IRMS.

No.	***Sample***	***Lab code***	***^{14}C conc. (pMC)***	***$\delta^{13}C_{VPDB}$ (‰)***	***Bio-based carbon content (%)***
1	QSCP-1 Sugarcane plates	GdS-4610	103.20 ± 0.74	-24.156 ± 0.059	103.20 ± 0.74
2	QPC-2 Paper cups	GdS-4611	114.65 ± 0.80	-29.465 ± 0.037	114.65 ± 0.80
3	QBP-3 Baking paper	GdS-4616	109.99 ± 0.78	-27.43 ± 0.23	109.99 ± 0.78
4	QPS-4 Paper straws	GdS-4617	110.36 ± 0.78	-26.97 ± 0.36	110.36 ± 0.78
5	QPP-5 Paper plates	GdS-4620	108.30 ± 0.72	-26.14 ± 0.21	108.30 ± 0.72
6	QWC-6 Wooden cutlery	GdS-4618	125.51 ± 0.87	-30.02 ± 0.16	125.51 ± 0.87
7	QBPP-7 Brown paper plates	GdS-4621	111.36 ± 0.74	-27.78 ± 0.24	111.36 ± 0.74
8	VWBP-8 Wheat plates	GdS-4622	103.56 ± 0.71	-14.24 ± 0.74	103.56 ± 0.71
9	BSCB-9 Sugar cane boxes	GdS-4623	102.45 ± 0.70	-15.84 ± 0.42	102.45 ± 0.70
10	BPP-10 Paper plates	GdS-4624	114.92 ± 0.76	-29.68 ± 0.16	114.92 ± 0.76

Graphs of ^{14}C concentration and δ^{13}C values based on the type of material are presented in **Figures 7a** and **7b**, and the detailed results are mentioned in **Table** 5. The same batch of packaging was used for LSC measurements as for AMS measurements in the case of the third publication. The LSC technique also confirmed the contemporary origin of the tested samples, determining that they were produced from biocomponents dating from 1955 to 2018.

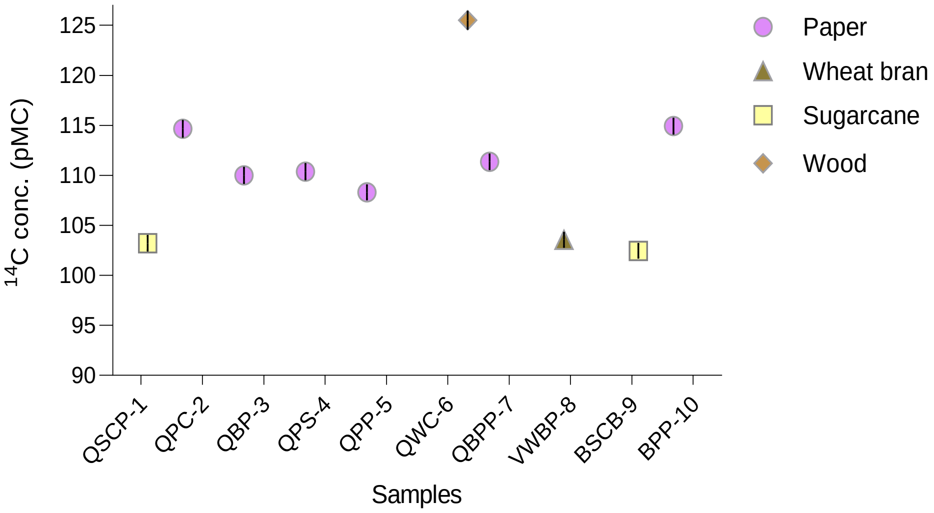

Fig. 7a Results for the ^{14}C concentration measurements in different DPMs by LSC.

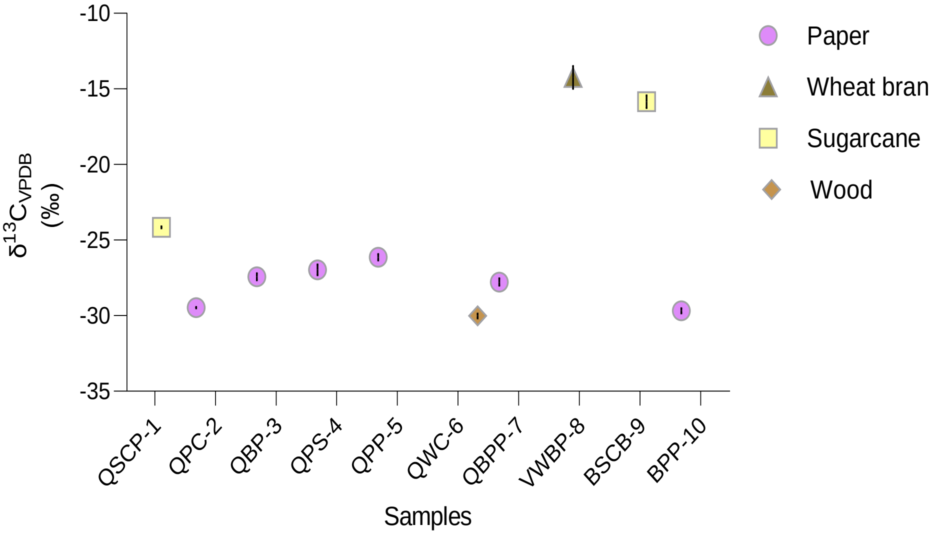

Fig. 7b Comparison of the δ^{13}C values with uncertainty across different DPM material categories by IRMS.

However, in some cases, there are differences between AMS and LSC measurements that are greater than within the limits of single uncertainties. **Figure 8** presents the comparison between LSC and AMS measurements. Although the differences between LSC and AMS results are greater than their laboratory uncertainties, it should be taken into account that in the case of the LSC technique, many pieces of a given type of material were used, while in the case of the AMS technique, a small piece of one tested material was used. The ASTM standard D6866 used in the United States (equivalent to the Polish and European EN16640 standard) takes into account the heterogeneity of samples taken from a large batch of tested material and recommends that the uncertainty of determining bio-based carbon in a sample be assumed as 3% (absolute). If this uncertainty value is applied to the measurements performed, it will turn out that the LSC and AMS results are consistent within the limits of a single uncertainty for 8 cases, and within the limits of double uncertainty for 2 cases.

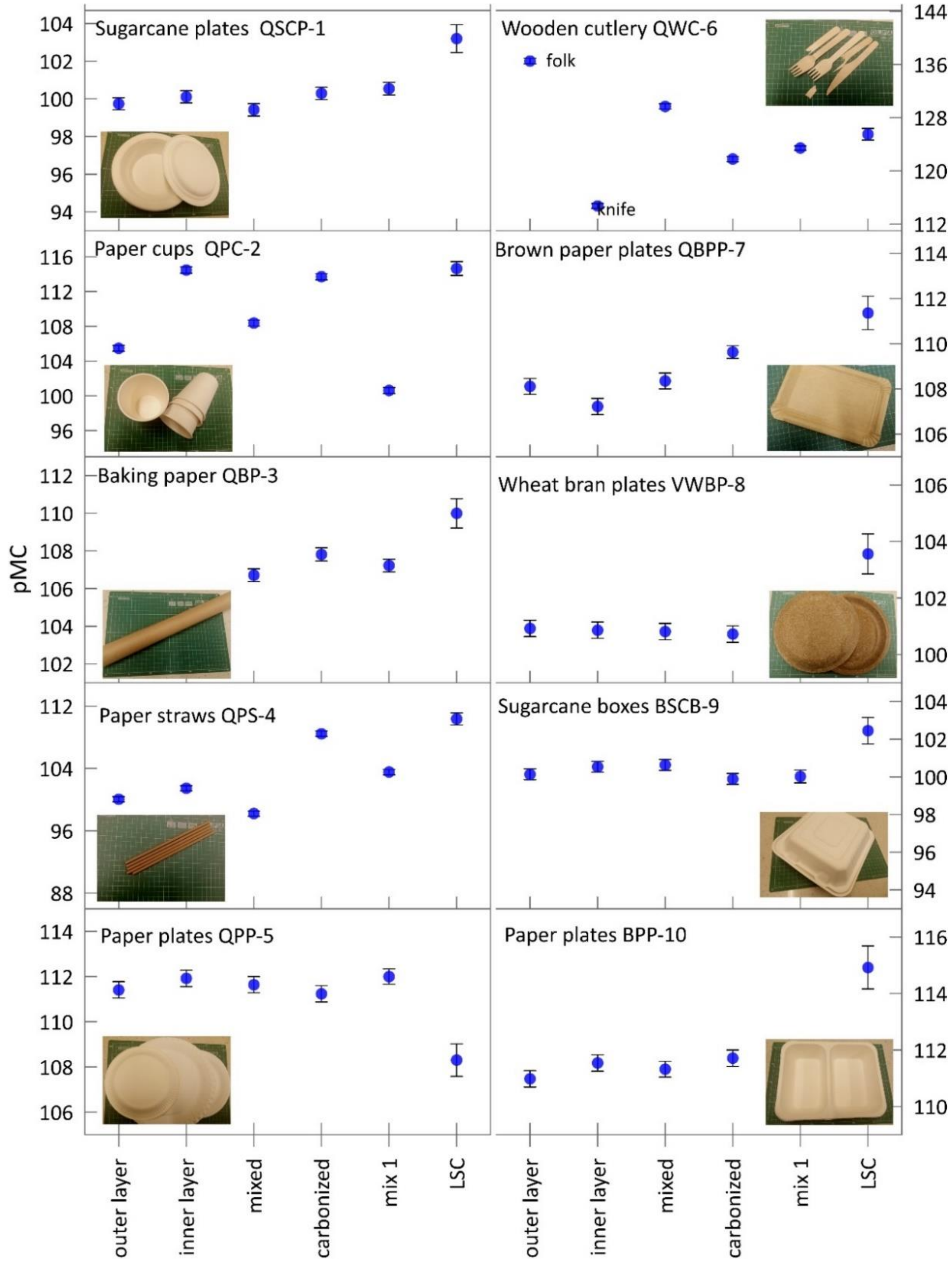

Fig. 8 Comparison of the ^{14}C concentration measurements of DPMs by LSC and AMS.

7. Summary of Own Contribution

7.1. Equipment Familiarization and Sample Preparation

Familiarization with equipment, sample preparation methods, and measurement procedures at the Gliwice ^{14}C and Mass Spectrometry Laboratory, followed by autonomous sample preparation for standard measurement purposes.

7.2. Implementing New Methodology at the Gliwice ^{14}C and Mass Spectrometry Laboratory

- Implementing the LSC radiocarbon methodology at the Gliwice ^{14}C and Mass Spectrometry Laboratory for the first time on tire rubber samples, tire pyrolysis samples, disposable paper materials, wooden cutlery, sugarcane paper material, wheat bran sample, and technical carbon black samples.
- Implementing the graphitization methodology of pyrolytic oil and recovered carbon black samples for the first time at the Gliwice ^{14}C and Mass Spectrometry Laboratory.
- Preparing samples for determination of the $\delta^{13}C$ by IRMS method for the standardized isotope fractionation correction of ^{14}C concentration values for all categories of samples obtained by LSC measurements.
- Preparing different layers of disposable packaging samples for AMS measurements at the Gliwice ^{14}C and Mass Spectrometry Laboratory.

7.3. Presenting the Obtained Results at Conferences and Workshops

- Participation and presentation in the one-week workshop, 18th Freiberg Colloquium of Young Researchers under EURECA-PRO, held in Freiberg, Germany in June 2024. Presentation title: ‘Recycling of End-of-Life Tires: A Greener Way of Energy and Sustainability’.
- Poster presentation in the 3rd EURECA-PRO Conference on Responsible Consumption and Production, in Chania, Crete, Greece, September 2023. Poster title:‘Green Packaging from Renewable Natural Resources – an Example of Disposable Packaging from Pakistan’.
- Poster presentation at the 14th International Conference Methods of Absolute Chronology, Gliwice, May 2023. Poster title: ‘Technical carbon black and green technology’.

- Lecture presentation during the opening ceremony of CEMIZ Center for Isotope Methods and VII Warsztaty Metod Datowania im. Profesora Mieczysława F. Pazdura, , Gliwice, December 2022. The lecture was delivered to the scientists, researchers, and students during session 'Application of Radiocarbon Method'. Lecture title: 'Monitoring of biogenic carbon fraction of wasted material''
- Participation and presentation at the 10th Environmental Protection and Energy Conference. Presentation title: 'Monitoring of biogenic carbon fraction of wasted material', Gliwice, December 2022.
- Participation and presentation during the one-week EURECA-PRO PhD Journey – European University on Responsible Consumption and Production, Freiberg, Germany, November 2022. Presentation title: 'Monitoring of biogenic carbon fraction of disposable packaging'.
- Poster presentation at the 24th International Radiocarbon Conference in Zurich, Switzerland, September 2022. Poster title: 'Monitoring of biogenic carbon fraction of disposable packaging'.
- Poster presentation at the 3rd International Radiocarbon in the Environment Conference, Gliwice, July 2021. Poster title: 'Tests for the content of the ^{14}C isotope in tires and their pyrolysis products'.

7.4. Collaboration

- Collaboration with Contec Inc. Company in Warsaw, Poland, for the collection of tire rubber and tire pyrolysis samples.
- Established cooperation with the National Laboratory for Age Determination, Trondheim, Norway, for the interlaboratory comparison of ^{14}C concentration results in tire samples and their pyrolysis products.
- Preparation and analysis of tire rubber and its pyrolysis product samples at Age Determination, Trondheim, Norway.
- Established cooperation with the Centro Nacional de Aceleradores (CNA), University of Seville, Seville, Spain, for the interlaboratory comparison of disposable packaging samples.
- Preparation and analysis of disposable packaging samples at CNA, University of Seville.

7.5. Internships

- One-month internship under the NAWA STER program in one of the best Universities and laboratories, Centro Nacional de Aceleradores (CNA), University of Seville, Seville, Spain. Project No. 32/014/NWD21/2001-04. October to November 2023.
- Two-week internship in one of the world's best universities and laboratories, National Laboratory for Age Determination, Norwegian University of Science and Technology, Trondheim, Norway. Project No. POWR.03.03.00-IP.08-00-P13/18 'PROM- International Scholarship Exchange of Doctoral Students and Academic Staff. September 2021.

7.6. Publications

Main author of a series of four monothematic publications, responsible for:

- Pretreatment of samples
- Synthesis of benzene for LSC measurements at the Gliwice ^{14}C and Mass Spectrometry Laboratory.
- Sample preparation and graphitization of samples for AMS measurements at the Gliwice ^{14}C and Mass Spectrometry Laboratory.
- Pressing of graphite and cathode tube preparation for AMS measurements.
- Analysis of samples by MICADAS at Gliwice ^{14}C and Mass Spectrometry Laboratory.
- Preparation of samples for IRMS measurements at the Gliwice ^{14}C and Mass Spectrometry Laboratory.
- Data analysis and interpretation of results.
- Preparation of figures, graphs, and tables of the manuscript.
- Manuscript writing.
- Established cooperation with the laboratories in Trondheim and Sevilla for interlaboratory comparison of samples.

Following is the list of publications:

- Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N, Kłusek M, Końska K, Wróblewski K, Nadeau M-J, Seiler M. (2022). Study of bio-based carbon fractions in tires and their pyrolysis products. Radiocarbon. 64(6):1457-1469. DOI: 10.1017/RDC.2022.88.

- Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N, Ustrzycka A. (2023). Technical carbon black and green technology. Geochronometria. 50(1):250-256. DOI: 10.2478/geochr-2023-0016.
- Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N. (2024). Monitoring of modern carbon fraction in disposable packaging. Radiocarbon, First View. DOI: 10.1017/RDC.2024.35.
- Gill KA, Michczyńska DJ, Michczyński A. Bio-carbon content determination in disposable packaging by liquid scintillation counting. [in:] POB6 Monograph "Climate and environmental protection, modern energy - selected issues", SUT (in press).

7.7. Publications with International Collaboration (not related to PhD)

- Riaz K, Gill KA, Muhammad S, Ali FI, Javed MN, Wasim AA, Henderson W, Bari A, Hashmi IA. (2024). 2-Mercaptobenzoic acid-based ionic liquids for metal extraction from water without additional chelating agent. Journal of Sulfur Chemistry. DOI: https://doi.org/10.1080/17415993.2024.2336618.
- Ali Z, Sajid M, Raza N, Sohail Y, Hayat M, Manzoor S, Shakeel N, Gill KA, Ifseisi AA, Ansari MZ. (2023). Study of modified biomass of Gossypium hirsutum as heavy metal biosorbent. Arabian Journal of Chemistry. DOI: 10.1016/j.arabjc.2023.105332.
- Raza H, Ashraf A, Shamim R, Manzoor S, Sohail Y, Khan MI, Raza N, Shakeel N, Gill KA, El-Marghany A, Aftab S. (2023). Synthesis and characterization of Hyaluronic Acid (HA) modified polymeric composite for effective treatment of wound healing by transdermal drug delivery system (TDDS). Scientific Reports. DOI: 10.1038/s41598-023-40593-9.
- Intisar A, Ramzan A, Hafeez S, Hussain N, Irfan M, Shakeel N, Gill KA, Iqbal A, Janczarek M, Jesionowski T. (2023). Adsorptive and photocatalytic degradation potential of porous polymeric materials for removal of pesticides, pharmaceuticals, and dyes-based emerging contaminants from water. Chemosphere. DOI: 10.1016/j.chemosphere.2023.139203.
- Muhammad S, Javed MN, Gill KA, Ali FI, Henderson W, Bari A, Musharraf SG, Baig JA, Hashmi IA. (2022). Selective extraction of heavy metals (Fe, Co, Ni) from their aqueous mixtures by task-specific salicylate functionalized imidazolium based ionic liquid. Journal of Cleaner Production. DOI: 10.1016/j.jclepro.2022.131119.

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Extended Abstract In Polish

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Rozszerzone Streszczenie Rozprawy Doktorskiej

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ZASTOSOWANIE METOD IZOTOPOWYCH DO OZNACZANIA ZAWARTOŚCI BIO-KOMPONENTÓW W MATERIAŁACH STAŁYCH

Promotor: Dr hab. inż. Danuta J. Michczyńska, prof. PŚ
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PODZIĘKOWANIA

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Nie mniej ważne podziękowania kieruję do mojego rodzeństwa, które było dla mnie opoką podczas pobytu za granicą.

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KOMAL AZIZ

Abstrakt

W szybko rozwijającym się współczesnym świecie produkcja coraz większej ilości odpadów budzi obawy związane z zanieczyszczeniem środowiska. Dlatego materiały oparte na węglu kopalnym są zastępowane współczesnymi materiałami biogenicznymi. Głównym celem tej pracy badawczej jest zbadanie zawartości węgla biobazowego w różnych materiałach, które są bezpośrednio lub pośrednio związane z codziennym użytkowaniem. W ramach badań pracowałam nad gumą z opon i jej produktami pirolizy, jednorazowymi materiałami opakowaniowymi oraz próbkami sadzy technicznej. Te materiały mają duży wpływ na zanieczyszczenie środowiska, ale jednocześnie są coraz częściej wykorzystywane do recyklingu, produkcji energii i zrównoważonej produkcji.

Próbki gumy z opon i produktów jej pirolizy (oleju pirolitycznego i odzyskanej sadzy) oraz próbki sadzy technicznej zostały dostarczone przez firmę Contec Inc. z Warszawy, która zajmuje się pirolizą opon. Guma z opon, olej pirolityczny i próbki odzyskanej sadzy pochodziły zarówno z opon samochodów ciężarowych, jak i osobowych.

Różne dostępne na rynku jednorazowe próbki opakowań, wykonane z papieru, otrąb pszennych, drewna i trzciny cukrowej zostały uzyskane od kilku firm (Quick Pack, Vigo i Bio-pack).

Wszystkie próbki zostały zbadane pod kątem zawartości izotopu ^{14}C i węgla biopochodnego za pomocą akceleratorowej spektrometrii mas (AMS) oraz techniki ciekłoscyntylacyjnej (LSC). Do wyznaczenia korekty ze względu na frakcjonowanie izotopowe dla techniki LSC użyto spektrometrii mas stosunków izotopowych (IRMS). Do oznaczania węgla pochodzenia biologicznego zastosowałam europejską normę EN 16640: 2017, która odnosi się do wszystkich produktów biopochodnych. Zastosowałam różne wartości współczynnika korekcji atmosferycznej REF w zależności od rodzaju próbki i założonego roku jej wyprodukowania.

Zastosowałam metodę radiowęglową, aby odróżnić materiały kopalne od materiałów współczesnych. Okres półtrwania izotopu ^{14}C wynosi 5700 ± 30 lat, w związku z czym materiały kopalne są pozbawione izotopu ^{14}C, podczas gdy materiały pochodzenia biologicznego zawierają izotop ^{14}C w koncentracji zbliżonej atmosferycznej.

Wszystkie próbki zostały przeanalizowane metodą radiowęglową w Laboratorium ^{14}C i Spektrometrii Mas w Gliwicach, przy czym próbki oleju pirolitycznego i odzyskanej sadzy zostały zgrafityzowane w laboratorium AMS w Gliwicach, a pomiary ^{14}C zostały przeprowadzone w Laboratorium Radiowęglowym w Poznaniu. Guma z opon i jej produkty pirolizy były dodatkowo analizowane w Narodowym Laboratorium Określania Wieku

w Trondheim, Norwegia. Koncentracje izotopu ^{14}C zostały podane jako procent współczesnego węgla (pMC).

Dla oleju pirolitycznego wartości koncentracji izotopu ^{14}C były zależne od proporcji opon do samochodów ciężarowych do osobowych w masie poddawanej pirolizie i wahały się w zakresie od ok. 41 do 50 pMC, przy czym im większy był wsad opon ciężarowych, tym wyższe były wartości koncentracji ^{14}C. Ten sam trend zaobserwowano dla odzyskanej sadzy. W tym przypadku wartości wahały się od ok. 5 do niecałych 7 pMC.

W przypadku próbek gumy otrzymano mocno rozrzucone wyniki pomiaru koncentracji ^{14}C w zakresie od 12 do 42 pMC. Fakt rozrzutu wyników wynika ze złożonej, warstwowej struktury opon i używania do jej produkcji zarówno kauczuku naturalnego jak i kauczuku wyprodukowanego z paliw kopalnych. Wynik pomiaru koncentracji izotopu ^{14}C w próbce o małej masie należy raczej traktować jako charakterystyczny dla danego miejsca w oponie, a nie partii opon poddawanych pirolizie, czy nawet dla pojedynczej całej opony.

Dziesięć różnych typów próbek opakowań jednorazowych wykazało koncentrację ^{14}C powyżej 100 pMC, co wskazuje na wyprodukowanie ich ze współczesnej biomasy. Próbki były analizowane warstowo przy użyciu techniki AMS. Warstwa zewnętrzna (wodoodporna) wykazuje stosunkowo wysokie stężenie ^{14}C, co wskazuje na zastosowanie bioplastików. W próbkach drewnianych sztućców zaobserwowano wysokie i zróżnicowane stężenia ^{14}C, w zakresie od 114 do 136 pMC, co sugeruje, że próbki pochodziły z drzew o różnym wieku.

Natomiast próbki sadzy technicznej dla czterech badanych klas wykazały niezwykle niskie stężenia ^{14}C, <1 pMC, co wskazuje na użycie do ich produkcji materiału kopalnego lub minimalny udział materiałów odnawialnych.

Wyniki pracy zostały opublikowane w trzech artykułach naukowych w czasopismach z listy JCR oraz w rozdziale w monografii naukowej:

1. Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N, Kłusek M, Końska K, Wróblewski K, Nadeau MJ, Seiler M. (2022). Study of bio-based carbon fractions in tires and their pyrolysis products. Radiocarbon. 64 (6): 1457-1469. DOI: 10.1017/RDC.2022.88.
2. Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N, Ustrzycka A. (2023). Technical carbon black and green technology. Geochronometria. 50 (1) : 250-256. DOI: 10.2478/geochr-2023-0016.
3. Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N. (2024). Monitoring of modern carbon fraction in disposable packaging. Radiocarbon, First View DOI: 10.1017/RDC.2024.35.
4. Gill KA, Michczyńska DJ, Michczyński A. Bio-carbon content determination in disposable packaging by liquid scintillation counting. [w:] Werle S, Ferdyn-

Grygierek J (red.) POB6 Monografia „Ochrona klimatu i środowiska, energetyka współczesna – wybrane zagadnienia”, Politechnika Śląska (w druku).

Wykonane badania pozwoliły na opracowanie procedur pomiarowych dla nowych typów próbek, dotychczas nie analizowanych w Laboratorium ^{14}C i Spektrometrii Mas w Gliwicach. Określono, że nie jest wymagana wstępna preparatyka chemiczna, z wyjątkiem przemycia wodą demineralizowaną. We wszystkich analizowanych próbkach oznaczono koncentrację izotopu ^{14}C oraz ilość węgla biobazowego. Badania umożliwiły również porównania wewnątrzlaboratoryjne między techniką LSC a AMS oraz porównania międzylaboratoryjne.

Badania pokazały, że zastosowane metody są odpowiednie i wiarygodne do badania testowanych typów materiałów.

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Lista Skrótów

AGE	*(Automated Graphitization Equipment) Zautomatyzowane Urządzenie Do Grafityzacji*
AMS	*(Accelerator Mass Spectrometry) Akceleratorowa Spektrometria Mas*
ASTM	*(American Society For Testing And Materials) Amerykańskie Stowarzyszenie Badań I Materiałów*
CB	*(Carbon Black) Sadza*
DPM	*(Disposable Packaging Material) Opakowania Jednorazowe*
ELT	*(End-Of-Life Tires) Zużyte Opony*
FIRI	*(Fourth International Radiocarbon Intercomparison) Czwarate Międzynarodowe Porównania Radiowęglowe*
GC	*(Gas Chromatography) Chromatografia Gazowa*
GdA	*(Gliwice Laboratory Code For AMS Technique) Gliwicki Kod Laboratoryjny Dla Techniki AMS*
GdS	*(Gliwice Laboratory Code For LSC Technique) Gliwicki Kod Laboratoryjny Dla Techniki LSC*
GPC	*(Gas Proportional Counters) Gazowe Liczniki Proporcjonalne*
IAEA	*(International Atomic Energy Agency) Międzynarodowa Agencja Energii Atomowej*
IRMS	*(Isotope Ratio Mass Spectrometry) Spektrometria Masowa Stosunków Izotopowych*
LSC	*(Liquid Scintillation Counting) Metoda Ciekłoscyntylacyjna*
MICADAS	*(Mini Carbon Dating System) Miniaturowy System Datowania Radiowęglowego*
POB	*(Priority Research Area) Priorytetowy Obszar Badawczy*
PW	*(Plastic Waste) Plastikowe Odpady*
rCB	*(Recovered Carbon Black) Odzyskana Sadza*
TC	*(Total Carbon) Węgiel Całkowity*
TCB	*(Technical Carbon Black) Sadza Techniczna*
TGA	*Thermogravimetric Analysis*
TRa	*(Trondheim Laboratory Code for AMS Technique) Trondheim Kod Laboratoryjny Dla Techniki AMS*
VPDB	*Vienna Peedee Belemnite*

1. Zakres badań

Gospodarki wielu krajów opierają się na węglowodorowych paliwach kopalnych, co powoduje wzrost emisji dwutlenku węgla. Pomimo braku określenia dokładnego wpływu takich gospodarek na bilans węgla w atmosferze, oceanach i na lądzie, a ostatecznie na ludzkość, obecnie wiele uwagi poświęca się redukcji emisji dwutlenku węgla. Służyć temu może m.in. recykling materiałów. W celu promowania zielonego recyklingu można przeprowadzić badania ilości współczesnego biowęgla w różnych rodzajach materiałów.

Przeprowadzone w ramach pracy doktorskiej badania koncentrują się na określeniu zawartości biobazowego węgla w badanych próbkach w oparciu o koncentrację w nich izotopu radiowęgla (^{14}C). Zawartość ^{14}C w materiale może pomóc w określeniu proporcji substancji kopalnych i współczesnych (nazywanych biokomponentami). Zawartość ta zależy od pochodzenia materiałów, z których wytworzono daną próbkę, gdyż współczesna biosfera zawiera radiowęgiel, natomiast paliwa kopalne nie.

Badaniami objęto powszechnie używane materiały, takie jak opony (wraz z produktami ich pirolizy), opakowania jednorazowe oraz próbki sadzy technicznej.

Rozprawa doktorska składa się ze zbioru opublikowanych i powiązanych tematycznie artykułów:

- Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N, Kłusek M, Końska K, Wróblewski K, Nadeau MJ, Seiler M. (2022). Study of bio-based carbon fractions in tires and their pyrolysis products. Radiocarbon. 64 (6): 1457-1469. DOI: 10.1017/RDC.2022.88.
- Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N, Ustrzycka A. (2023). Technical carbon black and green technology. Geochronometria. 50 (1) : 250-256. DOI: 10.2478/geochr-2023-0016.
- Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N. (2024). Monitoring of modern carbon fraction in disposable packaging. Radiocarbon, First View DOI: 10.1017/RDC.2024.35.
- Gill KA, Michczyńska DJ, Michczyński A. Bio-carbon content determination in disposable packaging by liquid scintillation counting. [w:] Werle S, Ferdyn-Grygierek J (red.) POB6 Monografia „Ochrona klimatu i środowiska, energetyka współczesna – wybrane zagadnienia”, Politechnika Śląska (w druku).

2. Cele i tezy badań

Celem pracy doktorskiej jest opracowanie, przetestowanie i zweryfikowanie metodologii określania zawartości biobazowego węgla przy użyciu metod izotopowych stosowanych w Laboratorium ^{14}C i Spektrometrii Mas w Gliwicach Instytutu Fizyki – Centrum Naukowo-Dydaktycznego Politechniki Śląskiej w Gliwicach dla próbek stałych, dla których istnieje potrzeba określania bądź weryfikowania zawartości biokomponentów. Próbki takie do tej pory nie były objęte badaniami w tym Laboratorium.

Podstawową stawianą tezą jest, że koncentrację biobazowego węgla można określić z wykorzystaniem metody pomiarów izotopu ^{14}C. Teza ta jest w pełni zgodna z normą unijną i polską EN16640: “*Bio-based products - bio-based carbon content - determination of the bio-based carbon content using the radiocarbon method*”.

Szczegółowe cele niniejszej pracy badawczej są następujące:

i. Określenie wymagań preparatyki wstępnej dla badanych materiałów.
ii. Opracowanie efektywnej metodologii oznaczania ^{14}C w różnych rodzajach materiałów stałych, dotychczas nie badanych przy użyciu techniki ciekłoscyntylacyjnej (LSC) i akceleratorowej spektrometrii mas (AMS).
iii. Określenie koncentracji ^{14}C w badanych materiałach stałych.
iv. Opracowanie efektywnych protokołów do określania zawartości biobazowego węgla.

Praca ta przyczynia się również do promowania zielonego recyklingu poprzez wykorzystywanie odnawialnych surowców w produkcji wszelkiego rodzaju materiałów i kontrolowanie emisji gazów cieplarnianych.

3. Opis przedmiotu badań

3.1. Radiowęgiel

Radioaktywny izotop węgla (radiowęgiel/^{14}C) jest najcięższym, niestabilnym, naturalnie występującym izotopem węgla. Radiowęgiel jest stosunkowo rzadkim izotopem węgla i występuje w ilości ~1×10^{-10} % w porównaniu do ~98,89% ^{12}C i ~1,11% ^{13}C (Wood 2015). Jest wytwarzany naturalnie poprzez oddziaływanie promieniowania kosmicznego na atomy azotu atmosferycznego i natychmiast uczestniczy w globalnym cyklu węglowym wraz z innymi izotopami węgla (Buchholz and Spalding 2010). Należy zauważyć, że cząsteczka CO_2 zawierająca ^{14}C ma podobne właściwości chemiczne do zwykłego CO_2 ze stabilnymi izotopami (^{12}C i ^{13}C). W ten sposób $^{14}CO_2$ jest przenoszony do roślin poprzez fotosyntezę i do zwierząt poprzez konsumpcję roślin, tak jak każda inna cząsteczka CO_2. ^{14}C jest również mieszany z nieorganicznymi formami węgla, takimi jak CO_2, HCO_3^- i CO_3^- , w oceanach poprzez proces wymiany molekularnej przez granicę powietrze-morze. W ten sposób radiowęgiel jest również pobierany przez biosferę morską. Cała materia żywa jest znakowana atomami ^{14}C, co daje bardzo szeroki zakres stosowalności metody radiowęglowej (Kusumgar et al. 1963; Quarta et al. 2021).

^{14}C jest stosowany jako narzędzie datowania do określania wieku materiałów zawierających węgiel, a także jako znacznik środowiskowy do śledzenia obiegu węgla w środowisku (Skinner and Bard 2022). Podstawowe prace nad pomiarami i zastosowaniem ^{14}C jako narzędzia datowania radiometrycznego przypisuje się W.F. Libby'emu (Arnold and Libby 1951; Libby et al. 1949). Okres półtrwania izotopu radiowęgla wynosi 5700 ± 30 lat (Kutschera 2019); dlatego po około dziesięciu okresach półtrwania próbki będą wolne od izotopu radiowęgla (Hajdas et al. 2021).

3.2. Pomiary radiowęglowe

Radiowęgiel dostarcza idealnego narzędzia do tworzenia chronologii archeologicznych i w wielu przypadkach może bezpośrednio datować interesujące wydarzenie. W stanowiskach archeologicznych materiały organiczne są często obfite i dostarczają wystarczającej ilości próbek do analizy. Oprócz datowania archeologicznego, analiza radiowęglowa jest szeroko stosowana w badaniach klimatu, środowiska i naukach o życiu (Szidat et al. 2014; Wood 2015).

3.3. Znaczenie metody radiowęglowej w określaniu zawartości materiałów biopochodnych

W XX wieku stężenie CO_2 w atmosferze wzrosło z powodu intensywnego wykorzystywania paliw kopalnych do produkcji energii oraz w transporcie. Aby zaradzić temu problemowi, Unia Europejska wyznaczyła nowe cele dotyczące zwiększenia wykorzystania materiałów odnawialnych (biogennych) w paliwach – 5,75% do 2010 roku zgodnie z Dyrektywą 2003/30/EC (Directive 2003) oraz co najmniej 10% biopaliw we wszystkich paliwach ciekłych do 2020 roku według (Directive 2009).. Ze względu na niższą rentowność produkcji biopaliw w porównaniu z paliwami kopalnymi, polityka środowiskowa Unii Europejskiej promuje biopaliwa poprzez obniżenie podatków akcyzowych i udzielanie ulg podatkowych (Krajcar Bronić et al. 2015). Dlatego też istnieje potrzeba określenia ilości materiału biogennego za pomocą wiarygodnej i dokładnej metody, nie tylko w różnych rodzajach paliw, ale także we wszystkich innych materiałach codziennego użytku, takich jak bioplastiki, opakowania jednorazowe, sprzęt drewniany itp. Każdy materiał jest uważany za biopochodny (biokomponent), jeśli zawiera znaczną część radiowęgla, który w idealnym przypadku odzwierciedla aktualną zawartość atmosferycznego ^{14}C. Metoda radiowęglowa jest dobrze znaną i niezawodną metodą określania zawartości biokomponentów w różnych rodzajach produktów. W metodzie radiowęglowej stężenie ^{14}C określa się jako procent współczesnego węgla (pMC), natomiast zawartość węgla biologicznego określa się według norm międzynarodowych na podstawie współczynnika korekcji atmosferycznej (REF) w określonym roku dla 100% zawartości węgla biobazowego.

W badaniach zajmowałam się gumą z opon i produktami jej pirolizy, sadzą techniczną (*z j. ang. technical carbon black – TCB*) i materiałami opakowaniowymi jednorazowego użytku (*z j. ang. disposable packaging materials – DPM*), ponieważ materiały te są szeroko stosowane do recyklingu i zrównoważonej produkcji. Głównym celem tego badania było zbadanie stężenia współczesnego węgla w wymienionych materiałach w celu sprawdzenia wdrażania przepisów uchwalonych przez agencje ochrony środowiska dla wprowadzania zielonej technologii i kontroli emisji gazów cieplarnianych.

3.4. Przetwarzanie odpadów

Zapotrzebowanie na energię i produkcja odpadów w codziennym życiu to dwa główne czynniki brane pod uwagę w rozwijającym się świecie. Spośród wytwarzanych odpadów organicznych i nieorganicznych tworzywa sztuczne i guma są uważane za najbardziej niebezpieczne źródło odpadów do przetwarzania, stanowiąc 31,2% całkowitej ilości odpadów (Hoang et al. 2020). Stałe odpady komunalne są znaczącym źródłem emisji gazów cieplarnianych (Wang and Nakakubo 2020) i są zbierane z odpadów domowych, w tym urządzeń elektronicznych, zużytych baterii, metali, papieru i tektury, metali, tworzyw sztucznych, drewna, mebli itp. (Directive 2008). Odzyskiwanie energii ze stałych odpadów komunalnych jest doskonałym sposobem na zmniejszenie zużycia paliw kopalnych do produkcji energii (Ngusale et al. 2017). Składowanie na wysypiskach, spalanie i kompostowanie są ogólnie klasyfikowane jako metody przetwarzania stałych odpadów komunalnych (Wang and Nakakubo 2020). Zgodnie z dyrektywą Komisji Europejskiej z 2008 r., zaktualizowanej w lutym 2024 r., poziomy priorytetów w zapobieganiu powstawaniu odpadów i zarządzaniu nimi są ustalone w następujący sposób: zapobieganie, ponowne wykorzystanie, recykling, odzysk energii i unieszkodliwianie. Wzięto pod uwagę ogólną ochronę środowiska, zrównoważony rozwój, wykonalność techniczną, ochronę zasobów, zdrowie ludzkie i skutki społeczne (Directive 2008).

Wskaźnik recyklingu odpadów rośnie w UE-27, co wskazuje na zwiększone wykorzystanie odpadów jako zasobów i osiąganie gospodarki o obiegu zamkniętym. Całkowity poziom przetwarzania odpadów w Europie znacznie wzrósł z 46% w 2004 r. Do 60% w 2020 r., podczas gdy całkowity poziom usuwania odpadów zmniejszył się z 54% w 2004 r. do 45% w 2020 r. (Eurostate 2020). W 2021 r. najwyższy wskaźnik recyklingu odnotowano dla opakowań – 64%, następnie dla odpadów komunalnych – 49% oraz odpadów elektrycznych i elektronicznych – 39%. Większość odpadów nadal była utylizowana poprzez spalanie w 2021 r. (European-Environmental-Agency 2023).

W Europie w latach 2010–2021 papier i tektura stanowiły główne materiały wytwarzane z odpadów opakowaniowych (34,0 mln ton w 2021 r.), a następnie tworzywa sztuczne (16,1 mln ton) i odpady opakowaniowe ze szkła (15,6 mln ton) (Eurostate 2023). Dwie kluczowe techniki – ponowne użycie i recykling, są wykorzystywane do rozwoju gospodarki o obiegu zamkniętym. (Di Foggia and Beccarello 2022).

Zanieczyszczenie plastikiem jest podkreślane jako globalny kryzys od jego produkcji do utylizacji. Bioplastiki to naturalne i chemicznie przetwarzane materiały pochodzące z odnawialnych lub opartych na ropie surowców, zaprojektowane w celu zapewnienia niskiej emisji dwutlenku węgla, wysokiej wartości recyklingu oraz pełnej biodegradowalności lub kompostowalności (Ramesh Kumar et al. 2020).

Produkcja plastiku przemysłowego rozpoczęła się około lat 50. XX wieku i wzrasta wykładniczo. W 2016 r. roczna produkcja plastiku wyniosła 330 milionów ton metrycznych (Lebreton and Andrady 2019), natomiast w 2022 r. osiągnęła 400,3 mln ton metrycznych (Statista 2023).

Według raportu Plastics Europe z 2020 r. wytworzono 24,5 mln ton odpadów z tworzyw sztucznych (*z j. ang. plastic waste - PW*). 14% tych odpadów zostało poddanych recyklingowi, co dostarczyło 3,5 miliona ton produktów z recyklingu. 50% europejskich odpadów plastikowych jest spalanych w celu odzyskania energii, co powoduje emisję 95 milionów ton dwutlenku węgla rocznie. Celem Komisji Europejskiej jest zakończenie zanieczyszczenia plastikiem do 2040 roku poprzez wprowadzenie gospodarki o obiegu zamkniętym, która pozwala na ponowne użycie, recykling i odpowiedzialne przetwarzanie wszystkich rodzajów produktów z plastiku, przy jednoczesnym ograniczeniu emisji gazów cieplarnianych związanych z gospodarowaniem plastikiem. Komisja zaleca również, aby przejście do osiągnięcia celów UE w zakresie zerowej emisji dwutlenku węgla i gospodarki o obiegu zamkniętym zostało ukończone do 2050 roku (Plastics-Europe).

Na całym świecie rocznie produkuje się ponad 1,7 miliarda opon (Tire-Grades 2023), a w Unii Europejskiej w 2020 r. wyprodukowano około 4,2 miliona ton metrycznych opon gumowych (Statista 2021). Według (Hoang et al. 2020) dwie trzecie opon trafia na wysypiska śmieci lub jest nielegalnie utylizowane, co stwarza poważne zagrożenie dla środowiska i zdrowia ludzi. Zużyte opony stają się wiodącym problemem środowiskowym na świecie, ponieważ zużyta guma stanowi duży procent odpadów stałych.

W przypadku opon wycofanych z eksploatacji (*z j. ang. end-of-life tires - ELT*), 80% jest wykorzystywanych jako paliwo lub materiał z recyklingu z wykorzystaniem utylizacji i bieżnikowania (Goksal 2022). W recyklingu opon stosuje się bieżnikowanie, spalanie, mielenie i odzysk, jednak każda z tych metod ma wiele wad. Opony trudno jest przetworzyć na nowo w ten sposób. Piroliza wydaje się być najbardziej odpowiednią metodą recyklingu. (De Marco Rodriguez et al. 2001). Efektywne wykorzystanie opon zmniejsza zużycie paliw kopalnych i energii, ponieważ same opony są wykorzystywane jako paliwo. W rezultacie następuje zmniejszenie emisji CO_2 pochodzącego z paliw kopalnych, ponieważ opony zawierają już w sobie węgiel pochodzenia kopalnego. Opony mają wysoką wartość opałową i zawierają około 60-70% węgla oraz 6-7% wodoru, więc ich właściwości spalania i skład są niemal równe węglowi (Rodríguez et al. 2017). W ten sposób spalanie opon zapewnia ciepło, ale zmniejsza dodatkową emisję CO_2 i SO_x do atmosfery (Krajcar Bronić et al. 2015; Rodríguez et al. 2017).

4. Próbki do analiz

W ramach pracy doktorskiej zbadałam kilka rodzajów próbek codziennego użytku. Pierwszy rodzaj próbek obejmował gumę z opon oraz produkty jej pirolizy, takie jak odzyskana sadza (*z j. ang. recovered carbon black - rCB*) i próbki oleju pirolitycznego. Próbki te zostały dostarczone przez firmę Contec Inc., mającą siedzibę w Warszawie, która wykorzystuje technologię pirolizy opon do produkcji przyjaznego dla środowiska zamiennika dla pierwotnej sadzy i surowca petrochemicznego, a także do rozwiązania globalnego problemu odpadów *ELT*. Contec Inc. dostarczył próbki w trzech partiach, przy czym za każdym razem próbki rozdrobnionej gumy stanowiły mieszankę opon ciężarowych i osobowych w różnych proporcjach, a olej pirolityczny i odzyskana sadza pochodziły z tej samej partii co próbki gumy.

W drugiej serii przeanalizowałam dziesięć różnych rodzajów materiałów opakowaniowych jednorazowego użytku (*DPM*) zebranych od firm Quick Pack, Vigo i Bio-pack. Próbki te obejmowały talerze papierowe, pudełka, słomki papierowe, kubki papierowe, papier do pieczenia, talerze i pudełka z trzciny cukrowej, talerze z otrębów pszennych i drewniane sztućce.

W trzeciej serii zbadałam zawartość materiału biogenicznego w próbkach sadzy technicznej (*TCB*) uzyskanych od Contec Inc. Przeanalizowałam cztery różne rodzaje próbek sadzy technicznej, które zostały wydzielone na podstawie wartości powierzchni właściwej, morfologii agregatów z nanostrukturami, zawartości popiołu i innych chemikaliów (Contec; Robertson and Hardman 2021). **Tabela 1** opisuje szczegółowo wszystkie kategorie badanych próbek.

Tabela 1. Opis analizowanych próbek.

NIE.	**Nazwa próbki**	**Kod próbki**	**Opis**
1.	Olej pirolityczny-1	CONT-1	Nieznana proporcja opon samochodów ciężarowych i osobowych.
2.	Olej pirolityczny-2	PCO-2	Opony w 100% przeznaczone do samochodów osobowych.
3.	Odzyskana sadza-1	rCB-2	Opony w 100% przeznaczone do samochodów osobowych.
4.	Guma-1	CR-2	Opony w 100% przeznaczone do samochodów osobowych.
5.	Olej pirolityczny-3	TCO-3	70% opon ciężarowych i 30% opon osobowych.
6.	Odzyskana sadza-2	rCB-3	70% opon ciężarowych i 30% opon osobowych.
7.	Guma-2	CR-3	70% opony ciężarowych i 30% opon osobowych.
8.	Talerze jednorazowe-1	QSCP-1	W kolorze białym, rodzaj jednorazowych talerzyków papierowych, z włókien trzciny cukrowej.
9.	Kubki jednorazowe	QPC-2	Jasnobiałe, z papieru.
10.	Papier do pieczenia	QBP-3	W kolorze brązowym, znany również jako pergamin roślinny; kompozyt na bazie celulozy.
11.	Słomki jednorazowe	QPS-4	Brązowe na zewnątrz i białe wewnątrz, z papieru.
12.	Talerze jednorazowe-2	QPP-5	W kolorze białym, z papieru.
13.	Sztućce drewniane	QWC-6	Drewniane łyżki, widelce i noże.
14.	Talerze jednorazowe-3	QBPP-7	W kolorze brązowym, z papieru.
15.	Talerze jednorazowe-4	VWBP-8	W kolorze brązowym, z otrębów pszennych.
16.	Pudełka jednorazowe	BSCB-9	Jasnobiałe, z trzciny cukrowej.
17.	Talerze jednorazowe-5	BPP-10	Jasnobiałe, z papieru.
18.	Sadza techniczna-1	TCB-N330	Powierzchnia właściwa 76-80 m^2/g; zapewnia średnio-wysokie wzmocnienie. Stosowana do bieżnika opon, osnowy i ścian bocznych.
19.	Sadza techniczna-2	TCB-N550	Powierzchnia właściwa 39-41 m^2/g; zapewnia średnio-wysokie wzmocnienie. Stosowana w warstwach wewnętrznych, osnowach i ścianach bocznych opon osobowych oraz w wyrobach gumowych.
20.	Sadza techniczna-3	TCB-N660	Powierzchnia właściwa 34-36 m^2/g; zapewnia średnie wzmocnienie. Stosowana w wewnętrznych warstwach i ścianach bocznych opon, pierścieniach uszczelniających, osłonach kabli, formach gumowych i produktach wytłaczanych.
21.	Sadza techniczna-4	TCB-N772	Powierzchnia właściwa 31-32 m^2/g, z półwzmocnieniem. Stosowana w warstwach wewnętrznych opon i wyrobach gumowych.

5. Metodologia

W pracy wykorzystałam zarówno konwencjonalną (ciekłoscyntylacyjną – LSC) jak i akceleratorową (AMS) technikę radiowęglową do określenia zawartości biobazowego węgla w próbkach. Spektrometria mas stosunków izotopowych (*z j. ang. isotope ratio mass spectrometry - IRMS*) została użyta do wyznaczenie poprawki na frakcjonowanie izotopowe dla próbek badanych techniką LSC.

Według (Rodríguez et al. 2017) piroliza-GC/MS, analiza termograwimetryczna (TGA) i analiza radiowęglowa (metoda ^{14}C) mogą być stosowane do określania zawartości biomasy w oponach wycofanych z eksploatacji (ELT), ale tylko analiza radiowęglowa jest uważana za wiarygodną technikę (Haverly et al. 2019).

Według (Krajcar Bronić alet. 2015) ręczne sortowanie, rozpuszczanie chemiczne i metody ^{14}C są stosowane do określania składników biologicznych we wszystkich rodzajach paliw lub odpadów, które są wykorzystywane w zakładach przetwarzających odpady na energię. Sortowanie ręczne jest czasochłonne i pracochłonne, natomiast selektywne rozpuszczanie wymaga personelu laboratoryjnego i sprzętu (Séverin et al. 2010). Metoda ^{14}C jest najbardziej niezawodna i może być stosowana do różnych rodzajów stałych odpadów komunalnych, zużytych opon samochodowych, płynów i paliw (Krajcar Bronić et al. 2015).

5.1. Techniki pomiarów radiowęglowych

Aby zmierzyć szybkość rozpadu ^{14}C, opracowano wysoce czułe techniki pomiaru niskich radioaktywności, wraz z odpowiednią wstępną preparatyką chemiczną próbki. Wymagana ilość węgla w próbce (1-5g) jest głównym ograniczeniem tych metod. Czułe techniki pomiaru niskich radioaktywności są wymagane ze względu na niską naturalną koncentrację izotopu ^{14}C (10^{-10} %), niską aktywność właściwą (226 Bq/kg) i niską energię elektronów (<156 keV) wytwarzaną w procesie rozpadu β. W początkach metody radiowęglowej powszechnie stosowano gazowe liczniki proporcjonalne (*z j. ang. gas proportional counters - GPC*), ale obecnie wyszły one już z użytku, a w technikach zliczania rozpadów dominuje technika ciekłoscyntylacyjna (*z j. ang. liquid scintillation counting - LSC*) (Krajcar Bronić et al. 2010; Wood 2015).

Około 50 lat temu opracowano technologię akceleratorowej spektrometrii masowej akceleratorowej (*z j. ang. accelerator mass spectrometry - AMS*), na którą nie ma wpływu niska aktywność właściwa ani energia elektronów. AMS mierzy stosunek ^{14}C/^{12}C lub ^{14}C/^{13}C w próbce w porównaniu do standardu. Niewielki rozmiar próbki (kilka mg) i ciągłe doskonalenie techniki AMS sprawiają, że jest to bardziej odpowiednia technika do różnych zastosowań (Hajdas et al. 2022; Krajcar Bronić et al. 2010).

5.2. Oznaczanie zawartości biowęgla

Obecnie wykorzystanie materiałów biogenicznych w różnych dziedzinach szybko wzrasta po stronie przemysłu, klientów i konsumentów. Materiały biogeniczne zastąpiły typowe materiały zawierające węgiel kopalny (European-Union 2019; Pandey and Singhal 2023). W ostatniej dekadzie (2010–2020) zauważono stały wzrost popytu na materiały pochodzenia biologicznego, nie tylko w dziedzinie bioplastików, ale także w biopolimerach, biosmarach, biorozpuszczalnikach, biosurfaktantach, enzymach i biofarmaceutykach (Pandey and Singhal 2023).

Zasada określania zawartości biokomponentów w badanym materiale opiera się na fakcie, że do jego produkcji wykorzystano materię organiczną o dobrze zdefiniowanej frakcji radiowęglowej odpowiadającej współczesnemu poziomowi atmosferycznego $^{14}CO_2$, a także materiały kopalne. Radiowęgiel ma okres półtrwania wynoszący 5700 ± 30 lat, co sprawia, że materiały kopalne są od niego wolne (Hua et al. 2022; Kutschera 2019).

Istnieją międzynarodowe i europejskie normy podające jak określać biobazowy węgiel, w zależności od rodzaju materiałów – szczegóły zawarto w pracy (Gill et al. 2022).

W ramach pracy zbadałam gumę oponową i produkty jej pirolizy, jednorazowe materiały opakowaniowe i próbki technicznej sadzy. Zawartość biowęgla w próbkach określiłam przy użyciu normy europejskiej (EN16640 2017), która ma zastosowanie do wszystkich towarów biopochodnych. Zawartość biowęgla (*z j. ang. biobased carbon content*) w próbkach jest określana przy użyciu poniższego wzoru:

$$biobased\ carbon\ \ content = \frac{pMC}{REF}, \tag{1}$$

gdzie:

pMC- stężenie ^{14}C wyrażone w procentach współczesnego węgla, uzyskane metodami radiowęglowymi (LSC i AMS).

REF- do obliczenia zawartości węgla biologicznego zastosowano współczynnik korekcji atmosferycznej w ustalonym roku 100% węgla pochodzenia biologicznego, zgodnie z danymi opublikowanymi przez (CIO 2022; Hua et al. 2022).

5.3. Określanie zawartości biokomponentu

Norma europejska EN-16785-1 definiuje jak poprawnie określić zawartość biokomponentu przy użyciu metody radiowęglowej i analizy pierwiastkowej. Zgodnie z nią ilość biomasy oblicza się jako ilość pierwiastków biologicznych (C, H, N, O) w próbce wyrażonych jako procent całkowitej masy próbki:

$$Bio - content = \frac{mass\ of\ bio\text{-}based\ content}{total\ mass\ of\ material} \times 100\ (\%) \tag{2}$$

Moje badania doktoranckie ograniczały się do metody radiowęglowej i określania zawartości węgla biobazowego.

5.4. Pomiary z użyciem akceleratorowej spektrometrii mas (AMS)

Technika radiowęglowa AMS jest wydajna, szybka i wygodna w przygotowywaniu próbek do pomiaru radiowęglowego (Wacker et al. 2010b). Pomiary AMS przeprowadzono w trzech laboratoriach. Wszystkie próbki wymienione w **Tabeli 1**, z wyjątkiem gumy z opon, przygotowano i przeanalizowano w Laboratorium ^{14}C i Spektrometrii Mas w Gliwicach w Instytucie Fizyki – Centrum Naukowo-Dydaktycznym. Gumę z opon i produkty jej pirolizy przeanalizowano dodatkowo w National Laboratory for Age Determination w Trondheim w Norwegii. Ponadto próbki grafitu z produktów pirolizy opon, które zostały zgrafityzowane w Gliwickim Laboratorium radiowęglowym, zostały zmierzone w Poznańskim Laboratorium Radiowęglowym (Goslar et al. 2004).

5.4.1. Przygotowanie i analiza próbek w Laboratorium ^{14}C i Spektrometrii Mas w Gliwicach

Dobrze wyposażone laboratorium do przygotowywania próbek do analizy ^{14}C istnieje w Politechnice Śląskiej, w Instytucie Fizyki – Centrum Naukowo-Dydaktycznym, Zakładzie Geochronologii i Badań Izotopowych Środowiska od końca lat 60 XX wieku. W ramach pracy doktorskiej miałam możliwość nauki korzystania ze światowej klasy sprzętu.

Do określenia całkowitej zawartości węgla w próbkach i grafityzacji wykorzystano analizator elementarny VarioMicroCube połączony z systemem automatycznej grafityzacji (AGE-3) firmy IonPlus AG z siedmioma reaktorami redukcyjnymi (**Rys. 1a**) (Němec et al. 2010; Wacker et al. 2010b). Przed rozpoczęciem mojej pracy doktorskiej Gliwickie Laboratorium Radiowęglowe AMS wytwarzało tarcze grafitowe z próbek szczątków roślinnych, drewna, węgla drzewnego, torfu, muszli i próbek kości (Piotrowska 2013). Opracowane wcześniej metody z powodzeniem zastosowałam do nowego typu próbek, tzn. oleju pirolitycznego, odzyskanej sadzy, próbek opakowań jednorazowych, drewnianych sztućców i próbek sadzy technicznej (Gill et al. 2024; Gill et al. 2022; Gill et al. 2023). W ramach przeprowadzonych badań ustalono, że dla wymienionych nowych typów próbek nie jest wymagana wstępna preparatyka chemiczna poza płukaniem wodą demineralizowaną.

Do pomiarów AMS używano kilku miligramów próbki (patrz **Tabela 2**). Próbkę ważono w cynowej kapsułce dla próbek ciekłych i cynowej kapsułce łódkowej dla próbek stałych. Cynowe kapsułki dla próbek ciekłych były odpowiednio uszczelnione za pomocą specjalnej prasy uszczelniającej. Ze względu na niejednorodność, tzn. warstwową strukturę opakowań jednorazowych, analizie poddano różne podpróbki (warstwę zewnętrzną, warstwę wewnętrzną i ich miks). Przeprowadzono również testy możliwości zastosowania zwęglania próbki przy ograniczonym dostępie tlenu dla celów ujednorodnienia próbek opakowań jednorazowych, gdyż wyniki pomiarów AMS wyraźnie wskazały, że wynik pomiaru zależy od proporcji poszczególnych warstw w małej (miligramowej) podpróbce. Do zwęglania używano próbki o masie 24g, którą umieszczano w metalowym reaktorze z pokrywą o bardzo małym otworze (aby zminimalizować dostęp tlenu) i spalono w piecu muflowym w temperaturze 700 °C przez około 7 do 10 minut. Próbkę następnie schładzano i rozdrabniano na proszek. W następnym kroku, analizator elementarny był stosowany do spalenia próbki w celu wytworzenia gazu CO_2, który następnie grafityzowano przy użyciu AGE-3 w obecności wodoru (H_2) i sproszkowanego żelaza (Fe) (Wacker et al. 2010b). Otrzymane próbki grafitu zaprasowywano w tarczach (katody) z użyciem specjalnej prasy pod ciśnieniem 4 barów (dwa razy w celu prawidłowego sprasowania i uszczelnienia).

Rys. 1a Analizator elementarny sprzężony z automatycznym systemem grafityzacji w Laboratorium ^{14}C i Spektrometrii Mas w Gliwicach.

Rys. 1b MICADAS w Laboratorium ^{14}C i Spektrometrii Mas w Gliwicach.

Jak napisali konstruktorzy, mały system AMS – MIni CArbon DAting System (MICADAS) (**Rys. 1b**) umożliwia analizy ^{14}C z porównywalną dokładnością i precyzją jak większe urządzenia AMS. Uproszczona konfiguracja urządzenia zmniejsza koszty eksploatacji i serwisu (Synal 2013; Synal et al. 2007; Wacker et al. 2010a). Magazynek mieści do 40 próbek. Opracowanie wyników jest wykonywane w programie BATS (Wacker et al. 2010a).

W przeprowadzonych pomiarach jako standard zastosowano kwas szczawiowy (II) (*z j. ang. Oxalic Acid (II*)). Do kontroli tła pomiarów AMS zastosowano bezwodnik ftalowy oraz antracyt. W pojedynczych przypadkach stosowano jako dodatkową kontrolę tła paliwo kopalne.

5.4.2. Przygotowanie i analiza próbek w National Laboratory for Age Determination w Trondheim w Norwegii

Guma oponowa i produkty jej pirolizy gumy zostały przeanalizowane w Narodowym Laboratorium Określania Wieku w Trondheim w Norwegii. Do próbek stałych i ciekłych zastosowano różne metody spalania. Stałe próbki gumy i odzyskanej sadzy zostały spalone i zredukowane w analizatorze elementarnym. Próbki ciekłego oleju pirolitycznego zostały najpierw zamrożone, a następnie wraz z tlenkiem miedzi (CuO) zostały zamknięte w rurach kwarcowych. Do spalania użyto pieca muflowego. CO_2 powstający w wyniku spalania został zredukowany w ręcznym systemie redukcji Fe-Zn. Praca (Seiler et al. 2019) dostarcza szczegółowych wyjaśnienie metod przygotowywania grafitu w tym laboratorium. Zautomatyzowane urządzenie do grafityzacji zostało użyty do wytworzenia tarcz grafitowych o masie 1mg. Urządzenie to łączy analizator elementarny z siedmioma reaktorami redukcyjnymi.

Rys. 2 Akceleratorowy spektrometr masowy w Narodowym Laboratorium Określania Wieku w Trondheim w Norwegii.

Pomiary ^{14}C przeprowadzono na układzie AMS (**Rys. 2**) o mocy 1 MV wyprodukowanym przez High Voltage Engineering Europa BV (Nadeau et al. 2015; Seiler et al. 2019). Typowy magazynek mieści do 50 próbek.

5.5. Metoda ciekłoscyntylacyjna (LSC)

Do oznaczania węgla pochodzenia biologicznego w gumie oponowej, produktach pirolizy opon i próbkach TCB zastosowano technikę ciekłoscyntylacyjną dostępną w Laboratorium ^{14}C i Spektrometrii Mas w Gliwicach w Instytucie Fizyki – Centrum Naukowo-Dydaktycznym Politechniki Śląskiej. Pomiary LSC poprzedzała synteza benzenu z próbek. Każda użyta substancja chemiczna była czysta pod względem analitycznym. Odłączalne szkło z linii do syntezy benzenu **(Rys. 3)** dokładnie oczyszczano wodą dejonizowaną i suszono w temperaturze 80 °C. Benzen syntezowano z oryginalnych próbek bez chemicznej preparatyki wstępnej; jedynie próbki gumy oponowej myto gorącą wodą dejonizowaną. Laboratorium Radiowęglowe w Gliwicach ma profesjonalną linię syntezy benzenu, z wyciągami spalin zapewniającymi bezpieczne etapy spalania i syntezy, a także dygestoria do bezpiecznego obchodzenia się z benzenem. Synteza benzenu obejmuje następujące kroki:

5.5.1. Produkcja CO_2 i synteza karbidu

Do syntezy węglika wykorzystywano reaktor metalowy, który był wcześniej mechanicznie oczyszczony i wypłukany wodą dejonizowaną, a następnie wysuszony i wygrzany w piecu muflowym w temperaturze 700 °C przez kilka godzin.

Analizowane próbki w postaci stałej, tzn. sadza techniczna, guma oponowa i odzyskanej sadzy były poddawane reakcji z litem metalicznym w stosunku 1:1 w oczyszczonym w sposób wyżej opisany, szczelnie zamkniętym reaktorze metalowym w temperaturze 700 °C pod kontrolą ciśnienia.

Próbki oleju pirolitycznego przechodziły dwuetapowy proces. W pierwszym etapie olej pirolityczny był wprowadzony do wewnętrznego małego reaktora i odparowywany na podgrzanym licie, który był umieszczony na dnie zewnętrznego reaktora. W drugim etapie, po schłodzeniu, pozostałości z wewnętrznego reaktora były przenoszone do zewnętrznego reaktora i dalej stosowano taką samą procedurę, jak w przypadku próbek stałych z dodatkowym litem metalicznym. Czas trwania reakcji różnił się w zależności od rodzaju materiału. W przypadku próbek sadzy technicznej reakcja była ukończona w ciągu około godziny, w przypadku oleju pirolitycznego potrzebne było około 40 minut, natomiast w przypadku próbek gumy oponowej od 1 do 2 godzin. Ogólną reakcję syntezy karbidu można zapisać następująco:

$$2CO_2 + 10Li \xrightarrow{700\,^{\circ}\mathrm{C}} Li_2C_2 + 4Li_2O \tag{3}$$

5.5.2. Synteza i oczyszczanie acetylenu

Li_2C_2 jest hydrolizowany w oddzielnej linii w celu wytworzenia acetylenu (C_2H_2) zgodnie z reakcją:

$$Li_2C_2 + H_2O \xrightarrow{\text{Room temperature}} C_2H_2 + 2LiOH \tag{4}$$

Następnie acetylen oczyszcza się, przepuszcza go przez higroskopijną pułapkę z dwuchromianu potasu ($K_2Cr_2O_7$) i kwasu siarkowego (H_2SO_4). Czysty C_2H_2 zbiera się w szklanej wymrażarce chłodzonej ciekłym azotem.

Rys. 3 Linia do syntezy benzenu w Laboratorium ^{14}C i Spektrometrii Mas w Gliwicach.

5.5.3. Synteza i Oczyszczanie Benzenu

Benzen powstaje z acetylenu w wyniku reakcji trymeryzacji, która jest przeprowadzana w temperaturze pokojowej na podgrzanym katalizatorze chromowym (wstępnie aktywowanym w temperaturze 600 °C przez 30 minut):

$$3C_2H_2 \rightarrow C_6H_6 \tag{5}$$

Benzen był oczyszczany z pary wodnej i radonu atmosferycznego. Benzen przechowywano w obecności metalicznego sodem przez noc w celu wysuszenia a następnie przez około miesiąc w zamrażarce (w temperaturze -15 ° C), aby uwolnić go od radonu. Ponieważ radon jest radioaktywny i ma okres półtrwania 3,8 dnia, to po miesiącu jego ilości w próbce benzenu są zaniedbywalne. Do usuwania radonu stosowałam również procedurę resublimacji (Tudyka et al. 2021). Do resublimacji używałam mieszaniny suchego lodu z etanolem (-78 °C).

Kiedy próbka była już wolna od radonu, to można było odmierzyć odpowiednią ilość niej (stosowano tzw. geometrię 2 ml) i po dodaniu scyntylatora w postaci butylu-PBD rozpocząć pomiary aktywności próbki (Pawlyta et al. 1997).

Pomiary ^{14}C wykonywano przy użyciu spektrometru ciekłoscyntylacyjnego β Quantulus 1220 ^{TM} (Pazdur et al. 2003). Jako tło zastosowano komercyjny polski benzen klasy cz.d.a, a jako standard zastosowano ANU-Sucrose.

5.6. Spektrometria masowa stosunków izotopowych (IRMS)

Do określenia względnej zawartości stabilnych izotopów węgla w próbkach, wyrażonej jako $\delta^{13}C$, zastosowano technikę spektrometrii masowej stosunków izotopowych. W moich badaniach wykorzystałam spektrometr IsoPrime 100 z ciągłym przepływem, połączony z systemem MultiFlow i automatycznym próbnikiem Gilson GX-271. System MultiFlow jest przeznaczony do automatycznego pobierania i transferu CO_2 z naczynek z próbkami do spektrometru masowego. Gaz pobierano za pomocą automatycznie sterowanej igły, rozdzielano chromatograficznie i przesyłano do IsoPrime w celu analizy izotopowej (Agnihotri et al. 2014; Multiflow 2012).

Pomiary izotopowe były konieczne do obliczenia poprawki na frakcjonowanie izotopowe dla pomiarów wykonanych techniką LSC. (Stuiver and Polach 1977). Do pomiarów IRMS używano benzenu wytworzonego z próbek na potrzeby pomiarów LSC. W tym celu w rurkach Simax umieszczano w szklanej kapilarze ~ 5 μl benzenu wraz z ~ 300 mg CuO. Po zamknięciu rurek z użyciem palnika umieszczano je w piecu w temperaturze 560 °C na ok. 12 h. Następnie w specjalnej linii próżniowej każda rurka była łamana, a wytworzony z próbki benzenu dwutlenek węgla był po przejściu przez pułapkę pary wodnej zbierany w szklanej wymrażarce przy użyciu ciekłego azotu. Po odmierzeniu odpowiedniej ilości CO_2 (kontrola poprzez pomiar ciśnienia w odpowiedniej gałęzi linii próżniowej) pobierano ręcznie specjalną strzykawką trzy podpróbki do naczynek dla systemu MultiFlow.

Jako standardów użyto materiałów dostarczanych przez IAEA: NBS-22 (olej; ~ 5 µl), IAEA-CH-6 (dawniej ANU Sucrose; ~ 3 mg) i IAEA-C3 (~ 1 mg) oraz standardu wewnątrzlaboratoryjnego WZS (osad jeziorny, ~ 2 µg) (Ustrzycka 2020). Standardy były spalane w rurkach Simax w tych samych warunkach co próbki i poddawane procedurze pomiarowej w sposób opisany powyżej.

Pomiary ^{14}C skorygowano, wykorzystując zmierzoną wartość $\delta^{13}C$, z użyciem następującego równania (Stuiver and Polach 1977):

$$A_{SN} = A_S \left[1 - \frac{2(25 + \delta^{13}C)}{1000}\right], \tag{6}$$

gdzie:
A_S- zmierzone stężenie ^{14}C
A_{SN}- skorygowane stężenie ^{14}C

6. Podsumowanie głównych wyników i wnioski

Koncentracja izotopu ^{14}C w próbce umożliwia odróżnienie próbek wyprodukowanych z materiałów współczesnych od wyprodukowanych z paliw kopalnych i przez to dostarcza informacji o potencjalnym wykorzystaniu do ich produkcji materiałów odnawialnych. W moich badaniach określiłam koncentrację ^{14}C (i ilość węgla biobazowego) w trzech różnych kategoriach próbek (guma oponowa i jej produkty pirolizy, próbki opakowań jednorazowych i próbki sadzy technicznej) przy użyciu wyżej wymienionych technik radiowęglowych.

Poniżej przedstawiam główne wyniki wraz z wnioskami opublikowanymi w poszczególnych publikacjach:

6.1. Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N, Kłusek M, Końska K, Wróblewski K, Nadeau MJ, Seiler M. (2022). Study of bio-based carbon fractions in tires and their pyrolysis products. Radiocarbon. 64 (6): 1457-1469. DOI: 10.1017/RDC.2022.88.

W artykule przedstawiono wyniki pomiarów stężenia biowęgla w oponach i produktach ich pirolizy. Ponadto przedstawiono wyniki pomiarów uzyskane dwiema technikami (AMS i LSC) w trzech różnych laboratoriach. Badanie stanowiło zatem również formę porównania międzylaboratoryjnego. Badania te zostały przeprowadzone we współpracy z firmą Contec Inc. z Warszawy, która zajmuje się pirolizą opon. W tych badaniach pracowałam nad produktami uzyskanymi z próbek opon samochodów osobowych, ciężarowych i ich mieszanin. Próbki oleju pirolitycznego i odzyskanej sadzy zostały przeanalizowane w Laboratorium ^{14}C i Spektrometrii Mas w Gliwicach (LSC i AMS) oraz Narodowym Laboratorium Oznaczania Wieku w Trondheim w Norwegii. Do obliczenia poprawki na frakcjonowanie izotopowe dla pomiarów LSC zastosowano metodę IRMS. Próbki gumy zostały przeanalizowane w Laboratorium ^{14}C i Spektrometrii Mas w Gliwicach wyłącznie techniką LSC oraz w Narodowym Laboratorium Oznaczania Wieku w Trondheim w Norwegii techniką AMS.

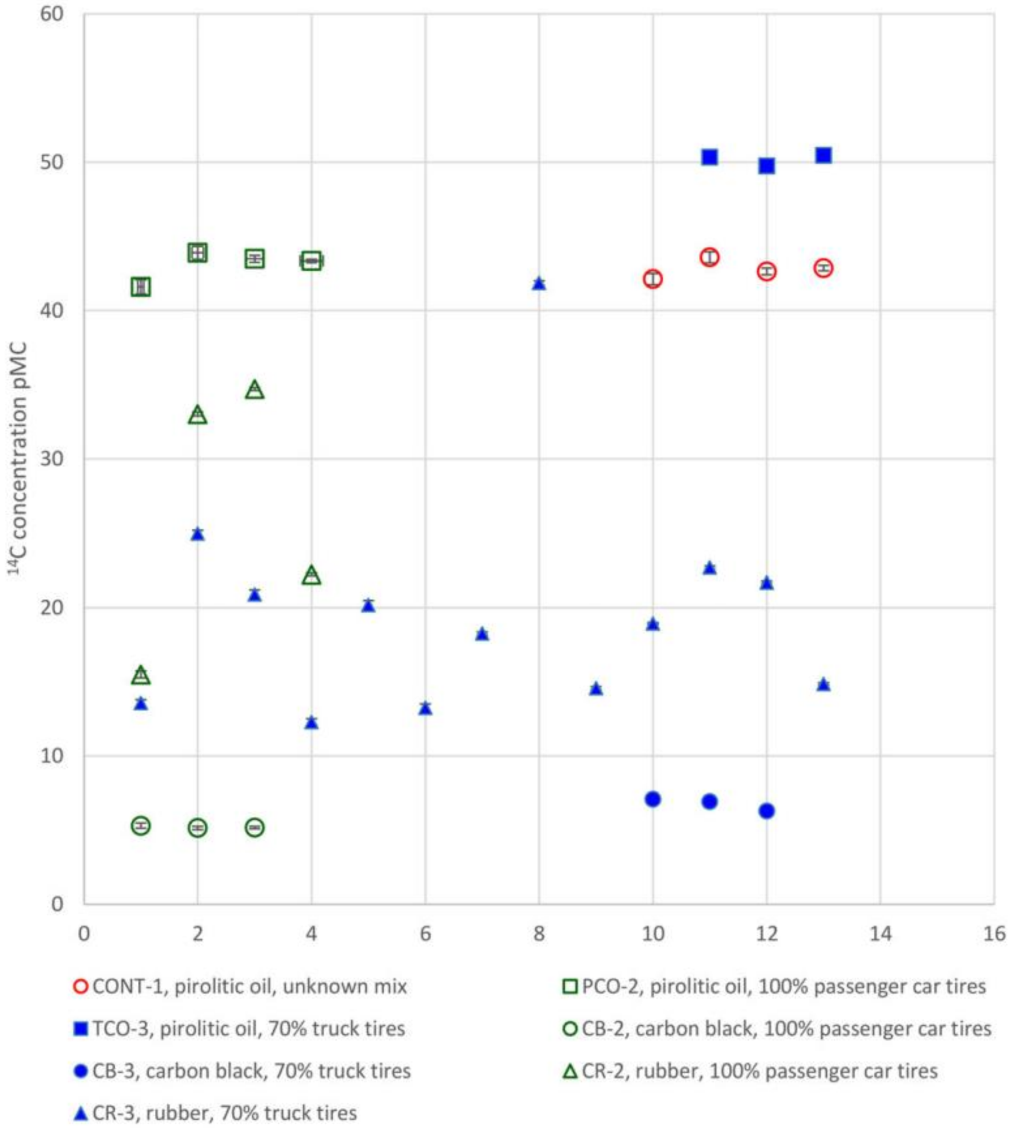
Szczegółowe wyniki zestawiono w **Tabeli** 2. Dla oleju pirolitycznego wartości koncentracji izotopu ^{14}C były zależne od ilości opon ciężarowych w masie poddawanej pirolizie i wahały się w zakresie od ok. 41 do 50 pMC, przy czym im większy był wsad opon ciężarowych, tym wyższe były wartości koncentracji ^{14}C. Ten sam trend zaobserwowano dla odzyskanej sadzy. W tym przypadku wartości wahały się od ok. 5 do niecałych 7 pMC. Próbki zbadano dwiema technikami, a trzy różne laboratoria wykazały dobrą zgodność (**Rys. 4**), a wszystkie metody wydają się być odpowiednie i niezawodne do badania produktów pirolizy z opon.

Tabela 2. Wyniki pomiarów koncentracji izotopu ^{14}C podane jako pMC dla poszczególnych rodzajów próbek otrzymane techniką LSC (kody laboratoryjne GdS-) oraz AMS (kody laboratoryjne GdA – (Gliwice) i TRa- (Trondheim)). Dla próbek oleju pirolitycznego i odzyskanej sadzy podano wyniki testu χ^2, przy czym krytyczna wartość χ^2 dla poziomu ufności α=0,01 i dla czterech pomiarów wynosi 11,34, a dla trzech – 9,21. Zawartość biobazowego węgla została wyznaczona zgodnie z normą EN16640 (EN16640:2017) dla trzech wartości REF (CIO 2022; Hua et al. 2022) - patrz Table. 4 w pracy (Gill et al. 2022).

Lp.	**Nazwa próbki**	**Kod lab.**	**Koncentracja ^{14}C (pMC)**	χ^2	**Całkowity węgiel (%)**	**Zawartość węgla biobazowego (%)**		
						REF$_{2011}$	**REF$_{2006}$**	**REF$_{1995}$**
1	CONT-1 Pyrolytic Oil	GdS-4257	41,95 ± 0,37	*8,48*	84,8 ± 0,50	40,6 ± 0,36	39,8 ± 0,35	37,5 ± 0,33
		GdS-4258	43,43 ± 0,38			42,0 ± 0,37	41,2 ± 0,36	38,8 ± 0,34
		GdA-6611	42,64 ± 0,23			41,3 ± 0,22	40,5 ± 0,22	38,1 ± 0,21
		TRa-16675	42,86 ± 0,18			41,5 ± 0,17	40,7 ± 0,17	38,3 ± 0,16
2	PCO-2 Pyrolytic Oil	GdS-4320	41,30 ± 0,47	*20,83; bez GdS-4320: 1,65*	83,5 ± 2,5	40,0 ± 0,45	39,2 ± 0,45	36,9 ± 0,42
		GdS-4365	43,90 ± 0,44			42,5 ± 0,43	41,7 ± 0,42	39,2 ± 0,39
		GdA-6612	43,49 ± 0,23			42,1 ± 0,22	41,3 ± 0,22	38,8 ± 0,21
		TRa-16676	43,35 ± 0,11			42,0 ± 0,11	41,1 ± 0,10	38,7 ± 0,10
3	TCO-3 Pyrolytic Oil	GdS-4373	50,35 ± 0,49	*7,46*	74,9 ± 7,2	48,7 ± 0,47	47,8 ± 0,46	45,0 ± 0,44
		GdA-6613	49,76 ± 0,24			48,2 ± 0,23	47,2 ± 0,23	44,4 ± 0,21
		TRa-16677	50,47 ± 0,10			48,9 ± 0,10	47,9 ± 0,09	45,1 ± 0,09
4	rCB-2 Recovered Carbon Black	GdS-4327	5,08 ± 0,18	*0,07*	71,7 ± 3,5	4,9 ± 0,17	4,8 ± 0,17	4,5 ± 0,16
		GdA-6615	5,14 ± 0,11			5,0 ± 0,11	4,9 ± 0,10	4,6 ± 0,10
		TRa-16679	5,17± 0,08			5,0 ± 0,08	4,9 ± 0,08	4,6 ± 0,07
5	rCB-3 Recovered Carbon Black	GdS-4394	6,89 ± 0,18	*19,31; bez TRa-16680*	78,9 ± 1,5	6,7 ± 0,17	6,5 ± 0,17	6,2 ± 0,16
		GdA-6616	6,92 ± 0,12			6,7 ± 0,12	6,6 ± 0,11	6,2 ± 0,11

		TRa-16680	6,29 ± 0,18	*0,02*		6,1 ± 0,17	6,0 ± 0,17	5,6 ± 0,16
6	CR-2 Rubber	GdS-4337	15,54 ± 0,23	χ^2 - NA; zakres: 15,54 – 34,71	83,7 ± 2,8	14,8 ± 0,22	14,5 ± 0,22	13,7 ± 0,21
		TRa-16682a	33,02 ± 0,13			32,0 ±0,13	31,3 ± 0,12	29,5 ± 0,12
		TRa-16682b	34,71 ± 0,10			33,6 ± 0,10	32,9 ± 0,09	31,0 ± 0,09
		TRa-16682c	22,21 ± 0,10			21,5 ± 0,10	21,1 ± 0,09	19,8 ± 0,09
7	CR-3 Rubber	GdS-4339	13,59 ± 0,23	χ^2 - NA zakres: 12,31 – 41,86	74,9 ± 2,3	12,9 ± 0,22	12,7 ± 0,22	11,9 ± 0,21
		GdS-4380	25,12 ± 0,22			24,2 ± 0,21	23,7 ± 0,21	22,3 ± 0,20
		GdS-4383	20,89 ± 0,32			19,9 ± 0,31	19,5 ± 0,30	18,4 ± 0,29
		GdS-4370	12,31 ± 0,21			11,7 ± 0,20	11,5 ± 0,20	10,8 ± 0,19
		GdS-4375	20,24 ± 0,31			19,4 ± 0,30	19,0 ± 0,29	17,8 ± 0,28
		GdS-4374	13,29 ± 0,25			12,6 ± 0,24	12,4 ± 0,24	11,7 ± 0,22
		TRa-16683a	18,25 ± 0,10			17,7 ± 0,10	17,3 ± 0,09	16,3 ± 0,09
		TRa-16683b	41,86 ± 0,15			40,5 ± 0,15	39,7 ± 0,14	37,4 ± 0,13
		TRa-16683c	14,57 ± 0,11			14,1 ± 0,11	13,8 ± 0,10	13,0 ± 0,10
		TRa-16683d	18,93 ± 0,07			18,3 ± 0,07	18,0 ± 0,07	16,9 ± 0,06
		TRa-16683e	22,68 ± 0,10			22,0 ± 0,10	21,5 ± 0,09	20,3 ± 0,09
		TRa-16683f	21,68 ± 0,09			21,0 ± 0,09	20,6 ± 0,09	19,4 ± 0,08
		TRa-16683g	14,85 ± 0,08			14,4 ± 0,08	14,1 ± 0,08	13,3 ± 0,07

W przypadku gumy z opon dostarczone próbki miały formę gumy pociętej na kawałki o rozmiarze od 0,5 do 1 cm. Dla potrzeb pomiarów LSC dla pojedynczego pomiaru wystarczało kilka fragmentów o łącznej masie 5-6 g, natomiast dla potrzeb AMS wycinano z jednego kawałka próbkę o masie rzędu 1 mg. Otrzymano mocno rozrzucone wyniki pomiaru koncentracji ^{14}C. Fakt rozrzutu wyników wynika ze złożonej struktury opon, gdyż do jej konstrukcji wykorzystuje się zarówno kauczuk naturalny (który można traktować jako biokomponent), jak i kauczuk wyprodukowany z paliw kopalnych. Zgodnie z danymi producentów opon, te różne rodzaje kauczuku są stosowane w różnych warstwach opony. Zatem, wynik pomiaru koncentracji izotopu ^{14}C w próbce o małej masie należy raczej traktować jako charakterystyczny dla danego miejsca w oponie, a nie partii opon poddawanych pirolizie, czy nawet dla pojedynczej całej opony.



Rys. 4 Porównanie pomiarów izotopu ^{14}C w gumie opon i produktach jej pirolizy dla trzech serii próbek zaznaczonych kolorami czerwonym, zielonym i niebieskim oraz różnych typów próbek (olej pirolityczny, odzyskana sadza i guma) zaznaczonych kształtami zgodnie z legendą. (patrz Fig. 2 w publikacji Gill et al. 2022).

Zawartość węgla pochodzenia biologicznego w badanych próbkach obliczono zgodnie z normą (EN16640 2017) stosując kilka wartości referencyjnych (REF). Biorąc pod uwagę zalecany okres eksploatacji opon (~5 lat), czas utylizacji opon (~10-15 lat) i wykorzystanie kauczuku naturalnego do produkcji opon z soku drzew (żyjących 5-25 lat) przeprowadzono obliczenia dla wartości REF charakterystycznych dla lat 2006, 2011 i 1995 (CIO 2022; Hua et al. 2022) – patrz Tabela 2 (Tabela 4 w omawianej publikacji).

Warto zaznaczyć, że część pomiarów wykonałam w Norwegii podczas 2-tygodniowego stażu badawczego. Staż dał mi możliwość zapoznania się z pracą w renomowanym laboratorium ^{14}C, a także upewnienia się, że protokoły przygotowania próbek i pomiarów stosowane w laboratorium w Gliwicach są zgodne ze światowymi standardami, a także zapoznania się z inną metodą grafityzacji i sprzętem pomiarowym.

Uzyskane wyniki badań mogą być przydatne dla firm zajmujących się pirolizą opon, gdyż pomagają określić zawartość węgla biologicznego w produktach pirolizy, co jest istotne zarówno pod względem ekologicznym, jak i ekonomicznym.

6.2. Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N, Ustrzycka A. (2023). Technical carbon black and green technology. Geochronometria. 50 (1) : 250-256. DOI: 10.2478/geochr-2023-0016.

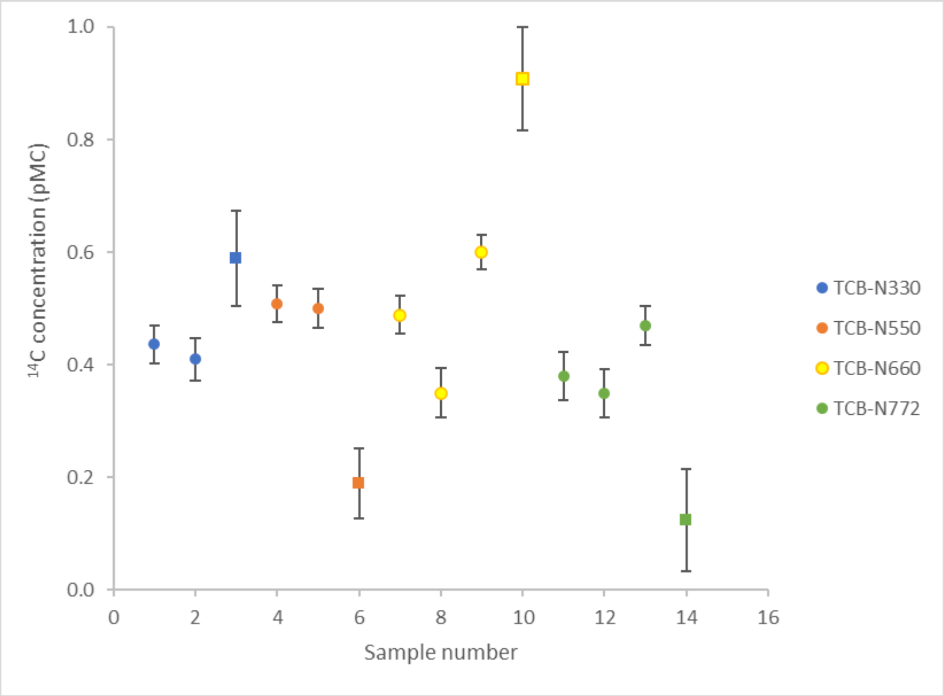
Badania w tym artykule zostały przeprowadzone na próbkach sadzy technicznej. Cztery rodzaje próbek TCB o różnym stopniu rozdrobnienia i powierzchni właściwe zostały przeanalizowane dwiema technikami radiowęglowymi (LSC i AMS) w Laboratorium ^{14}C Spektrometrii Mas w Gliwicach. Dla wyników techniką LSC zastosowałem metodę IRMS do obliczenia poprawki na frakcjonowanie izotopowe. Próbki do badań otrzymano od firmy Contec Inc. Oczekiwano, że próbki będą zawierały większy udział biokomponentów, ale próbki dają bardzo niskie wartości koncentracji ^{14}C pomiędzy 0,124 ± 0,091 pMC i 0,908 ± 0,092 pMC (<1 pMC) dla obu technik. Szczegółowe podsumowanie wyników koncentracji ^{14}C i zawartości węgla biobazowego w próbkach TCB przedstawiono w **Tabeli** 3. Niskie wartości koncentracji ^{14}C w próbkach TCB świadczą o ich produkcji z materiałów kopalnych. Wyniki sugerują potrzebę opracowania przyjaznych dla środowiska alternatyw i zwiększenia wykorzystania materiałów odnawialnych w produkcji TCB.

Tabela 3. Wyniki koncentracji izotopu ^{14}C i zawartość biobazowego węgla w próbkach sadzy technicznej (TCB) - patrz Table 2 w pracy (Gill et al. 2023). Wartości $\delta^{13}C$ values otrzymane z pomiarów IRMS oznaczono (*), a te z pomiarów AMS jako (**).

Lp.	**Nazwa próbki**	**Kod lab.**	**Masa próbki**	**Całkowity węgiel (%)**	**$\delta^{13}C_{VPDB}$ (‰)**	**^{14}C (pMC)**	**Zawartość węgla biobazowego (%)**
1.	TCB-N330	GdS-4543	6,08 g	-	–32,44 ± 0,11*	0,589 ± 0,084	0,589 ± 0,084
2.		GdA-7138.1.1	1,81 mg	99,75 ± 0,93	–29,20**	0,436 ± 0,033	0,436 ± 0,033
3.		GdA-7138.1.2	0,99 mg		–30,60**	0,410 ± 0,038	0,410 ± 0,038
4.	TCB-N550	GdS-4552	4,02 g	-	–30,417 ± 0,072*	0,189 ± 0,063	0,189 ± 0,063
5.		GdA-7137.1.2	0,98 mg	97,5 ± 2,3	–25,70**	0,508 ± 0,033	0,508 ± 0,033
6.		GdA-7137.1.3	2,05 mg		–28,80**	0,500 ± 0,035	0,500 ± 0,035
7.	TCB-N660	GdS-4554	3,91 g	-	–31,82 ± 0,44*	0,908 ± 0,092	0,908 ± 0,092
8.		GdA-7139.1.1	2,19 mg	98,1 ± 1,9	–28,80**	0,489 ± 0,033	0,489 ± 0,033
9.		GdA-7139.1.2	1,90 mg		–36,60**	0,350 ± 0,043	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	0,124 ± 0,091
12.		GdA-7140.1.2	2,03 mg	98,9 ± 1,0	–33,00**	0,380 ± 0,043	0,380 ± 0,043
13.		GdA-7140.1.3	2,03 mg		–32,90**	0,350 ± 0,043	0,350 ± 0,043
14.		GdA-7140.1.4	1,01 mg		–28,90**	0,470 ± 0,035	0,470 ± 0,035

Wyniki pomiarów ^{14}C wszystkich próbek z laboratoriów LSC i AMS przedstawiono na **Rys. 5.** Badanie stanowiło również porównanie wewnątrzlaboratoryjne, wykazując niezawodność stosowania technik LSC i AMS do pomiaru stężeń izotopów ^{14}C w próbkach TCB. Dla próbek TCB-N550 i TCB-N660 zaobserwowano statystyczne niezgodności między wynikami uzyskanymi technikami LSC i AMS. Mogą one wynikać z niejednorodności próbki (na co mogą wskazywać różnice w wartościach $\delta^{13}C$ pomiędzy podpróbkami) i zanieczyszczenia popiołem.

Do obliczenia zawartości biobazowego węgla użyto wartości REF dla roku 2022, czyli 100%. Dlatego też jest ona równa koncentracji izotopu ^{14}C w próbce (CIO 2022; EN16640 2017).



Rys. 5 Porównanie pomiarów izotopów ^{14}C w próbkach sadzy technicznej metodą AMS i LSC. '•' Wyniki pomiarów AMS, '▪' Wyniki pomiarów LSC. (patrz rys. 1 w Gill et al. 2023).

Badania dostarczają cennych informacji na temat zawartości węgla pochodzenia biologicznego w próbkach TCB, podkreślając znaczenie zasobów odnawialnych i wyzwania związane z obecnymi praktykami produkcyjnymi.

6.3. Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N. (2024). Monitoring of modern carbon fraction in disposable packaging. Radiocarbon. First View,1-9. DOI: 10.1017/RDC.2024.35.

Niniejszy artykuł badawczy koncentruje się na określeniu frakcji współczesnego węgla w próbkach opakowań jednorazowych wykonanych z czterech różnych materiałów: papieru, drewna, trzciny cukrowej i otrąb pszennych. Próbki otrzymano od różnych producentów opakowań. Próbki te obejmowały kubki papierowe, talerze papierowe, słomki papierowe, brązowe talerze papierowe, papier do pieczenia, drewniane sztućce, talerze z trzciny cukrowej, talerze z otrąb pszennych, pudełka z trzciny cukrowej i pudełka papierowe. Wybrałam te próbki do badania ze względu na ich codzienne użytkowanie i powszechny recykling.

W tym badaniu próbki analizowano przy użyciu radiowęglowej techniki AMS w Laboratorium ^{14}C i Spektrometrii Mas w Gliwicach. Próbki analizowano w dwóch partiach. W pierwszej partii analizowano małą, losową część, natomiast w drugiej partii próbki analizowano warstwowo, z wyjątkiem próbek papieru do pieczenia i drewnianych sztućców. Wszystkie próbki okazały się być współczesne, ponieważ wykazały koncentrację izotopu ^{14}C powyżej 100 pMC (**Tabela** 4). Próbki wykonane z papieru wykazywały koncentrację ^{14}C między 100 a 112 pMC. Próbki drewnianych sztućców miały najwyższe wartości koncentracji izotopu ^{14}C, w zakresie od nieco ponad 114 do ok. 136,5 pMC. Rozproszone wyniki przypisano faktowi, że sztućce nie zostały wyprodukowane z drewna z tego samego drzewa, a różny wiek drzew zaskutkował różnymi wartościami ^{14}C.

Próbki z trzciny cukrowej i otrąb pszennych miały najniższe wartości stężenia ^{14}C, które są niemal równe obecnej wartości stężenia ^{14}C w atmosferze, co wskazuje, że materiał pochodził z współczesnych upraw roślinnych. Nieco niższe stężenia ^{14}C (ale nadal odpowiadające współczesnym wartościom ^{14}C) stwierdzono w warstwach zewnętrznych w porównaniu z warstwami wewnętrznymi niektórych próbek, co sugeruje, że zostały one pokryte bioplastikiem, aby były wodoodporne.

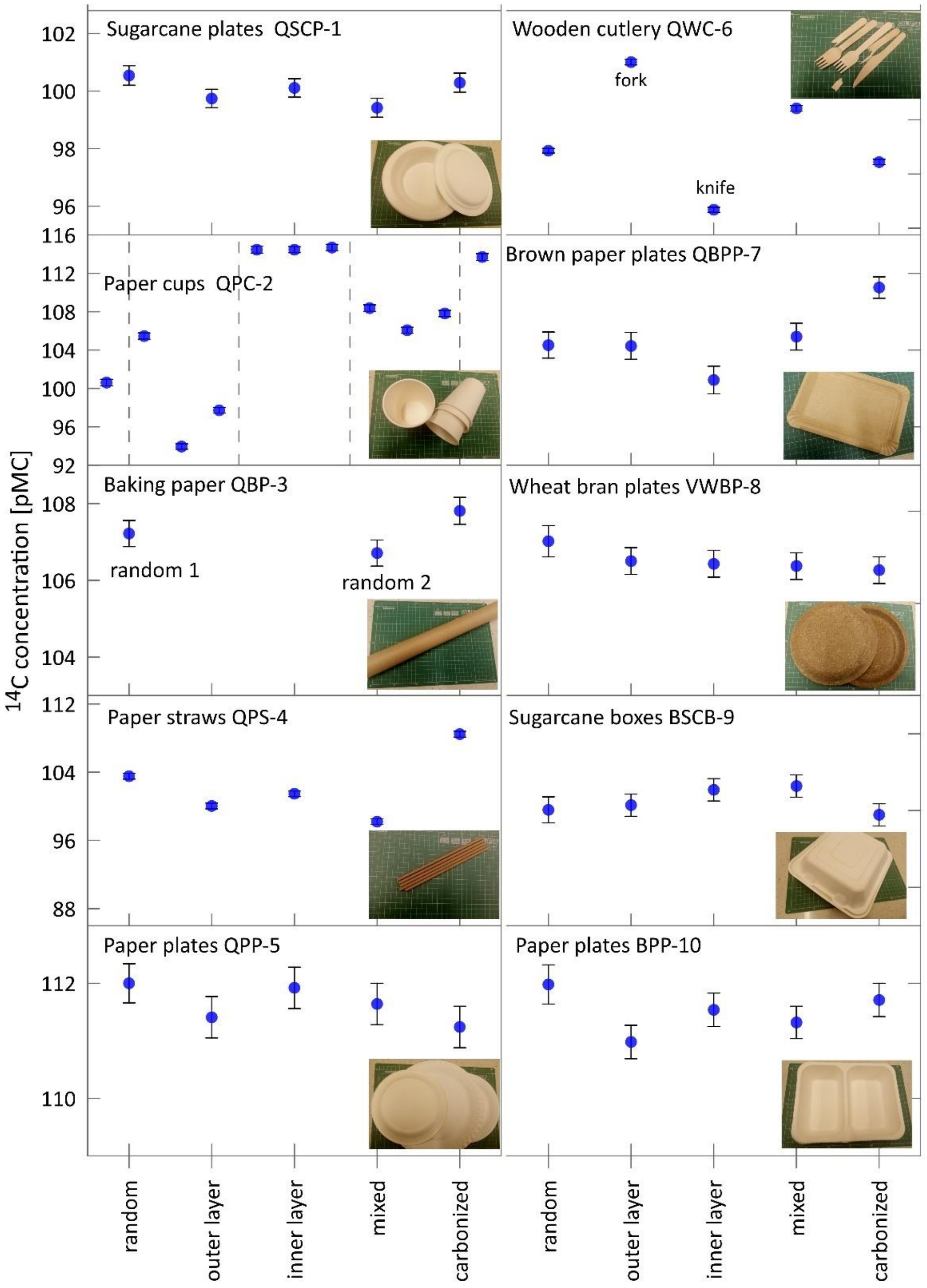
Tabela 4. Koncentracja izotopu ^{14}C i zawartość węgla biobazowego w próbkach opakowań jednorazowych. Cytowane wyniki pomiarów $\delta^{13}C$ zostały zmierzone przy okazji pomiarów AMS. (patrz Suplement do pracy Gill et al. 2024).

Lp.	**Nazwa próbki**	**Materiał**	**Podpróbka**	**Kod lab.**	**Całkowity węgiel (%)**	**^{14}C (pMC)**	**$\delta^{13}C_{AMS}$ ‰**
1.	QSCP-1	Talerze z trzciny cukrowej	Przypadkowa	GdA-6805.1.1	41,74 ± 0,40	100,54 ± 0,34	-18,94
			Warstwa zewnętrzna	GdA-6805.2.1	42,47 ± 0,69	99,74 ± 0,32	-16,00
			Warstwa wewnętrzna	GdA-6805.3.1	42,41 ± 0,64	100,11 ± 0,32	-15,80
			Miks warstw	GdA-6805.4.1	42,53 ± 0,73	99,42 ± 0,33	-17,40
			Zwęglona	GdA-6805.5.1	91,25 ± 1,83	100,29 ± 0,33	-23,50
2.	QPC-2	Kubki papierowe	Przypadkowa	GdA-6806.1.1	42,30 ± 0,42	100,61 ± 0,34	-25,74
			Warstwa zewnętrzna	GdA-6806.2.1	49,24 ± 0,93	105,46 ± 0,33	-21,10
				GdA-6806.2.2		93,95 ± 0,28	-21,5
				GdA-6806.2.4		97,72 ± 0,29	-22,0
			Warstwa wewnętrzna	GdA-6806.3.1	44,14 ± 0,52	114,47 ± 0,36	-25,70

				GdA-6806.3.2		114,47 ± 0,31	-26,4
				GdA-6806.3.3		114,69 ± 0,33	-27,3
			Miks warstw	GdA-6806.4.1	45,31 ± 0,95	108,37 ± 0,34	-22,70
				GdA-6806.4.2		106,07 ± 0,30	-24,1
				GdA-6806.4.3		107,81 ± 0,32	-25,8
			Zwęglona	GdA-6806.5.1	90,82 ± 1,08	113,7 ± 0,36	-32,10
3.	QBP-3	Papier do pieczenia	Przypadkowa 1	GdA-6807.1.1	41,71 ± 0,37	107,22 ± 0,34	-25,51
			Przypadkowa 2	GdA-6807.2.1	42,41 ± 0,64	106,71 ± 0,34	-26,20
			Zwęglona	GdA-6807.3.1	87,38 ± 0,93	107,81 ± 0,35	-31,80
4.	QPS-4	Słomki papierowe	Przypadkowa	GdA-6808.1.1	43,55 ± 0,55	103,53 ± 0,34	-25,74
			Warstwa zewnętrzna	GdA-6808.2.1	44,47 ± 0,73	100,04 ± 0,33	-25,90
			Warstwa wewnętrzna	GdA-6808.3.1	44,28 ± 0,68	101,47 ± 0,33	-26,20
			Miks warstw	GdA-6808.4.1	44,95 ± 0,52	98,21 ± 0,33	-25,50
			Zwęglona	GdA-6808.5.1	87,16 ± 2,65	108,46 ± 0,35	-31,40
5.	QPP-5	Talerze papierowe	Przypadkowa	GdA-6809.1.1	42,12 ± 0,41	112,00 ± 0,34	-25,65
			Warstwa zewnętrzna	GdA-6809.2.1	40,38 ± 0,12	111,41 ± 0,36	-24,60
			Warstwa wewnętrzna	GdA-6809.3.1	44,26 ± 0,37	111,92 ± 0,36	-25,90
			Miks warstw	GdA-6809.4.1	42,98 ± 0,42	111,64 ± 0,36	-25,00
			Zwęglona	GdA-6809.5.1	69,74 ± 2,52	111,24 ± 0,36	-30,60
6.	QWC-6	Sztućce drewniane	Przypadkowa	GdA-6810.1.1	46,02 ± 0,43	123,44 ± 0,34	-26,49
			Widelec	GdA-6810.2.1	47,05 ± 1,19	136,53 ± 0,42	-26,00
			Nóż	GdA-6810.3.1	45,12 ± 3,03	114,72 ± 0,37	-26,20
			moks noża I widelca	GdA-6810.4.1	46,70 ± 1,35	129,7 ± 0,40	-26,20
			Zwęglona	GdA-6810.5.1	92,50 ± 3,43	121,77 ± 0,39	-35,20

7.	QBPP-7	Beżowe talerze papierowe	Przypadkowa	GdA-6811.1.1	44,11 ± 0,25	108,13 ± 0,34	-26,21
			Warstwa zewnętrzna	GdA-6811.2.1	44,15 ± 0,64	108,11 ± 0,35	-25,80
			Warstwa wewnętrzna	GdA-6811.3.1	45,86 ± 0,77	107,22 ± 0,36	-25,20
			Miks warstw	GdA-6811.4.1	44,67 ± 0,19	108,35 ± 0,35	-24,80
			Zwęglona	GdA-6811.5.1	90,90 ± 1,65	109,63 ± 0,28	-31,30
8.	VWBP-8	Talerze z otrąb pszennych	Przypadkowa	GdA-6812.1.1	44,22 ± 1,02	101,35 ± 0,34	-27,84
			Warstwa zewnętrzna	GdA-6812.2.1	43,56 ± 0,63	100,92 ± 0,29	-27,60
			Warstwa wewnętrzna	GdA-6812.3.1	43,39 ± 0,52	100,86 ± 0,29	-27,50
			Miks warstw	GdA-6812.4.1	43,52 ± 0,56	100,81 ± 0,29	-27,00
			Zwęglona	GdA-6812.5.1	65,99 ± 1,25	100,72 ± 0,29	-32,10
9.	BSCB-9	Pudełka z trzciny cukrowej	Przypadkowa	GdA-6813.1.1	43,01 ± 1,01	100,02 ± 0,34	-14,72
			Warstwa zewnętrzna	GdA-6813.2.1	43,26 ± 0,13	100,14 ± 0,29	-13,90
			Warstwa wewnętrzna	GdA-6813.3.1	43,28 ± 0,15	100,54 ± 0,29	-14,50
			Miks warstw	GdA-6813.4.1	43,32 ± 0,12	100,64 ± 0,29	-14,10
			Zwęglona	GdA-6813.5.1	91,31 ± 0,12	99,89 ± 0,29	-21,50
10.	BPP-10	Talerze papierowe	Przypadkowa	GdA-6814.1.1	43,14 ± 0,14	111,98 ± 0,34	-25,62
			Warstwa zewnętrzna	GdA-6814.2.1	44,79 ± 0,30	110,98 ± 0,29	-26,00
			Warstwa wewnętrzna	GdA-6814.3.1	45,10 ± 0,12	111,54 ± 0,29	-25,40
			Miks warstw	GdA-6814.4.1	45,09 ± 0,11	111,32 ± 0,28	-25,10
			Zwęglona	GdA-6814.5.1	94,97 ± 3,77	111,71 ± 0,29	-33,30

Co prawda uzyskane wartości koncentracji ^{14}C wskazały, że wszystkie próbki były wyprodukowane z biomasy, to cztery spośród dziesięciu badanych próbek charakteryzował duży rozrzut wyników. Wskazuje to, że w ich przypadku istnieje potrzeba homogenizacji większej objętości próbki dla uzyskania wyniku reprezentatywnego dla danej partii badanego DPM. Koncentracje ^{14}C wszystkich badanych opakowań, uzyskane techniką AMS przedstawiono na **Rys. 6** oraz w **Tabeli 4**.



Rys. 6 Porównanie pomiarów izotopu ^{14}C w DPM metodą AMS. (patrz rys. 1 w Gill et al. 2024).

Zawartość węgla pochodzenia biologicznego można obliczyć korzystając z równania (1). Ponieważ każda próbka wykazuje koncentrację ^{14}C wyższą niż 100 pMC i jest uważana za współczesną i całkowicie biogeniczną, a konkretny rok pochodzenia materiału był nieznany, wartość REF wynoszącą 100 dla roku 2022 (CIO 2022) została użyta dla wszystkich próbek w celu obliczenia zawartości węgla pochodzenia biologicznego. W związku z tym zawartość węgla pochodzenia biologicznego będzie równa zmierzonym wartościom stężenia ^{14}C.

Badanie podkreśla znaczenie zapewnienia jednorodności próbek dla dokładnych pomiarów. Proste zwęglanie okazało się niewystarczające do homogenizacji; dlatego w przyszłych badaniach zaleca się pełne spalanie w linii próżniowej, aby zapobiec utracie lekkiego węgla i zmniejszyć frakcjonowanie izotopowe. Wyniki wspierają stosowanie materiałów opakowaniowych pochodzenia biologicznego i nadających się do recyklingu w celu zmniejszenia wpływu na środowisko oraz promowania zrównoważonego rozwoju, zgodnie z Europejską Dyrektywą w sprawie Odpadów (UE) 2018/852.

6.4. Gill KA, Michczyńska DJ, Michczyński A. Bio-carbon content determination in disposable packaging by liquid scintillation counting. [w:] Monografia POB6 „Ochrona klimatu i środowiska, nowoczesna energetyka – wybrane zagadnienia", Politechnika Śląska (w druku).

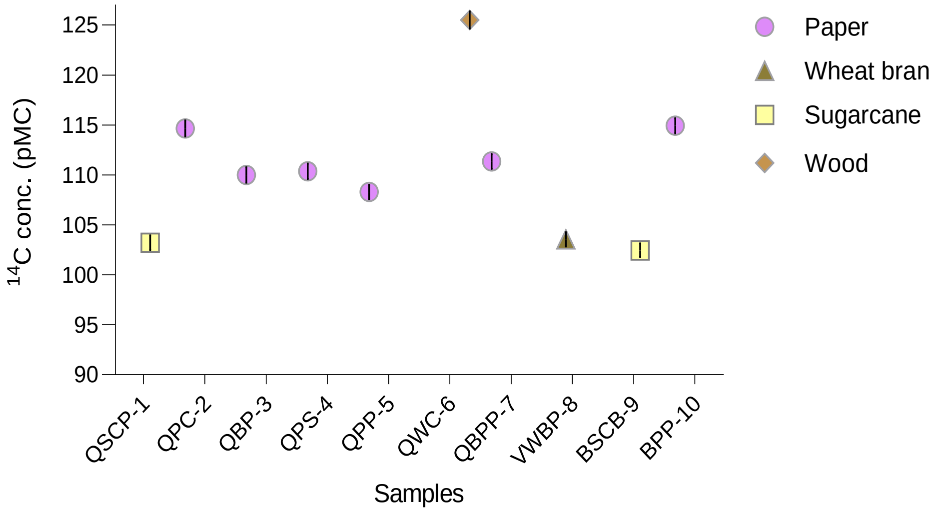
Niniejsza praca badawcza stanowiła kontynuację wcześniejszej pracy (Monitoring of modern carbon fraction in disposable packaging) polegającej na pomiarach ^{14}C w próbkach opakowań jednorazowych z użyciem techniki AMS. W niniejszej pracy koncentrację ^{14}C i ilość biowęgla określono przy użyciu techniki LSC w Laboratorium ^{14}C i Spektrometrii Mas w Gliwicach. Metodę IRMS zastosowano do zmierzenia względnego stosunku stabilnych izotopów węgla (^{13}C/^{12}C) w próbkach, a następnie obliczenia poprawki na frakcjonowanie izotopowe.

Tabela 5. Koncentracja ^{14}C i zawartość węgla biobazowego w próbkach opakowań jednorazowych. Wartości δ^{13}C mierzono metodą IRMS.

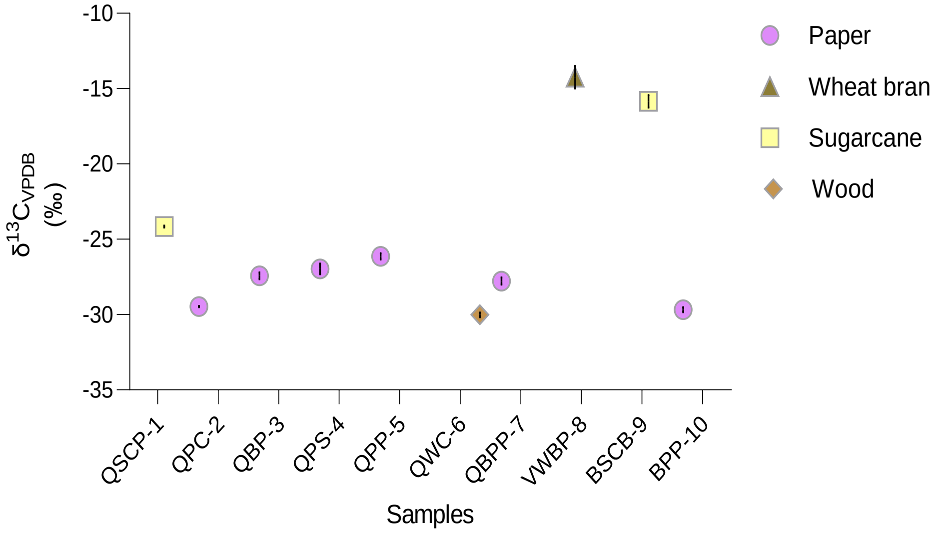
Lp.	**Nazwa i opis próbki**	**Kod lab.**	**^{14}C (pMC)**	**$\delta^{13}C_{VPDB}$ (‰)**	**Zawartość węgla biobazowego (%)**
1	QSCP-1 Talerze z trzciny cukrowej	GdS-4610	103,20 ± 0,74	-24,156 ± 0,059	103,20 ± 0,74
2	QPC-2 Kubki papierowe	GdS-4611	114,65 ± 0,80	-29,465 ± 0,037	114,65 ± 0,80
3	QBP-3 Papier do pieczenia	GdS-4616	109,99 ± 0,78	-27,43 ± 0,23	109,99 ± 0,78
4	QPS-4	GdS-4617	110,36 ± 0,78	-26,97 ± 0,36	110,36 ± 0,78

	Słomki papierowe				
5	QPP-5 Talerze papierowe	GdS-4620	108,30 ± 0,72	-26,14 ± 0,21	108,30 ± 0,72
6	QWC-6 Sztućce drewniane	GdS-4618	125,51 ± 0,87	-30,02 ± 0,16	125,51 ± 0,87
7	QBPP-7 Beżowe talerze papierowe	GdS-4621	111,36 ± 0,74	-27,78 ± 0,24	111,36 ± 0,74
8	VWBP-8 Talerze z otrąb pszennych	GdS-4622	103,56 ± 0,71	-14,24 ± 0,74	103,56 ± 0,71
9	BSCB-9 Pudełka z trzciny cukrowej	GdS-4623	102,45 ± 0,70	-15,84 ± 0,42	102,45 ± 0,70
10	BPP-10 Talerze papierowe	GdS-4624	114,92 ± 0,76	-29,68 ± 0,16	114,92 ± 0,76

Wykresy koncentracji węgla ^{14}C i wartości $\delta^{13}C$ w zależności od rodzaju materiału pokazano na **Rys. 7a** i **7b**, a szczegółowe wyniki podano w **tabeli 5**. Do pomiarów LSC użyto opakowań z tej samej partii, co do pomiarów AMS w przypadku trzeciej publikacji. Pomiary z wykorzystaniem techniki LSC również wskazały na współczesne pochodzenie badanych próbek, określając, że wyprodukowano je z biokomponentów pochodzących z lat 1955-2018. Jednak zaobserwowano, że w niektórych przypadkach występują różnice między pomiarami AMS i LSC, które są większe niż w granicach pojedynczych niepewności.

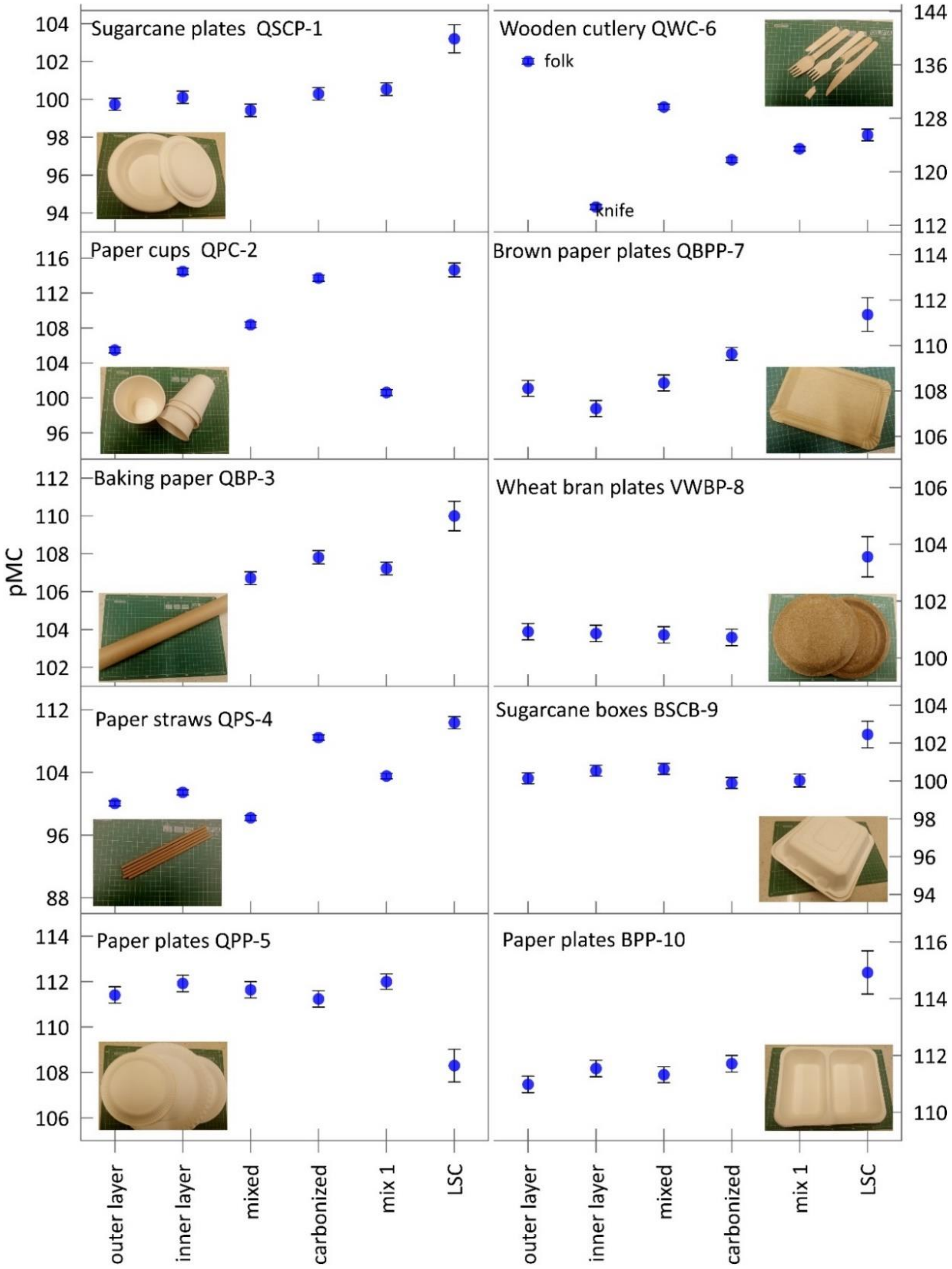


Rys. 7a Wyniki pomiarów koncentracji ^{14}C w różnych opakowaniach metodą LSC.



Rys. 7b Porównanie wartości δ^{13}C dla różnych kategorii materiałów opakowań metodą IRMS.

Rys. 8 przedstawia porównanie pomiarów LSC i AMS. Chociaż różnice między wynikami LSC i AMS są większe niż ich niepewności laboratoryjne, należy wziąć pod uwagę, że w przypadku techniki LSC wykorzystano wiele kawałków danego rodzaju materiału, podczas gdy w przypadku techniki AMS wykorzystano mały kawałek jednego badanego materiału. Norma ASTM D6866 stosowana w Stanach Zjednoczonych (równoważna polskiej i europejskiej normie EN16640) uwzględnia niejednorodność próbek pobranych z dużej partii badanego materiału i zaleca, aby niepewność oznaczania węgla biopochodnego w próbce przyjąć na poziomie 3% (bezwzględnie). Jeśli tę wartość niepewności zastosuje się do wykonanych pomiarów, okaże się, że wyniki LSC i AMS są spójne w granicach pojedynczej niepewności dla 8 przypadków i w granicach podwójnej niepewności dla 2 przypadków.



Rys. 8 Porównanie pomiarów stężenia ^{14}C w DPM metodą LSC i AMS.

7. Podsumowanie wkładu własnego

7.1. Zapoznanie się ze sprzętem i preparatyką próbek

Po zapoznaniu się ze sprzętem, metodami preparatyki próbek oraz procedurami pomiarowymi w Laboratorium ^{14}C i Spektrometrii Mas w Gliwicach, samodzielne przygotowanie próbek do standardowych pomiarów.

7.2. Laboratorium Spektrometrii Mas i ^{14}C w Gliwicach

- Po raz pierwszy wdrożono metodologię radiowęglową LSC w Laboratorium Spektrometrii Mas i ^{14}C w Gliwicach do badań próbek gumy z opon, próbek z pirolizy opon, jednorazowych materiałów papierowych, drewnianych sztućców, papieru z trzciny cukrowej, próbek otrębów pszennych i próbek sadzy technicznej.
- Wdrożenie po raz pierwszy w Laboratorium Spektrometrii Mas ^{14}C w Gliwicach metodyki grafityzacji próbek oleju pirolitycznego oraz odzyskanej sadzy.
- Przygotowanie próbek do oznaczania δ^{13}C metodą IRMS w celu określenia poprawki na frakcjonowanie izotopowe dla wyników koncentracji ^{14}C dla wszystkich kategorii próbek zmierzonych techniką LSC.
- Przygotowywanie różnych warstw próbek opakowań jednorazowych do pomiarów AMS w Laboratorium Spektrometrii Mas i ^{14}C w Gliwicach.

7.3. Prezentowanie uzyskanych wyników na konferencjach i warsztatach

- Udział i prezentacja na tygodniowych warsztatach 18th Freiberg Colloquium of Young Researchers w ramach EURECA-PRO, które odbyły się w czerwcu 2024 r. w Freibergu w Niemczech. Tytuł prezentacji: ‘Recycling of End-of-Life Tires: A Greener Way of Energy and Sustainability’.
- Prezentacja plakatu na 3rd EURECA-PRO Conference on Responsible Consumption and Production, która odbyła się we wrześniu 2023 w Chanii na Krecie w Grecji. Tytuł plakatu: ‘Green Packaging from Renewable Natural Resources – an Example of Disposable Packaging from Pakistan’.
- Prezentacja plakatu podczas 14th International Conference Methods of Absolute Chronology, która odbyłą się w maju 2023 w Gliwicach. Tytuł plakatu: ‘Sadza techniczna i zielone technologie’.

- Wykład podczas uroczystości otwarcia Centrum Metod Izotopowych CEMIZ i VII Warsztatów Metod Datowania im. Profesora Mieczysława F. Pazdura w Gliwicach w grudniu 2022. Tytuł wykładu: ‘Monitoring of biogenic carbon fraction of wasted material’. Wykład wygłoszono dla naukowców, badaczy i studentów w ramach sesji Zastosowania Metod Radiowęglowych.
- Udział i prezentacja na 10th Environmental Protection and Energy Conference w Gliwicach w grudniu 2022. Tytuł prezentacji: ‘Monitoring of biogenic carbon fraction of wasted material’.
- Udział i prezentacja podczas ‘EURECA-PRO PhD Journey - European University on Responsible consumption and production’ we Freibergu w Niemczech, listopad 2022 r. Tytuł prezentacji: ‘Monitoring of biogenic carbon fraction of disposable packaging’.
- Prezentacja plakatu podczas 24th International Radiocarbon Conference w Zurychu, Szwajcaria, wrzesień 2022 r. Tytuł plakatu: ‘Monitoring of biogenic carbon fraction of disposable packaging’.
- Prezentacja plakatu podczas 3rd International Radiocarbon in the Environment Conference, Gliwice, lipiec 2021. Tytuł plakatu: Tests for the content of the ^{14}C isotope in tires and their pyrolysis products’.

7.4. Współpraca

- Współpraca z firmą Contec Inc. z Warszawy w zakresie pobierania próbek gumy z opon i produktów jej pirolizy.
- Nawiązano współpracę z Narodowym Laboratorium Oznaczania Wieku w Trondheim w Norwegii w celu międzylaboratoryjnego porównania wyników koncentracji ^{14}C w próbkach opon i produktach ich pirolizy.
- Przygotowanie i analiza próbek gumy z opon oraz produktów jej pirolizy Narodowym Laboratorium Oznaczania Wieku w Trondheim w Norwegii.
- Nawiązano współpracę z Centro Nacional de Aceleradores (CNA) Uniwersytetu w Sewilli, Sewilla, Hiszpania, w celu międzylaboratoryjnego porównania pomiarów próbek opakowań jednorazowych.
- Przygotowanie i analiza próbek opakowań jednorazowych w CNA na Uniwersytecie w Sewilli.

7.5. Staże

- Miesięczny staż w ramach programu NAWA STER w jednym z najlepszych uniwersytetów i laboratoriów, Centro Nacional de Aceleradores (CNA), University of Sevilla, Sewilla, Hiszpania. Projekt nr 32/014/NWD21/2001-04. Październik-listopad 2023.
- Dwutygodniowy staż w jednym z najlepszych uniwersytetów i laboratoriów na świecie, National Laboratory for Age Determination, Norwegian University of Science and Technology, Trondheim, Norwegia. Numer projektu: POWR.03.03.00-IP.08-00-P13/18 'PROM- Międzynarodowa wymiana stypendialna doktorantów i pracowników naukowych. Wrzesień 2021 r.

7.6. Publikacje

Główny autor serii czterech monotematycznych publikacji, odpowiedzialny za:

- Przygotowanie próbek
- Syntezę benzenu do pomiarów LSC w Laboratorium ^{14}C i Spektrometrii Mas w Gliwicach.
- Przygotowanie próbek i grafityzację próbek do pomiarów AMS w Laboratorium ^{14}C i Spektrometrii Mas w Gliwicach.
- Prasowanie grafitu i przygotowanie katod do pomiarów AMS.
- Analizę wyników uzyskanych za pomocą MICADAS w Laboratorium ^{14}C i Spektrometrii Mas w Gliwicach.
- Przygotowanie próbek do pomiarów IRMS w Laboratorium ^{14}C i Spektrometrii Mas w Gliwicach.
- Analizę danych i interpretację wyników.
- Przygotowanie wykresów, tabel oraz rycin do manuskryptu.
- Pisanie manuskryptów.
- Nawiązanie współpracy z laboratoriami w Trondheim i Sewilli w celu porównania międzylaboratoryjnego próbek.

Poniżej znajduje się lista publikacji:

- Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N, Kłusek M, Końska K, Wróblewski K, Nadeau M-J, Seiler M. (2022). Study of bio-based carbon fractions in tires and their pyrolysis products. Radiocarbon. 64(6):1457-1469. DOI: 10.1017/RDC.2022.88.

- Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N, Ustrzycka A. (2023). Technical carbon black and green technology. Geochronometria. 50(1):250-256. DOI: 10.2478/geochr-2023-0016.
- Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N. (2024). Monitoring of modern carbon fraction in disposable packaging. Radiocarbon, First View. DOI: 10.1017/RDC.2024.35.
- Gill KA, Michczyńska DJ, Michczyński A. Bio-carbon content determination in disposable packaging by liquid scintillation counting. [w:] Monografia POB6 'Ochrona klimatu i środowiska, nowoczesna energetyka – wybrane zagadnienia', Politechnika Śląska (w druku).

7.7. Publikacje we współpracy międzynarodowej (niezwiązane z doktoratem)

- Riaz K, Gill KA, Muhammad S, Ali FI, Javed MN, Wasim AA, Henderson W, Bari A, Hashmi IA. (2024). 2-Mercaptobenzoic acid-based ionic liquids for metal extraction from water without additional chelating agent. Journal of Sulfur Chemistry. DOI: https://doi.org/10.1080/17415993.2024.2336618.
- Ali Z, Sajid M, Raza N, Sohail Y, Hayat M, Manzoor S, Shakeel N, Gill KA, Ifseisi AA, Ansari MZ. (2023). Study of modified biomass of Gossypium hirsutum as heavy metal biosorbent. Arabian Journal of Chemistry. DOI: 10.1016/j.arabjc.2023.105332.
- Raza H, Ashraf A, Shamim R, Manzoor S, Sohail Y, Khan MI, Raza N, Shakeel N, Gill KA, El-Marghany A, Aftab S. (2023). Synthesis and characterization of Hyaluronic Acid (HA) modified polymeric composite for effective treatment of wound healing by transdermal drug delivery system (TDDS). Scientific Reports. DOI: 10.1038/s41598-023-40593-9.
- Intisar A, Ramzan A, Hafeez S, Hussain N, Irfan M, Shakeel N, Gill KA, Iqbal A, Janczarek M, Jesionowski T. (2023). Adsorptive and photocatalytic degradation potential of porous polymeric materials for removal of pesticides, pharmaceuticals, and dyes-based emerging contaminants from water. Chemosphere. DOI: 10.1016/j.chemosphere.2023.139203.
- Muhammad S, Javed MN, Gill KA, Ali FI, Henderson W, Bari A, Musharraf SG, Baig JA, Hashmi IA. (2022). Selective extraction of heavy metals (Fe, Co, Ni) from their aqueous mixtures by task-specific salicylate functionalized imidazolium based ionic liquid. Journal of Cleaner Production. DOI: 10.1016/j.jclepro.2022.131119.

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Publications and Co-Author Statements

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List of Publications:

1. Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N, Kłusek M, Końska K, Wróblewski K, Nadeau M-J, Seiler M. (2022). Study of bio-based carbon fractions in tires and their pyrolysis products. Radiocarbon. 64(6):1457-1469. DOI: 10.1017/RDC.2022.88.
2. Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N, Ustrzycka A. (2023). Technical carbon black and green technology. Geochronometria. 50(1):250-256. DOI: 10.2478/geochr-2023-0016.
3. Gill KA, Michczyńska DJ, Michczyński A, Piotrowska N. (2024). Monitoring of modern carbon fraction in disposable packaging. Radiocarbon, First View DOI: 10.1017/RDC.2024.35.
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STUDY OF BIO-BASED CARBON FRACTIONS IN TIRES AND THEIR PYROLYSIS PRODUCTS

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ABSTRACT. Wasted tires are the great source of fuel and valuable components but could be a cause of environmental and land pollution. This study shows the detailed method for the determination of radiocarbon isotope (^{14}C) concentration in tires and their pyrolysis products. Samples are taken from truck and passenger car tires in the form of shredded rubber, pyrolysis oil and recovered carbon black. Liquid scintillation counting (LSC) and accelerator mass spectrometry (AMS) techniques were used for the investigation at Gliwice Radiocarbon and Mass Spectrometry Laboratory, and National Laboratory for Age Determination, Trondheim, Norway. The results are in good agreement. Radiocarbon concentration of the rubber varies significantly because of its complex structure and composition within the tires. The ^{14}C concentration values were found to be higher in pyrolytic oil compared to rubber, and greater in truck tires rather than car tires.

KEYWORDS: bio-based carbon content, ^{14}C isotope concentration, pyrolysis, radiocarbon methods, waste tires.

INTRODUCTION

Worldwide, the number of scrapped tires that are produced is estimated to be 1 billion per year, and around 250 million car and truck tires are scrapped each year in Europe, which corresponds to 3 million tonnes by weight (Kyari et al. 2005). Any kind of recycling may be extensively limited because of the irreversible chemical structure of the elastomer. Rubber is the main chemically cross-linking polymer of tires, which is insoluble and non-fusible, and therefore, cannot be remolded into other shapes without its severe degradation. Therefore, these scrap tires represent an important environmental problem that needs to be solved (Kaminsky and Mennerich 2001; Olazar et al. 2008).

Two European Commission directives were attempts by the European Union to control the management of tires. The first one is the European Commission's End-of-Life Vehicles Directives 2000 (Directive 2000), which specified the separate collection of tires from vehicle dismantlers and boosts the recycling of tires. The second one is Waste Landfill Directives 1999 (Directive 1999) that banned land filling with tires. Consequently, these two Directives had an impact on waste tires management throughout the European Union (Kyari et al. 2005). Directive (EU) 2018/850 which amends Directive 1999/31/EC (Directive 2018) introduced limits on landfilling from 2030 for all wastes that is suitable for recycling. In the European Union, the disposal rate of tires is close to 100% directed towards overcoming landfill problems (Sebola et al. 2018), approximately 58% of the tires are recycled and around 36% are used as energy recovery (ETRma 2021).

There are many ways to effectively deal with waste tires, which are based on two approaches. The first one involves the energy production by combustion or incineration of the tire; the other

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*Corresponding author. Email: komal.aziz@polsl.pl one is recovery of their components either by hydrogenation, liquefaction, or by the pyrolysis (Olazar et al. 2008).

Tires are a complex mixture of different materials not only rubber (ca. 40%) but also carbon black and silica (ca. 25%), metal (steel cord ca. 13% in passenger car tires and ca. 21% in truck tires) and, moreover, small organic and inorganic components such as oils and resins (6%), chemicals for vulcanization (6%), and anti-ageing agents. The composition of the tire depends on its type and, to a lesser extent, the producer (since each producer uses its own proportions). The main source of biogenic carbon in tires is the natural rubber and, to a much smaller degree, there are oils, stearic acid, rayon, natural fibers, and cotton in old tires. The ratio of natural to synthetic rubber is different in passenger car tires compared to truck tires. (Pehlken and Essadiqi 2005) reported that for passenger car tires it is 14% to 27%, and, for trucks, it is 27% to 14%. The U.S. Tire Manufacturers Association reported 19% to 24% for passenger car tires and, 34% to 11% for truck tires (APSnet. 2021). It is noteworthy that tires have a layered structure, different layers may contain various types of rubber. Starting from the tire part that is closest to the road surface and moving towards the center of the tire, the following elements can be distinguished (Continental 2022): (1) tread—natural and synthetic rubber, (2) jointless cap plies—nylon, embedded in rubber, (3) steel cord for belt plies—high-strength steel cords, (4) textile cord ply—rubberized artificial silk or polyester, (5) inner liner—butyl rubber, (6) sidewall—natural rubber, (7) bead reinforcement—nylon or aramid, (8) bead apex—synthetic rubber, and (9) bead core—steel wire embedded in rubber.

For the recycling of tires, there are many alternatives, like retreading, reclaiming, incineration grinding, etc., that have been used but all of them have many drawbacks. Pyrolysis is, currently, gaining new attention for tire recycling purposes; it can be considered as an unconventional method but it seems to be the most appropriate for complex materials, such as tires that cannot be remolded (De Marco Rodriguez et al. 2001). Tires are used as fuels and their effective application decreases the consumption of fossil fuels and energy costs. In this way the emission of further fossil-based carbon dioxide is also reduced, since the tires contain carbon from fossils themselves. The composition and combustion properties of tires are almost equivalent or even much improved compared to coal because of the presence of about 60–70% carbon, 6–7% hydrogen, and high calorific values (Rodríguez et al. 2017). As a result, the combustion of tires supplies heat and, in addition, this help to reduce the additional release of CO_2 and SO_x into the atmosphere (Krajcar Bronić et al. 2015; Rodríguez et al. 2017).

The use of biogenic fuels can prevent additional CO_2 emission into the atmosphere. Until 2010, the required biogenic content in fuel was 5.75% and, according to EU directives 2009/28/EC, it was increased to 10% in 2020. Therefore, it is important to determine the biogenic content in wasted tires in order to check whether the materials and their recycling are eco-friendly. For this purpose, several methods have been used, but the radiocarbon method is well-known to provide a perfect means for distinguishing between carbonaceous material of biological and fossil origin (Krajcar Bronić et al. 2017; Oinonen et al. 2010). The dispersal of ^{14}C on Earth from the atmosphere is governed by the carbon cycle. The radiocarbon method has a wide range of applications, due to this large scale labelling (Hajdas et al. 2021). The half-life of the ^{14}C isotope is 5730 years. Therefore, after about 10 half-lives, there is almost no ^{14}C isotope in the sample. By detecting the ratio of $^{14}C/^{12}C$ isotopes in a sample, the radiocarbon analysis can distinguish between the bio and fossil-based carbon (Haverly et al. 2019). Fossil carbon does not contain ^{14}C anymore, while biomass material contains a certain amount (depending on the $^{14}CO_2$ value in the atmosphere at the time of uptake). In this paper, we

Table 1 Characteristics of the standards for determining the content of biocarbon in brief.

Standard	Application	Short description
International standards: American Society for Testing Materials (ASTM) and International Standardization Organization (ISO)		
ASTM D6866	All bio-based products	Bio-based carbon defined as a fraction of the total organic carbon in a sample. ISO 16620-2 is equivalent to this standard
ISO 16620-2	Plastics Part 2: Determination of bio-based carbon content	Bio-based carbon content defined as a fraction of total carbon. Note: it corresponds to “biogenic carbon content” defined in ASTM D6866.
ISO 19984	Rubber and rubber products	Bio-based carbon content defined as in the ISO 16620-2.
European standards (EN)		
EN 16640	All bio-based products	Bio-based carbon content defined as in the ISO 16620-2.
EN 16575	Vocabulary. All bio-based products	Bio-based carbon content defined as in the ISO 16620-2.

investigate the concentration of ^{14}C isotope in waste tire pyrolysis products (such as rubber, oil, and recovered carbon black) to determine the bio-based carbon content. This investigation is conducted using liquid scintillation counting (LSC) and accelerator mass spectrometry (AMS) methodologies at Gliwice Radiocarbon and Mass Spectrometry Laboratory and National Laboratory for Age Determination, Trondheim, Norway. The purpose of these studies was not only a quantification of the biocarbon content in the tires, but also the testing of different measurement techniques. The research with tires from Poland was inspired by the tests performed on end-of-life tires (ELT) in France and Spain. The reported radiocarbon concentration in a passenger car, truck and, agro tires was 27–29 pMC, 50–51 pMC and, ca. 30 pMC, respectively (Rodríguez et al. 2017).

There are numerous standards that concern bio-based carbon content, which are founded on radiocarbon analysis that are applicable to different kinds of samples. Table 1 presents only those standards that could be applied to the bio-based carbon content found in the investigated samples.

SAMPLES

The tire rubber and the pyrolysis products, i.e., the recovered carbon black and pyrolysis oil, analyzed in this project are obtained from Contec Inc. in Warsaw, who deal with tire pyrolysis. The subsequent stages of the technological process applied by Contec Inc. can be described as follows:

- In its first stage, the cord and steel wire are separated from the tires;
- In the mechanical grinding process, different sizes of rubber particles are obtained: rubber dust, finely ground rubber, granules, or grits;
- The raw material prepared using this method is s placed into the reactor via a feeder. In order to remove air from the feeder, the load is purged with nitrogen at the end of the feeder;

Table 2 Detailed composition of the samples. Rubber samples were taken immediately after the mechanical grinding process, rCB samples were collected after their exit from the reactor at a dedicated sampling point, oil samples were obtained from the oil tanks after passing through a filtration and sedimentation separation system.

No.	Sample production cycle	Sample code	Type of sample	Description
1	1st cycle	CONT-1	Pyrolytic oil	Unknown mixture of truck and passenger car tires
2	2nd cycle	PCO-2	Pyrolytic oil	100% passenger car tires
3		rCB-2	Recovered carbon black	100% passenger car tires
4		CR-2	Rubber	100% passenger car tires
5	3rd cycle	TCO-3	Pyrolytic oil	70% truck and 30% passenger car tires
6		rCB-3	Recovered carbon black	70% truck and 30% passenger car tires
7		CR-3	Rubber	70% truck and 30% passenger car tires

- In the reactor, with the shape of a horizontal and stationary cylinder, the material is heated by a heating medium (a mixture of molten salts) with an auger, an anaerobic, and at low pressure. As a result, low-temperature hydrocarbon decomposition of the organic compounds occurs and pyrolysis gas and rCB (recovered carbon black) is produced. The temperature of the reactor is kept at 500°C;
- Approximately 62% (by weight) of the feedstock is decomposed and received as pyrolysis gas, which is then cooled and liquefied, resulting in an oil fraction and non-condensable pyrolysis gas. The remaining mass leaves the reactor in solid form as rCB. A special system collects the recovered carbon black (rCB) from the reactor outlet. The temperature of the rCB is lowered using a conveyor cooling jacket;
- At the recovered carbon black processing station, the material is subjected to magnetic separation with a yield of steel by the amount of 4% of the total weight of the wire (96% is recovered in the first stage); and
- Pyrolytic gas that is collected from the reactor is directed to the process gas separation node. The fuel gas produced from the non-condensing part of the pyrolysis gas is then burned and the heat is used in the process.

Samples were delivered by Contec Inc. in three cycles with different proportions of truck and passenger car tires. Samples coming from the production cycle are numbered respectively 1, 2, and 3. The detailed samples categories are described in Table 2.

METHODS

The radiocarbon method was used because of its reliability when determining biogenic carbon fraction in materials. Benzene-LSC (GdS=GADAM Scintillation), EA-graphite-AMS (GdA=GADAM AMS), and quratz tubes CuO-graphite-AMS (TRa= Trondheim Radiocarbon AMS), are used to measure the ^{14}C concentrations in LSC Gliwice Radiocarbon Laboratory, AMS Gliwice Radiocarbon Laboratory, and National

Table 3 Details of the pretreatment samples.

	Pyrolytic oil		Recovered carbon black		Rubber	
Lab ID	Method	Subsample size	Method	Subsample size	Method	Subsample size
GdS	Benzene-LSC	~7 g	Benzene-LSC	~5 g	Benzene-LSC	5–6 g
GdA	EA-graphite AMS	~2 mg	EA-graphite AMS	~2 mg	—	—
TRa	Quartz tubes CuO	~2–4 mg	EA-graphite AMS	1 mg	EA-graphite AMS	1 mg

Laboratory for Age Determination, Trondheim, Norway, respectively. Total carbon content in samples was analyzed using VarioMicroCube Elemental Analyzer in Gliwice Radiocarbon Laboratory with different masses in various experiments, mean of these values together with the uncertainties are mentioned in the Table 4. Different pretreatment methods are used for three different laboratories. The type of method and the mass of samples are mentioned in Table 3.

On the basis of these results the variability of the ^{14}C concentration within the different batches of tires was analyzed. The differences in the content of the ^{14}C isotope in the passenger and truck tires were also examined.

Benzene Preparation for LSC

For the LSC measurements in the Gliwice Radiocarbon Laboratory, the samples were converted into benzene (Pazdur et al. 2003). Benzene was prepared by use of carbide synthesis, hydrolysis, and trimerization of acetylene for each sample. Metal reactors, in which the carbide synthesis was carried out, were mechanically cleaned before their use, rinsed with deionized water, and heated in a muffle furnace at a temperature of 700°C. Removable glass elements from the benzene production line were carefully washed with deionized water and dried at 80°C. All the chemicals were analytically pure, and the samples from Contec Inc. were not subjected to chemical pretreatment. Only the rubber samples were rinsed with boiling water.

Recovered carbon black was directly reacted with lithium to obtain Li_2C_2. Rubber, as well as the pyrolytic oil samples in the first step were placed into the internal reactor and then evaporated in hot lithium positioned at the bottom of the outer reactor. In the second step, the remainder of each sample from the internal reactor was transferred to the external reactor, then the reaction of synthesizing lithium carbide with a new batch of lithium was repeated. For all the samples, a reaction temperature of 700°C was used. The next steps involve hydrolysis (in which the product is acetylene C_2H_2) and trimerization (the product is benzene C_6H_6). The whole scheme for the preparation of benzene is presented in Figure 1. Benzene was dried by removal of water molecules with sodium metal and atmospheric radon was removed by keeping the benzene sample in a refrigerator for a month, since the half-life of radon is 3.8 days. For the removal of radon, we also followed a re-sublimation process for the two samples (CONT-1 and PCO-2), (Tudyka et al. 2021) and involves a mixture of dry ice with ethanol (–78°C) or ice with salt (–21°C).

Table 4 Results on the concentration of ^{14}C for each sample. Also reported χ^2 values for the samples of pyrolytic oil and recovered carbon black. The critical χ^2values for four measurements = 11.34, and for three measurements = 9.21 (with confidence level, $\alpha = 0.01$). Biocarbon content was calculated according to the standard (EN16640 2017) for three different REF values.

No.	Sample	Lab code	^{14}C concentration (pMC)	χ^2	Total carbon TC (%)	Biobased carbon content (%) REF$_{2011}$	REF$_{2006}$	REF$_{1995}$
1	CONT-1	GdS-4257	41.95 ± 0.37	*8.48*	84.8 ± 0.50	40.6 ± 0.36	39.8 ± 0.35	37.5 ± 0.33
	Pyrolytic Oil	GdS-4258	43.43 ± 0.38			42.0 ± 0.37	41.2 ± 0.36	38.8 ± 0.34
		GdA-6611	42.64 ± 0.23			41.3 ± 0.22	40.5 ± 0.22	38.1 ± 0.21
		TRa-16675	42.86 ± 0.18			41.5 ± 0.17	40.7 ± 0.17	38.3 ± 0.16
2	PCO-2	GdS-4320	41.30 ± 0.47	*20.83*	83.5 ± 2.5	40.0 ± 0.45	39.2 ± 0.45	36.9 ± 0.42
	Pyrolytic Oil	GdS-4365	43.90 ± 0.44	*without GdS-4320:*		42.5 ± 0.43	41.7 ± 0.42	39.2 ± 0.39
		GdA-6612	43.49 ± 0.23	*1.65*		42.1 ± 0.22	41.3 ± 0.22	38.8 ± 0.21
		TRa-16676	43.35 ± 0.11			42.0 ± 0.11	41.1 ± 0.10	38.7 ± 0.10
3	TCO-3	GdS-4373	50.35 ± 0.49	*7.46*	74.9 ± 7.2	48.7 ± 0.47	47.8 ± 0.46	45.0 ± 0.44
	Pyrolytic Oil	GdA-6613	49.76 ± 0.24			48.2 ± 0.23	47.2 ± 0.23	44.4 ± 0.21
		TRa-16677	50.47 ± 0.10			48.9 ± 0.10	47.9 ± 0.09	45.1 ± 0.09
4	rCB-2	GdS-4327	5.08 ± 0.18	*0,07*	71.7 ± 3.5	4.9 ± 0.17	4.8 ± 0.17	4.5 ± 0.16
	Recovered Carbon	GdA-6615	5.14 ± 0.11			5.0 ± 0.11	4.9 ± 0.10	4.6 ± 0.10
	Black	TRa-16679	5.17 ± 0.08			5.0 ± 0.08	4.9 ± 0.08	4.6 ± 0.07
5	rCB-3	GdS-4394	6.89 ± 0.18	*19.31*	78.9 ± 1.5	6.7 ± 0.17	6.5 ± 0.17	6.2 ± 0.16
	Recovered Carbon	GdA-6616	6.92 ± 0.12	*without TRa-16680*		6.7 ± 0.12	6.6 ± 0.11	6.2 ± 0.11
	Black	TRa-16680	6.29 ± 0.18	*0.02*		6.1 ± 0.17	6.0 ± 0.17	5.6 ± 0.16
6	CR-2	GdS-4337	15.54 ± 0.23	χ^2- N/A	83.7 ± 2.8	14.8 ± 0.22	14.5 ± 0.22	13.7 ± 0.21
	Rubber	TRa-16682a	33.02 ± 0.13			32.0 ± 0.13	31.3 ± 0.12	29.5 ± 0.12
		TRa-16682b	34.71 ± 0.10	range:		33.6 ± 0.10	32.9 ± 0.09	31.0 ± 0.09
		TRa-16682c	22.21 ± 0.10	15.54–34.71		21.5 ± 0.10	21.1 ± 0.09	19.8 ± 0.09

Table 4 (*Continued*)

No.	Sample	Lab code	^{14}C concentration (pMC)	χ^2	Total carbon TC (%)	Biobased carbon content (%) REF$_{2011}$	REF$_{2006}$	REF$_{1995}$
7	CR-3 Rubber	GdS-4339	13.59 ± 0.23	χ^2- N/A	74.9 ± 2.3	12.9 ± 0.22	12.7 ± 0.22	11.9 ± 0.21
		GdS-4380	25.12 ± 0.22			24.2 ± 0.21	23.7 ± 0.21	22.3 ± 0.20
		GdS-4383	20.89 ± 0.32	range:		19.9 ± 0.31	19.5 ± 0.30	18.4 ± 0.29
		GdS-4370	12.31 ± 0.21	12.31–41.86		11.7 ± 0.20	11.5 ± 0.20	10.8 ± 0.19
		GdS-4375	20.24 ± 0.31			19.4 ± 0.30	19.0 ± 0.29	17.8 ± 0.28
		GdS-4374	13.29 ± 0.25			12.6 ± 0.24	12.4 ± 0.24	11.7 ± 0.22
		TRa-16683a	18.25 ± 0.10			17.7 ± 0.10	17.3 ± 0.09	16.3 ± 0.09
		TRa-16683b	41.86 ± 0.15			40.5 ± 0.15	39.7 ± 0.14	37.4 ± 0.13
		TRa-16683c	14.57 ± 0.11			14.1 ± 0.11	13.8 ± 0.10	13.0 ± 0.10
		TRa-16683d	18.93 ± 0.07			18.3 ± 0.07	18.0 ± 0.07	16.9 ± 0.06
		TRa-16683e	22.68 ± 0.10			22.0 ± 0.10	21.5 ± 0.09	20.3 ± 0.09
		TRa-16683f	21.68 ± 0.09			21.0 ± 0.09	20.6 ± 0.09	19.4 ± 0.08
		TRa-16683g	14.85 ± 0.08			14.4 ± 0.08	14.1 ± 0.08	13.3 ± 0.07

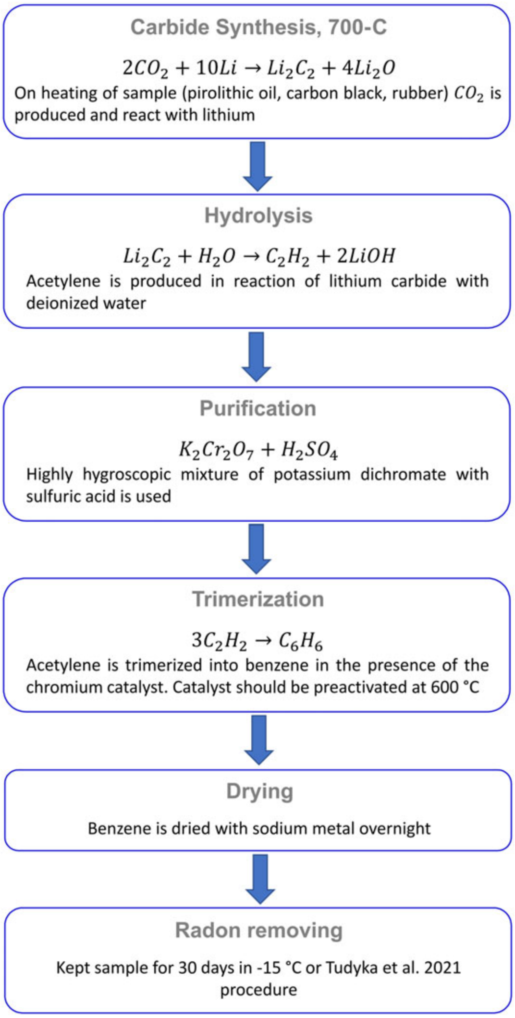

Figure 1 Benzene preparation methodology for LSC measurements in Gliwice.

The isotope ratio mass spectrometry (IRMS) is applied when calculating the standardized isotope fractionation correction and it was used for the measurement of the relative ratio of the stable carbon isotopes ($^{13}C/^{12}C$) in the samples. The catalytic combustion of the benzene samples was performed to produce CO_2 with CuO. ANU-sucrose, NBS-22(oil), and IAEA-C3 standards were used for the determination of $\delta^{13}C$ of the samples. LSC measurements were done by a Quantulus 1220^{TM} spectrometer, butyl-PBD was used as scintillation agent with benzene (Pawlyta et al. 1997).

Graphite Preparation for AMS

AMS measurements were done in two laboratories. All the samples were combusted, graphitized and measured at the National Laboratory for Age Determination, Trondheim, Norway. In addition, the pyrolytic oil and recovered carbon black samples were graphitized in the Gliwice Radiocarbon Laboratory and the ^{14}C isotope concentration measurements were made at Poznan Radiocarbon Laboratory.

Graphite Preparation at Gliwice Radiocarbon Laboratory

For the AMS measurements, the graphite was prepared from samples by combustion in an Elemental Analyzer VarioMicroCube (Elementar) coupled to an AGE-3 graphitization system by IonPlus AG (Wacker et al. 2010). The radiocarbon backgrounds, and the graphite preparation method are described in (Piotrowska 2013). The method is used for the preparation of graphite targets from common samples (plant fossils, charcoal, peat, shells, and bones) and we used the same method for the oil and recovered carbon black. Tin boats were used for the solid samples, and tin capsules for the liquid samples were sealed by a special sealing press. The graphite was analyzed for its ^{14}C concentration by Poznan Radiocarbon Laboratory (Goslar et al. 2004).

Graphite Preparation at the National Laboratory for Age Determination, Trondheim, Norway

Prior to graphitization of the CO_2, the CO_2 was obtained by certain combustion methods (which are different for the solids compared to the liquids). Solid samples of rubber and recovered carbon black were combusted and reduced in an Elemental Analyzer. The oil samples were frozen and then sealed with CuO in quartz tubes. After combustion in a muffle oven, the CO_2 was reduced in the Fe-Zn manual reduction system. Graphite preparation methods, with backgrounds, are clearly explained in (Seiler et al. 2019).

The determination of the bio-carbon content was based on the standard (EN16640 2017) Bio-based products–Bio-based carbon content–Determination of the bio-based carbon content using the radiocarbon method (Polish standard PN-EN 16640).

RESULTS

The results of the ^{14}C isotope concentration in the pyrolysis products of the tires and their obtained by LSC and AMS measurements from both laboratories, alongside the bio-based carbon content according to (EN16640 2017), are listed in Table 4. The ^{14}C concentration in samples is reported as the percent modern carbon (pMC), according to (Stuiver and Polach 1977). Biocarbon content calculations require the adoption of the reference (REF) value, which amounts to an estimation of the age of the biochar in the tires that are subjected to pyrolysis. It should be noted, however, that this required an assumption on the age of the recycled tires. The REF value of 100% bio-based carbon in the determined year was used and expressed in pMC,based on the data reported by University of Groningen (Palstra and Meijer 2018; CIO 2022). The recommended service life of tires is around 5 years, but tires are usually 10–15 years old on disposal. Account for the natural rubber used in the production of tires should also be considered, which originates from the sap of trees that are 5–25 years old. Therefore, the biocarbon content calculations were performed using REF values for 2006 = 105.4, 2011 = 103.3 (CIO 2022), and 1995 = 112 (Hua et al. 2021)

DISCUSSION

Figure 2 presents comparisons of the results. The measurement results for the pyrolytic oil and recovered carbon black, using two techniques and in three different laboratories, display show good agreement (see the χ^2 values in Table 4). These are homogenized by the pyrolysis process and should therefore provide reproducible results. We calculated the bio-based content using

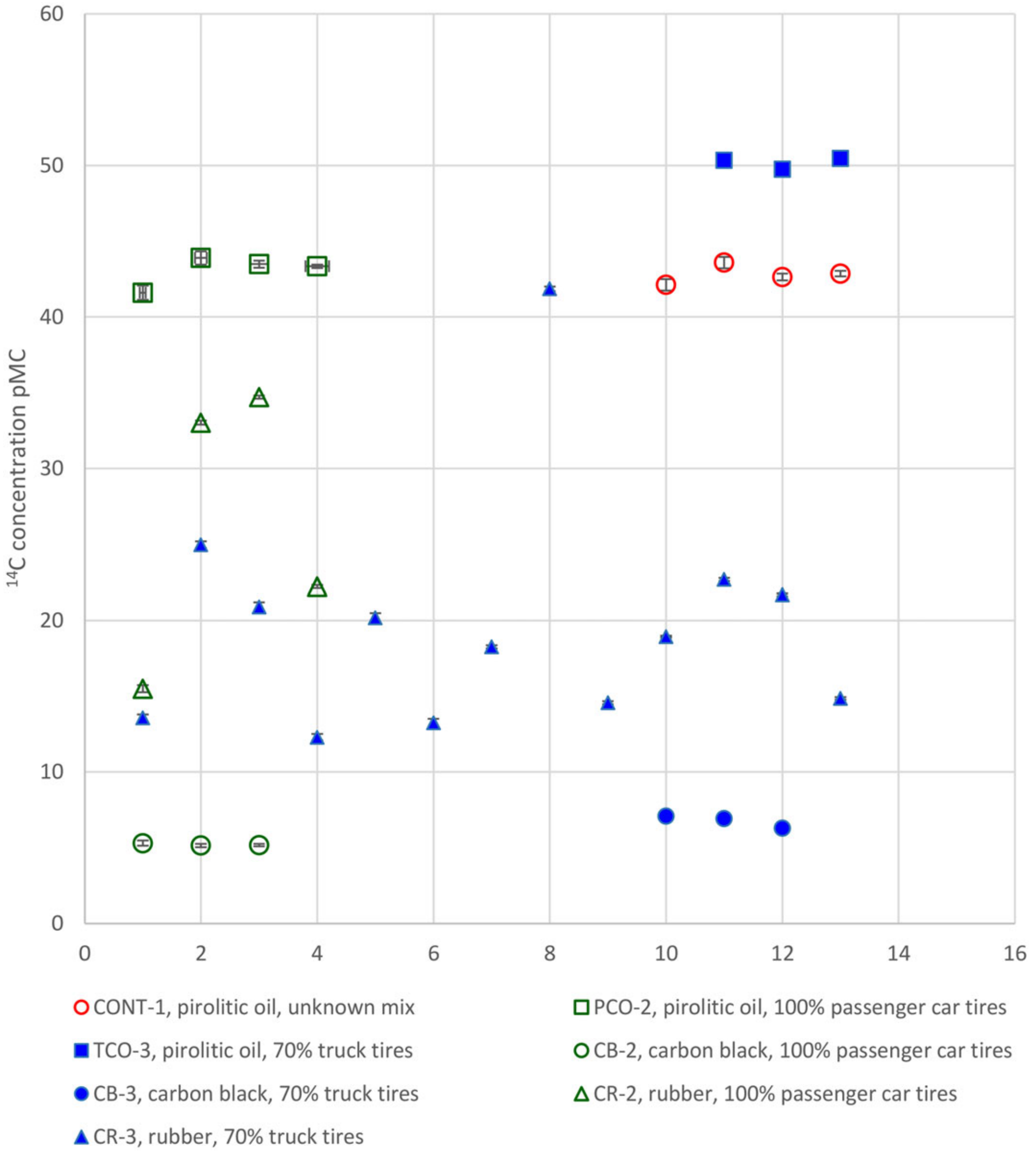

Figure 2 Comparison of the ^{14}C isotope measurements. Measurement uncertainties are smaller than the size of the symbols used.

different REF values and receive some differences. For each sample, the differences in the biobased carbon content values calculated for different REF values are proportional to the measured ^{14}C isotope.

Pyrolytic oil from trucks, passenger cars and an unknown mixture of tires give ^{14}C concentrations of 50.19 ± 0.22 pMC, 43.01 ± 0.58 pMC and 42.72 ± 0.31 pMC, respectively. Recovered carbon black (rCB) from car tires give ^{14}C concentrations of 5.13 ± 0.03 pMC, while from truck tires give ^{14}C concentrations of 6.70 ± 0.21 pMC, it is, thus, clear that some of the modern carbon from natural rubber converts to recovered carbon black in the pyrolysis process. Obviously, most of the organics that results from the decomposition of these rubbers is found in the pyrolysis oil and its non-condensing fraction, i.e., pyro gas. Nevertheless, some of the carbon molecules remain in the rCB structure as shown by the BET results (not presented in this work).

The radiocarbon concentration of the pyrolytic oil and rCB for truck tire samples are higher than those for passenger car tire since the natural rubber composition is higher in truck tires (APSnet. 2021). Pyrolytic oil samples have greater ^{14}C concentrations when compared to rubber samples. In the oil, only the hydrocarbon parts (or such an essence) are present.

The measurement results for the rubber samples are extensively scattered and require a special discussion. For passenger car tires the ^{14}C concentrations were found in the range 15.54–34.71 pMC, and for truck tires in the range 12.31–41.86 pMC. Most of these results are lower than the values obtained in the studies of (Rodríguez et al. 2017): 27–29 pMC for passenger car tires and 50–51 pMC for truck tires. The authors also examined different pieces of rubber from the same sample, by AMS measurements at the National Laboratory for Age Determination, Trondheim, Norway, and obtained variations in the results of the ^{14}C concentrations ranging from 22–34 pMC in passenger car tires and 14–42 pMC in truck tires.

Small cut pieces of the rubber samples were provided for this study, as a result of a mechanical grinding process and mixing. LSC results are the average of the multiple pieces, while AMS results should be considered as point values. We expected that LSC results would converge, while the AMS results could be scattered. However, a significant spread occurs for both measurement techniques. This created suspicion that the obtained samples were not representative samples. Indeed, the co-authors from Contec Inc. explained that the rubber samples that were sent for testing mainly originated from the tread area, which explains the much lower concentration of ^{14}C in the rubber compared to the pyrolysis oil. To obtain a representative sample, it would be necessary, for example, to sieve a finer fraction from a large batch of material. Since this action is not necessary from the point-of-view of the company dealing with tire pyrolysis, any tests can be performed for the selected type of tire by collecting sub-samples by yourself.

CONCLUSION

Three different sample pretreatment methods and two different ^{14}C measurement methods were applied in the study. All the methods seem to be suitable and reliable for the investigation of the pyrolysis products from tires, as the measurements were performed in various laboratories and using different techniques that showed a compliance of the results. Only in the case of the measurements for the shredded tire rubber was it found that the provided samples were not representative of the entire batch of tires, which were subjected to the pyrolysis. In subsequent tests, it is planned to perform the measurements for rubber from different parts of a given type of tire. Further tests are required to determine the optimal REF value for calculating the biocarbon fraction in the type of samples that were tested.

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‘Study of bio-based carbon fractions in tires and their pyrolysis products’, 2022. Radiocarbon Vol 64, Nr 6, 2022, p 1457–1469.
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My participation consisted of;

- Selection of organic solvent for Pretreatment of rubber samples for measurements.
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- Sample preparation and graphitization of samples for AMS measurements at the Gliwice ^{14}C and Mass Spectrometry Laboratory.
- Preparation of samples for IRMS measurements at the Gliwice ^{14}C and Mass Spectrometry Laboratory
- Established cooperation with the National Laboratory for Age Determination, Norwegian University of Technology, Trondheim, Norway.
- Preparation and analysis of samples at the National Laboratory for Age Determination, Trondheim, Norway.
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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 CO_2 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 ^{14}C isotope concentration. Liquid scintillation counting (LSC) and accelerator mass spectrometry (AMS) radiocarbon techniques were employed for measuring the ^{14}C isotope concentration, while isotope ratio mass spectrometry (IRMS) corrected standardised isotope fractionation correction. The investigation revealed that the examined TCB samples contain extremely low ^{14}C concentrations, measuring <1 per cent modern carbon (pMC). This finding raises concerns regarding potential environmental ramifications.

Key words:

technical carbon black, ^{14}C 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 tine 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 CO_2 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 $^{14}C/^{12}C$ isotope ratio within the sample (Haverly *et al*., 2019; Gill *et al*., 2022). Fossil materials do not contain ^{14}C isotope after about 50,000 years, as the half-life of the ^{14}C 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 ^{14}C 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 ^{14}C 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 ^{14}C 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 δ^{13}C by IRMS

Quantulus 1220^{TM} 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 ($K_2Cr_2O_7$) 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 δ^{13}C (^{13}C/^{12}C). About 5 µL 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; ~2 µg, [Ustrzycka, 2020]) were directly combusted with CuO under same conditions. Standard δ^{13}C values of NBS-22 (oil; $\delta^{13}C$ = -30.03‰ (IAEA-NBS), IAEA-CH-6 (formerly, Sucrose ANU; $\delta^{13}C = -10.45$‰; [IAEA-CH-6]) and WZS (lake sediment, $\delta^{13}C$ = -5.06‰, [Ustrzycka, 2020]) were used for the correction of δ^{13}C measurements. The IsoPrime 100 spectrometer with a continuous flow regime was used for the δ^{13}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 δ^{13}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 δ^{13}C according to Stuiver and Polach (1977) equation:

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

where

A_S – measured ^{14}C concentration

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

The uncertainty for δ^{13}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}C/^{12}C and ^{13}C/^{12}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 CO_2 gas. This gas was subsequently graphitised using AGE in the presence of H_2 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 ^{14}C concentrations were measured by MICADAS accelerator mass spectrometer (Synal *et al*., 2007) and BATS software was used for the ^{14}C 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 ^{14}C 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**. ^{14}C concentrations are reported in per cent modern carbon (pMC) (Stuiver and Polach, 1977). δ^{13}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 ^{14}C 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 ^{14}C isotope concentrations of TCB samples, categorised into four different grades, were measured by LSC and AMS spectrometry. **Table 2** presents the ^{14}C concentration obtained via LSC and AMS, the corresponding δ^{13}C values, and bio-based carbon content calculated in accordance with (EN16640, 2017) for each sample. **Fig. 1** provides a graphical representation of the ^{14}C concentration values along with their associated uncertainty.

Table 2. *The ^{14}C isotope concentrations are mentioned in pMC for the four different classification categories of TCB samples. δ^{13}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 (%)	δ^{13}C$_{VPDB}$ (‰)	^{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 0.28	0.436 ± 0.033
3.		GdA-7138.1.2	0.99 mg		−30.60**	0.410 ± 0.038		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 0.03	0.508 ± 0.033
6.		GdA-7137.1.3	2.05 mg		−28.80**	0.500 ± 0.035		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 24.17	0.489 ± 0.033
9.		GdA-7139.1.2	1.90 mg		−36.60**	0.350 ± 0.043		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 5.58	0.380 ± 0.043
13.		GdA-7140.1.3	2.03 mg		−32.90**	0.350 ± 0.043		0.350 ± 0.043
14.		GdA-7140.1.4	1.01 mg		−28.90**	0.470 ± 0.035		0.470 ± 0.035

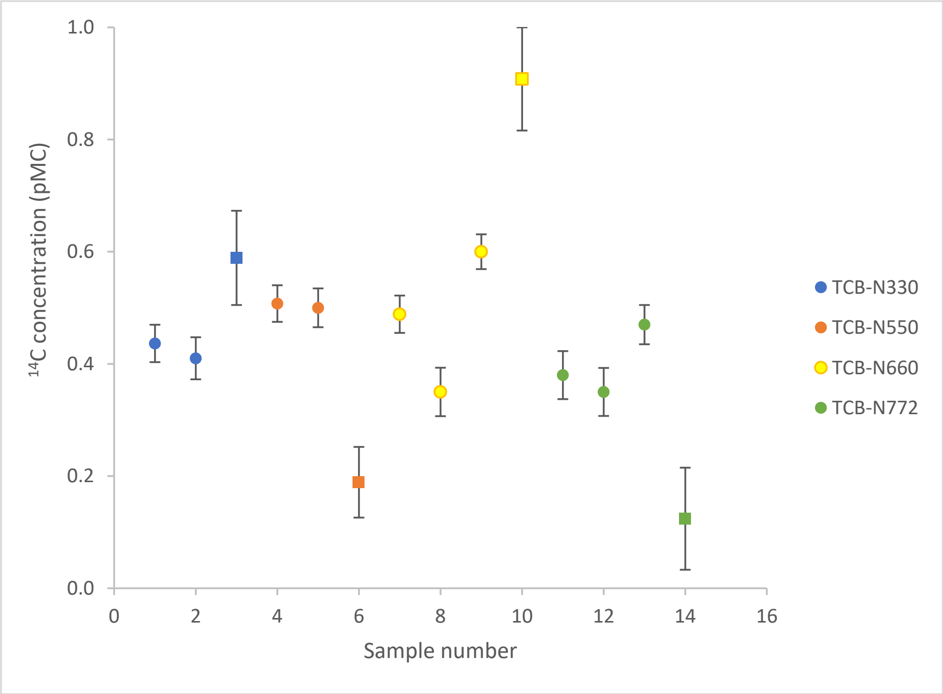

Fig 1. *Comparison between AMS and LSC ^{14}C isotope measurements. '•' AMS measurement results, '▪' LSC measurement results.*

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 δ^{13}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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Co-authorship statement

I hereby declare that my contribution to the paper:

‘Technical carbon black and green technology’, (2023). Geochronometria 50(1):250-256. DOI: 10.2478/geochr-2023-0016.
Authors: Komal Aziz Gill, Danuta J. Michczyńska, Adam Michczyński, Natalia Piotrowska, Alicja Ustrzycka.
My participation consisted of;

- Synthesis of benzene for LSC measurements at the Gliwice ^{14}C and Mass Spectrometry Laboratory.
- Sample preparation and graphitization of samples for AMS measurements at the Gliwice ^{14}C and Mass Spectrometry Laboratory.
- Pressing of graphite and cathode tube preparation for AMS measurements.
- Analysis of samples by MICADAS at Gliwice ^{14}C and Mass Spectrometry Laboratory.
- Preparation of samples for IRMS measurements at the Gliwice ^{14}C and Mass Spectrometry Laboratory.
- Data analysis and interpretation of results.
- Preparation of figures, graphs, and tables of the manuscript.
- Manuscript writing.

My participation in the work was 55%.

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MONITORING OF MODERN CARBON FRACTION IN DISPOSABLE PACKAGING

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ABSTRACT. Radiocarbon (^{14}C) methodology was used to investigate the presence of biocarbon in different bio-based disposable packaging products. Packaging waste contributes to a municipal solid waste, which is increasing environmental concerns and resulting in the enhancement of EU regulations that aim to reduce packaging waste. The ^{14}C amount in samples reflects how much of the biocarbon has been used. In this study, the concentration of ^{14}C was determined in commonly used types of disposable packaging, such as cups, plates, straws, cutlery, and baking paper. Samples were made of materials such as paper, wheat bran, sugarcane, and wood. The mean concentration of the ^{14}C isotope, measured by the accelerator mass spectrometry (AMS) technique, is greater than 100 pMC in all tested samples, indicating that the samples are modern. The relatively high ^{14}C concentration values in the waterproof layer of the sample indicate that bioplastic, rather than plastic, was used in its production. The highest ^{14}C isotope concentration values were measured for samples that used the oldest biomass (wood and paper), and the lowest for products from current crops (sugarcane and wheat bran), which is consistent with the trend of changes in ^{14}C concentration in the biosphere. The study also addresses the problem of heterogeneity and representativeness of subsamples.

KEYWORDS: AMS, ^{14}C concentration, disposable packaging, environmental protection.

INTRODUCTION

Disposable packaging materials (DPMs) are typically single use items and commonly used for enclosing or protecting food products during storage, sale, delivery and for the regular use mainly at restaurants (Tallentire and Steubing 2020). For packaging applications, a variety of materials are used, comprising plastic, bioplastics, paper or pulp-based products, metal, wood, glass, and a variety of composites made from multiple elements(Davis and Song 2006). In Europe, from 2009 to 2019, paper and cardboard (32.3 million tons in 2019) were the main packaging material followed by plastic (15.4 million tons in 2019) and glass (15.2 million tons in 2019) (Eurostate 2022). The aim of this paper closely falls within the European waste Directive (EU) 2018/852, which intends to harmonize national measures for packaging and waste management policies in order to prevent environmental impacts (Davis and Song 2006; Directive2018/852(EU)).

Reuse and recycling are the two most crucial techniques in the development of the circular economy (Di Foggia and Beccarello 2022). In Europe the recovery in total waste treatment increased significantly from 46% in 2004 to 60% in 2020 (39% for recycling, 15% for backfilling, and 6% for energy recovery), whereas the disposal in total waste treatment decreased from 54% in 2004 to 45% in 2020 (Eurostate 2020).

Regarding energy use, greenhouse gas emissions, and their contribution to an increase in trash, plastic food packaging has an impact on the environment (Jeżewska-Zychowicz and Jeznach 2015). Biodegradable polymers have become the topic of current research due to their potential biodegradability and nontoxicity, but still there is a long way to go in order to overcome the global plastic pollution through biodegradable plastics (Shen et al. 2020). Growing emphasis has been paid in recent years, especially in European (EU) members, to the development of biodegradable packaging materials made from renewable natural resources (mainly from corn

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*Corresponding author. Email: komal.aziz@polsl.pl and sugarcane) in order to contribute for sustainable development and also can reduce environmental impact upon disposal, if managed properly (Davis and Song 2006).

Green packaging is the one of the main aspects of green logistics activity, which aimed to minimize resource utilization and environmental pollution. Green packaging is being developed to make packages that are lightweight, recyclable, reusable, and biodegradable and to prohibit the use of non-ecological products (Zhang and Zhao 2012).

By using agro-industrial plants products and by-products to produce biodegradable packaging can be turned into goods with a high added value while using less conventional nonrenewable packaging. The pandemic scenario increased the food packaging market (Barone et al. 2021).

According to Directive2018/852(EU), bio-based recyclable packaging and compostable biodegradable packaging could be a way to promote renewable sources for packaging production. DPMs prepared from sugarcane or paper can be a source of valuable resources and can overcome the plastic problem. Sugarcane plates are made from renewable sugarcane pulp so the compositing takeaway packaging minimizes the greenhouse gas emissions and improves the soil quality (APSnet 2022). Production or recycling of DPMs in industries causes CO_2 emission, which is seen as a global hazardous because of its properties like greenhouse gas. CO_2 emission can be reduce by the use of renewable (biogenic/bio-based) resources (Rodin et al. 2020). New paper production from waste paper requires less energy and emits less amount of greenhouse gases than producing the same amount of paper from virgin materials, thus the recycling of waste paper could be beneficial to the environment (Merrild et al. 2008). Recycling of about 1 ton of paper can save slightly more than 2 tons of wood. The energy information administration that 40% reduction in energy paper is produced by paper recycling verses paper production by unrecycled pulp, while the Bureau of International Recycling (BIR) claims a 64% reduction (WKPD). Radiocarbon analysis can distinguish between fossil and bio-based carbon by detecting $^{14}C/^{12}C$ isotope ratio in the sample (Haverly et al. 2019; Gill et al. 2022). After about 50,000 years, samples do not contain ^{14}C isotope, as its half-life is 5700 years (Kutschera 2019). Several methods have been used to determine the biocomponent content in different materials, but the radiocarbon method is known to distinguish between carbonaceous material of fossil and biological origin (Krajcar Bronić et al. 2017). Many studies have been done to check the renewability in different kinds of materials in terms of biogenic carbon determination. Stable carbon isotope ratio measurements have proved to be an acceptable method of distinguishing between C_4 plant plastics and petroleum plastics (Santos et al. 2019). Quarta et al. (2013) determined biobased content in plastic (polyester resins). Ploykrathok and Chanyotha (2017), Santos et al. (2019), and Telloli et al. (2019) measured biogenic carbon fraction in plastic materials, and Huels et al. (2017) and Pigorsch et al. (2022) analyzed paper materials.

In this paper ^{14}C isotope concentration in DPMs was monitored, to make sure if indeed, the materials contain some concentration of biogenic carbon to cause a green effect in recycling.

MATERIALS AND METHODS

In this study we examine 10 different kinds of DPMs, which include paper, wood, sugarcane, and wheat bran type materials. Samples were collected from different packaging production companies in order to investigate different varieties of typical packages: paper cups, plates, straws, food boxes, and also baking paper, wheat bran plates, and wooden cutlery.

^{14}C Analysis by AMS

All of the samples were prepared and analyzed at Gliwice ^{14}C and Mass Spectrometry Laboratory in Institute of Physics – Centre for Science and Education, Division of Geochronology and Environment Isotopes. A VarioMicroCube Elemental Analyzer (EA) coupled to an AGE-3 graphitization system by IonPlus AG was used for the determination of total carbon content in samples and for graphitization, as it is the efficient, fast and convenient sample preparations for radiocarbon measurement (Wacker et al. 2010b). Tin boat capsules were used with ~4 mg of sample. CO_2 is produced by the sample combustion with the Elemental Analyzer, and Automated Graphitization Equipment (AGE) produces graphite by reducing this CO_2 with H_2 on iron powder. The obtained graphite is pressed into the target holders (cathodes), two times at a pressure of 4 bar for the proper pressing. A Cu pin is used to seal the graphite.

MICADAS accelerator mass spectrometer was used for ^{14}C concentration measurements (Synal et al. 2007) and BATS software for calculations of ^{14}C concentration (Wacker et al. 2010a). Oxalic Acid II was used as standard. Anthracite, phthalic acid, and fossil fuel were used as backgrounds.

For DPMs, no chemical pretreatments were used for AMS measurements. Only small masses of the tested material are used for AMS measurements, which in the case of samples with complex structures may be a source of non-representative results if only one subsample is selected for measurements. Therefore, two batches of samples were analyzed. In the first batch, a small subsample was taken from a random place in the case of each sample, whereas in the second batch, different layers of samples were tested. Other than baking paper and wooden cutlery, all DPMs samples are taken as outer layer, inner layer, mixture of outer and inner layer. In case of paper cup samples, three AMS measurements were performed for each of the tested layers to check the consistency of the results. The measurements for the thin outer layer which potentially contains plastic seemed particularly interesting. In the case of baking paper, only two types of subsamples were analyzed, including the original form (two random subsamples) and carbonized form. In the case of wooden cutlery, samples from the fork, knife, their mixture, were analyzed. We examine the different subsamples to test whether plastic or bioplastic was used to make the waterproof layer.

Due to the different weight ratio of the possible plastic or bioplastic layer to the inner layer, depending on the sampling site, small samples may not be representative. In order to avoid the influence of different mass proportions of the waterproof layer and the inner paper layer, and its effect on the results of ^{14}C concentration measurements, samples need to be homogenized. Mechanical homogenization of samples can be time-consuming. The best solution would be to combust a larger mass of the sample in vacuum conditions in the presence of reagents (Ag and CuO), and then convert the resulting CO_2 into graphite. This is typical solution used for small samples in AMS laboratories. Due to the lack of dedicated vacuum line for combustion larger masses of samples, it was decided to test applicability of carbonization with limited oxygen available. Carbonization of large mass (~24 g) of samples was carried out in a metal reactor with a small hole in the lid, minimizing the access of air, in a muffle furnace at a temperature of 700°C for 7 to 10 minutes and grinded into powder form after cooling.

RESULTS

^{14}C concentration results of DPMs from AMS laboratory (with lab code GdA) are listed in supplement. ^{14}C concentration in samples is reported as percent modern carbon (pMC), according to (Stuiver and Polach 1977). Total carbon concentration data is obtained by combusting samples in EA with different masses in three experiments, mean of the three values are provided in Supplementary Material.

DISCUSSION

Determination of ^{14}C concentration in disposable packaging was conducted. Supplement represents the total carbon content, ^{14}C concentrations, and δ^{13}C of each sample. It should be noted that the given δ^{13}C values are values measured using the AMS method and therefore also take into account the isotopic fractionation that takes place during the measurement. Figure 1 presents the graphical view of pMC values with uncertainties.

All samples gave a mean of ^{14}C concentration higher than 100 pMC, which means the samples are modern thus the recycling of such samples will be a green recycling. All DPMs from paper material gives ^{14}C concentration between 100–112 pMC in random subsamples, corresponding to the ^{14}C concentration in packaging paper reported in (Huels et al. 2017; Pigorsch et al. 2022).

It is well visible that for samples of sugarcane plates (QSCP-1) and boxes (BSCB-9), paper plates (QPP-5, QBPP-7 and BPP-10), backing paper (QBP-3), and wheat bran plates (VWBP-8), the ^{14}C concentration values for small subsamples are consistent within a single or double uncertainty. This agreement is confirmed by the results of the chi-square test presented in Table 1, and for these samples, the weighted mean, as a measure of the ^{14}C isotope content in the whole tested sample, can be calculated. The remaining three tested packages (QPC-2, QPS-4, QWC-6) are characterized by a large dispersion of results. This can be a result of the non-homogeneity of the samples. We selected one of these samples, namely QPC-2, to test which layer was causing the scatter. For that sample, we performed three measurements for the outer layer, the inner layer and the mixed outer and inner layers (see Supplement).

The sample QPC-2 was a paper cup, coated with waterproof material in outer most part (both sides) with a thin inner layer. The ^{14}C concentration from the outer layer are varied between 93.95 ± 0.28 and 105.46 ± 0.33 pMC showing non-homogeneity of this layer. These values are much lower than for the inner layer. Similar, lowered pMC values in plastic packaging materials are reported in Ploykrathok and Chanyotha 2017; Santos et al. 2019; Telloli et al. 2019.

Measurements for the inner layer are highly consistent, and weighted mean for this layer is equal to 114.54 ± 0.19 pMC. The mixture of outer and inner layer subsamples gives ^{14}C concentration from the value range 106.07 ± 0.30 - 108.37 ± 0.34 pMC, which is consistent with the average value calculated from results of outer and inner layers (106.79 ± 0.32 pMC). The sample with lab code of GdA-6806.1.1 (random sample) yielded ^{14}C concentration of 100.61 ± 0.34 pMC. As random sample was taken directly without selecting any layer so the decreased ^{14}C concentration could be the result of the bigger proportion of outer to the inner layer in it. The carbonized sample yielded 113.7 ± 0.36 pMC. This value is between the extremes obtained for the small subsamples. It may therefore represent a realistic average value for the concentration of ^{14}C in the total sample.

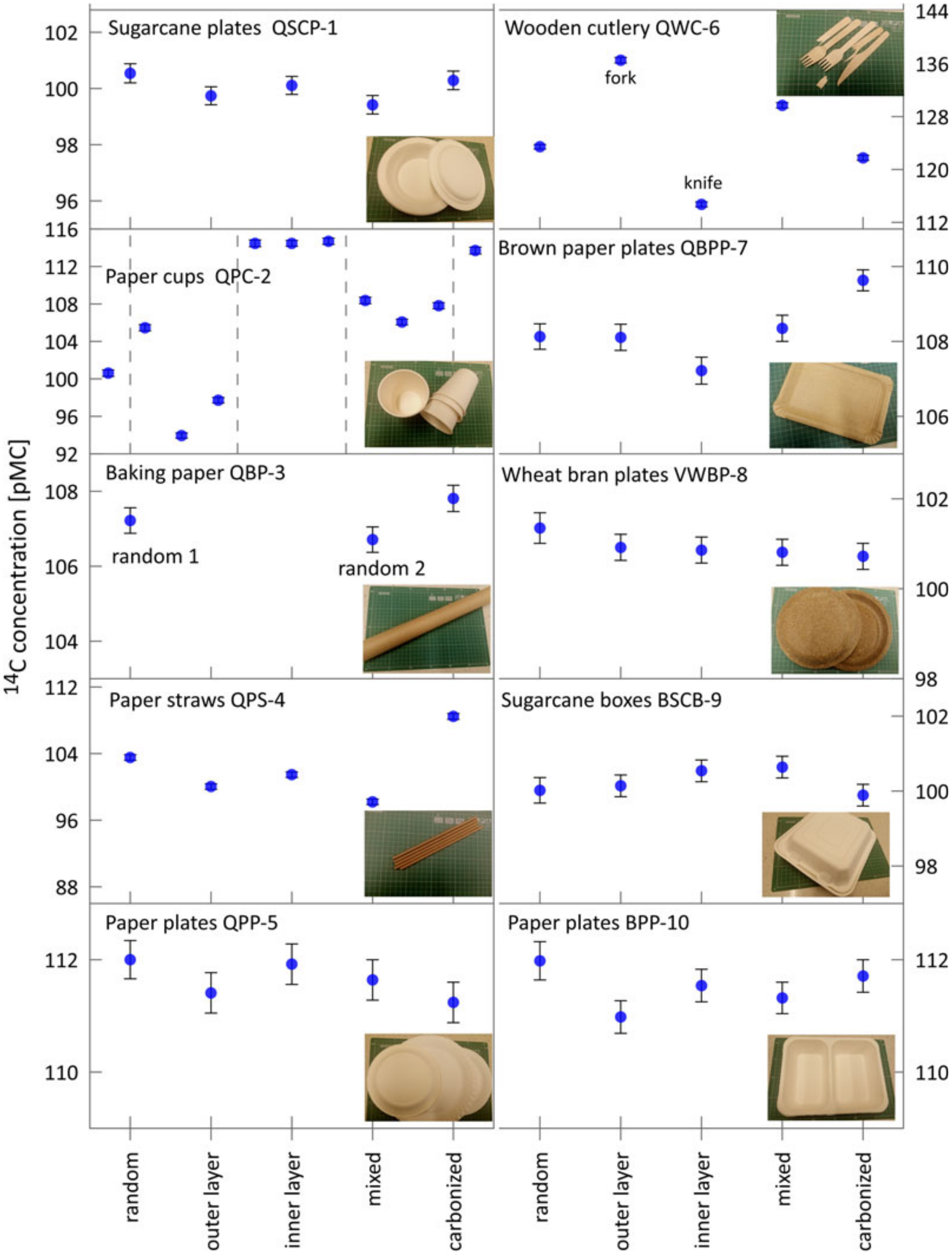

Figure 1 Comparison of the ^{14}C isotope measurements (see Supplementary Material).

For sample QPS-4, there is visible high variation in ^{14}C concentrations for all subsamples. The sample was from the paper straws, composed of thick waterproof layer and a thin paper layer. The ^{14}C concentration from the outer layer is 100.04 ± 0.33 pMC which is little lower than the

Table 1 Results of testing the consistency of received results. A) testing the consistency of small subsamples (random, inner layer, outer layer, and mixed) results by meaning of chi-square (χ^2) test. Critical χ^2 values for confidence level $\alpha = 0.05$ and for 4 measurements = 7.81, for 3 measurements = 5.99, and for 2 measurements = 3.84. For consistent results weighted mean was calculated. B) testing the consistency of weighted mean for small subsamples and result for large (carbonized) sample by meaning of t-test.

Sample code	Statistical consistency of small samples results, test χ^2	Weighted mean with uncertainty for small samples [pMC]	Statistical consistency of the weighted mean for small subsamples and results for carbonized sample, t-test
QSCP-1	$6.27 < 7.81$ → consistent results	99.94 ± 0.16	0.95 → consistent results
QPC-2:	Inconsistent results	NA; range 93.95–114.69	NA
QPC-2: Random	NA	NA	NA
QPC-2: Outer layer	Inconsistent results	NA; range 93.95–105.46	NA
QPC-2: Inner layer	$0.29 < 5.99$ → consistent results	114.54 ± 0.19	2.07 → consistent results
QPC-2: Mixed layer	Inconsistent results	NA; range 106.07–108.37	NA
QBP-3	$1.13 < 3.84$ → consistent results	106.97 ± 0.24	1.99 → consistent results
QPS-4	Inconsistent results	NA; range 98.21–108.46	NA
QPP-5	$1.75 < 7.81$ → consistent results	111.75 ± 0.18	1.27 → consistent results
QWC-6	Inconsistent results	NA; range 114.72–136.53	NA
QBPP-7	$5.90 < 7.81$ → consistent results	107.96 ± 0.18	5.04
VWBP-8	$1.72 < 7.81$ → consistent results	100.96 ± 0.15	0.72 → consistent results
BSCB-9	$2.89 < 7.81$ → consistent results	100.36 ± 0.15	1.43 → consistent results
BPP-10	$5.31 < 7.81$ → consistent results	111.41 ± 0.15	0.91 → consistent results

^{14}C concentration from the inner thin layer i.e., 101.47 ± 0.33 pMC. The mixed layers sample yielded the lowest ^{14}C concentration i.e., 98.21 ± 0.33 pMC. This indicates that the sample material is highly inhomogeneous. Carbonized sample gave a measurement result 108.46 ± 0.35 pMC. Even the highest ^{14}C concentration for small subsample GdA-6808.1.1 (random sample) is far away from such result. The hypothesis that the lighter carbon isotopes may have been preferentially removed as a gas fraction during the carbonization procedure and that this was not sufficiently corrected by the measurement of the δ^{13}C can be considered in this situation. However, the results for six samples: QSCP-1, QBP-3, QPP-5, VWBP-8, BSCB-9, and BPP-10 contradict such a hypothesis. This suggest the selected small subsamples were not representative of the packaging tested.

For sample QWC-6, the subsamples were from the wooden cutlery in knife and fork forms. The ^{14}C concentrations for the fork, knife, mixed form of fork and knife, random and carbonized samples, are high and coming from the range 136.53 ± 0.42 to 114.72 ± 0.37 pMC. We got quite different ^{14}C concentrations for each subsample, as the samples are not prepared only from a single tree which significantly affect the ^{14}C concentrations. According to (Krajcar Bronić et al. 2015) if wooden products are produced from wood grown in the second half of the 20th century, ^{14}C activities may vary between 105 and 190 pMC depending on the year of growth.

For sample QBPP-7, there is a little variation in ^{14}C concentrations for all subsamples. The sample was from the brown paper plates, composed of waterproof layer and inner paper layer. All subsamples other than carbonized give the ^{14}C concentrations between 107.22 ± 0.36 pMC and 108.35 ± 0.35, whereas for carbonized sample is 109.63 ± 0.28 pMC. Thus, the situation for this material is analogous to that for sample QPS-4.

Admittedly, measurements of the δ^{13}C at AMS do not correctly reflect its value in the samples, but they do make it possible to observe certain trends. For carbonized samples we received the lowest δ^{13}C values as during carbonization the lighter isotopes of carbon evacuated from the sample with other gases. δ^{13}C values for QSCP-1 and BSCB-9 samples are the highest (between –13‰ to –18‰) as the samples are from sugarcane material, the values are in the range of δ^{13}C values measured in sugarcane-based plastic bags (Santos et al. 2019).

Instead of carbonization complete combustion would be a better way of homogenization. Such combustion of the samples carried in a vacuum line with the ability to control the temperature rise and combustion time and using (Quarta et al. 2013) would be necessary. It would prevent light carbon loss and reduce isotope fractionation which we observe in the case of carbonization.

One more thing to be noted here, the outer surface of three samples: QPC-2, QPS-4 and QBPP-7 was more waterproof and greasy as compared to the rest of the samples.

CONCLUSIONS

the AMS ^{14}C technique was tested in Gliwice ^{14}C and Mass Spectrometry Laboratory for the determination of ^{14}C concentration in disposable samples. The research was carried out on paper, wheat bran, sugarcane, and wooden materials from different production companies.

According to the current, post-bomb changes in ^{14}C concentrations in the biosphere, the highest ^{14}C concentration values could be expected for samples made from wood, followed by samples containing paper (produced from wood and/or recycled). In contrast, the lowest concentrations should yield materials from current plant crops. The results obtained are as expected. The highest values were obtained for sample QWC-6 (wooden cutlery) and the lowest for sugarcane (QSCP-1, BPP-10) and wheat bran (VWBP-8) products. Paper packaging gives intermediate results.

All samples turned out to be contemporary. The mean concentration of the ^{14}C isotope for all samples is above 100 pMC, indicating that the disposables tested were produced from modern biomass. Relatively high ^{14}C concentrations for the outer (waterproof) layer indicate that bioplastic was used. However, in the case of paper cups, one of the subsamples gave the lowest measured results, which may indicate a small addition of ordinary plastic. Significant differences and high ^{14}C concentrations in the wooden samples indicate the production of samples from different trees with different ages.

Four packaging samples tested are characterized by a large scatter in the results of ^{14}C isotope concentration measurements. This demonstrates the need to homogenize a larger volume of samples, since a sample selected for analysis from a random part may not be representative. Such homogenization may be particularly important when determining the biomass content of material used for co-firing in energy production.

Simple carbonization is not an appropriate way for the homogenization of sample although 6 of the 10 packaging types tested, the results obtained for the large sample subjected to simple carbonization are in agreement with the results for the small subsamples. The results are promising, but further comparative studies with a specially designed line and carbonization of samples in an oxygen-free atmosphere are needed to conclusively answer the question of whether carbonizing a sample can be a good way for homogenization.

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SUPPLEMENTARY MATERIAL

To view supplementary material for this article, please visit https://doi.org/10.1017/RDC.2024.35

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Supplement. Results of the ^{14}C concentration measurements expressed as pMC for the 10 analyzed types of disposable packaging. All results were corrected for isotope fractionation by δ^{13}C ,measured by AMS. Total carbon percentages measured in VarioMicroCube Elemental Analyzer (EA) coupled to an AGE-3 graphitization system are also given.

No.	Sample code	Material	Subsample	Lab code	Total Carbon (%)	^{14}C conc. (pMC)	$\delta^{13}C_{AMS}$ ‰
1.	QSCP-1	Sugar cane plates	Random	GdA-6805.1.1	41.74 ± 0.40	100.54 ± 0.34	-18.94
			Outer layer	GdA-6805.2.1	42.47 ± 0.69	99.74 ± 0.32	-16.00
			Inner layer	GdA-6805.3.1	42.41 ± 0.64	100.11 ± 0.32	-15.80
			Mixed layers	GdA-6805.4.1	42.53 ± 0.73	99.42 ± 0.33	-17.40
			Carbonized	GdA-6805.5.1	91.25 ± 1.83	100.29 ± 0.33	-23.50
2.	QPC-2	Paper cups	Random	GdA-6806.1.1	42.30 ± 0.42	100.61 ± 0.34	-25.74
			Outer layer	GdA-6806.2.1	49.24 ± 0.93	105.46 ± 0.33	-21.10
				GdA-6806.2.2		93.95 ± 0.28	-21.5
				GdA-6806.2.4		97.72 ± 0.29	-22.0
			Inner layer	GdA-6806.3.1	44.14 ± 0.52	114.47 ± 0.36	-25.70
				GdA-6806.3.2		114.47 ± 0.31	-26.4
				GdA-6806.3.3		114.69 ± 0.33	-27.3
			Mixed layers	GdA-6806.4.1	45.31 ± 0.95	108.37 ± 0.34	-22.70
				GdA-6806.4.2		106.07 ± 0.30	-24.1
				GdA-6806.4.3		107.81 ± 0.32	-25.8
			Carbonized	GdA-6806.5.1	90.82 ± 1.08	113.7 ± 0.36	-32.10
3.	QBP-3	Baking paper	Random 1	GdA-6807.1.1	41.71 ± 0.37	107.22 ± 0.34	-25.51
			Random 2	GdA-6807.2.1	42.41 ± 0.64	106.71 ± 0.34	-26.20
			Carbonized	GdA-6807.3.1	87.38 ± 0.93	107.81 ± 0.35	-31.80
4.	QPS-4	Paper straws	Random	GdA-6808.1.1	43.55 ± 0.55	103.53 ± 0.34	-25.74
			Outer layer	GdA-6808.2.1	44.47 ± 0.73	100.04 ± 0.33	-25.90
			Inner layer	GdA-6808.3.1	44.28 ± 0.68	101.47 ± 0.33	-26.20
			Mixed layers	GdA-6808.4.1	44.95 ± 0.52	98.21 ± 0.33	-25.50
			Carbonized	GdA-6808.5.1	87.16 ± 2.65	108.46 ± 0.35	-31.40
5.	QPP-5	Paper plates	Random	GdA-6809.1.1	42.12 ± 0.41	112.00 ± 0.34	-25.65
			Outer layer	GdA-6809.2.1	40.38 ± 0.12	111.41 ± 0.36	-24.60
			Inner layer	GdA-6809.3.1	44.26 ± 0.37	111.92 ± 0.36	-25.90
			Mixed layers	GdA-6809.4.1	42.98 ± 0.42	111.64 ± 0.36	-25.00
			Carbonized	GdA-6809.5.1	69.74 ± 2.52	111.24 ± 0.36	-30.60
6.	QWC-6	Wooden cutlery	Random	GdA-6810.1.1	46.02 ± 0.43	123.44 ± 0.34	-26.49
			Fork	GdA-6810.2.1	47.05 ± 1.19	136.53 ± 0.42	-26.00
			Knife	GdA-6810.3.1	45.12 ± 3.03	114.72 ± 0.37	-26.20
			Mixed fork & knife	GdA-6810.4.1	46.70 ± 1.35	129.7 ± 0.40	-26.20
			Carbonized	GdA-6810.5.1	92.50 ± 3.43	121.77 ± 0.39	-35.20
7.	QBPP-7	Brown paper plates	Random	GdA-6811.1.1	44.11 ± 0.25	108.13 ± 0.34	-26.21
			Outer layer	GdA-6811.2.1	44.15 ± 0.64	108.11 ± 0.35	-25.80
			Inner layer	GdA-6811.3.1	45.86 ± 0.77	107.22 ± 0.36	-25.20
			Mixed layers	GdA-6811.4.1	44.67 ± 0.19	108.35 ± 0.35	-24.80
			Carbonized	GdA-6811.5.1	90.90 ± 1.65	109.63 ± 0.28	-31.30
8.	VWBP-8	Wheat bran plates	Random	GdA-6812.1.1	44.22 ± 1.02	101.35 ± 0.34	-27.84
			Outer layer	GdA-6812.2.1	43.56 ± 0.63	100.92 ± 0.29	-27.60
			Inner layer	GdA-6812.3.1	43.39 ± 0.52	100.86 ± 0.29	-27.50

			Mixed layers	GdA-6812.4.1	43.52 ± 0.56	100.81 ± 0.29	-27.00
			Carbonized	GdA-6812.5.1	65.99 ± 1.25	100.72 ± 0.29	-32.10
9.	BSCB-9	Sugar cane boxes	Random	GdA-6813.1.1	43.01 ± 1.01	100.02 ± 0.34	-14.72
			Outer layer	GdA-6813.2.1	43.26 ± 0.13	100.14 ± 0.29	-13.90
			Inner layer	GdA-6813.3.1	43.28 ± 0.15	100.54 ± 0.29	-14.50
			Mixed layers	GdA-6813.4.1	43.32 ± 0.12	100.64 ± 0.29	-14.10
			Carbonized	GdA-6813.5.1	91.31 ± 0.12	99.89 ± 0.29	-21.50
10.	BPP-10	Paper plates	Random	GdA-6814.1.1	43.14 ± 0.14	111.98 ± 0.34	-25.62
			Outer layer	GdA-6814.2.1	44.79 ± 0.30	110.98 ± 0.29	-26.00
			Inner layer	GdA-6814.3.1	45.10 ± 0.12	111.54 ± 0.29	-25.40
			Mixed layers	GdA-6814.4.1	45.09 ± 0.11	111.32 ± 0.28	-25.10
			Carbonized	GdA-6814.5.1	94.97 ± 3.77	111.71 ± 0.29	-33.30

Gliwice, 19th Feb 2024

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Co-authorship statement

I hereby declare that my contribution to the paper:

‘Monitoring of modern carbon fraction in disposable packaging’, (2024). Radiocarbon, First View DOI: 10.1017/RDC.2024.35.
Authors: Komal Aziz Gill, Danuta J. Michczyńska, Adam Michczyński, Natalia Piotrowska.
My participation consisted of;

- Carbonization of samples in a metal reactor at 700 °C.
- Sample preparation from different layers of packaging materials.
- Graphitization of samples for AMS measurements at the Gliwice ^{14}C and Mass Spectrometry Laboratory.
- Pressing of graphite and cathode tube preparation for AMS measurements
- Analysis of samples by MICADAS at Gliwice ^{14}C and Mass Spectrometry Laboratory.
- Data analysis and interpretation of results.
- Preparation of figures, graphs, and tables of the manuscript.
- Manuscript writing.

My participation in the work was 70%.

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Zaświadczam, że Wydawnictwo Politechniki Śląskiej przyjęło do opublikowania monografię POB6 Werle S., Ferdyn-Grygierek J. (eds.) 2024 „Ochrona klimatu i środowiska, nowoczesna energetyka – wybrana problematyka”, w której znajduje się rozdział:
Gill K.A., Michczyńska D.J., Michczyński A. „Bio-carbon content determination in disposable packaging by liquid scintillation counting”.

Z poważaniem

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CONTENTS

CONTENTS

1. BIO-CARBON CONTENT DETERMINATION IN DISPOSABLE PACKAGING BY LIQUID SCINTILLATION COUNTING (OZNACZANIE ZAWARTOŚCI BIOWĘGLA W OPAKOWANIACH JEDNORAZOWYCH METODĄ CIEKŁOSCYNTYLACYJNĄ)

1.1. Introduction

Liquid scintillation counting (LSC) is one of the most common radiocarbon technique that has been used for the biocomponent content determination in various materials since its first application in the 1950's [1]. The LSC technique is considered a mature method of measurement. In LSC measurements, the energy released from the radioactive decay is converted into light by the scintillator, which is then detect by photomultipliers. Cost-effectiveness, portability, ease of sample preparation, and a possibly comparable detection limit of 0.4 weight percent to AMS are among the benefits of LSC [2]. LSC measurements can be used to distinguish between fossil and biogenic components which is difficult by classical analytical techniques because of their similar physical and chemical properties [3].

Carbon-14 (^{14}C) is the heaviest and radioactive isotope of carbon. It's formed in the upper atmosphere when cosmic rays collide with nitrogen atoms, converting them into ^{14}C, which is then oxidized to $^{14}CO_2$ and transferred to plants and other living organisms. Hence, living organisms contain ^{14}C. During the life of an organism, there is a dynamic balance between the absorbed ^{14}C and that which undergoes radioactive decay. After the death of the organism, exchange with the environment ceases and the amount of ^{14}C decreases according to the law of radioactive decay. After undergoing beta decay, this radioactive isotope becomes stable nitrogen-14 by emitting a beta particle. With a half-life of approximately 5,700 years [4], carbon-14 can be utilized to date geological and archaeological samples up to 50,000 years old using a method known as radiocarbon dating [4-6]. As fossil fuels (natural gas, oil, coal, lignite) do not contain ^{14}C, it is possible to verify using the radiocarbon method whether a product (e.g. disposable packaging) has been produced from modern biomass or whether fossil components have been used in its production [7-10].

It is only in the last fifteen years that the industry has begun to make polymers utilizing renewable sources of carbon, such as plants, as opposed to the beginning of the third millennium, when all raw materials used for the synthesis of plastic products were derived from petroleum. In 2003, the market saw the first unsaturated polyester resins with an 18% bio-content [11, 12]. The material reflects the current value of atmospheric $^{14}CO_2$ activity if the radioactive carbon content is significantly different from that of fossil material, indicating that the ^{14}C coexisted with biological material during its production. [11]. In this regard, ^{14}C is used to assess biobased content in packaging [6], oil [13], diesel [14], plastic [15, 16], used car tyres and their pyrolysis products [17, 18], carbon black [19], vinegar [20], and various other products [3] for which bio-based content is required.

Three standards, EN 16785-1, ASTM D6866, and EN 16640, are mainly used for bio-based content determination. ASTM D6866 is used to determine the bio-based carbon content in materials by radiocarbon analysis. Bio-based carbon content is determined as the amount of bio-based carbon in the material as a percent of mass of the total organic carbon in the material. The bio-based carbon represents the carbon directly related to the renewable materials like wood, and other recently living organisms. In contrast, organic carbon content represents the bio-based carbon together with the fossil-based carbon (carbon from non-renewable materials such as petroleum, coal, natural gas, etc). EN 16640 is slightly different from ASTM D6866. The bio-based carbon content is determined in relation to the total carbon content, which represents the total amount of carbon from bio-based carbon, fossil-based carbon and inorganic carbon (from minerals or rocks) [21].

In present days many studies focus on the determination of bio-based carbon content in different materials. Many laboratories use accelerator mass spectrometry (AMS) for bio-based carbon content determination. The aim of this research is to measure the modern carbon percentage by the LSC method for the determination of bio-carbon content of the final products used for packaging.

1.2. Materials and method

In this research, the LSC technique was used to analyse disposable packaging materials (DPMs) for bio-based carbon content determination. We worked on total ten samples. The samples were made of paper, wheat bran, sugar cane and wood. We tested packaging of various shapes (for various applications). These were plates, cups, baking paper, cutlery, boxes. Samples were collected from different DPMs manufacturing companies. Samples were prepared and analysed at the Gliwice ^{14}C and Mass Spectrometry Laboratory within the Institute of Physics – Centre for Science and Education, SUT, Poland [17, 22, 23].

1.2.1. LSC measurements at Gliwice ^{14}C and Mass Spectrometry Laboratory

DPM samples were analysed by LSC technique using the benzene synthesis method [23]. Each sample was directly used without any pretreatment and passed through carbide synthesis, hydrolysis (acetylene preparation), trimerization of acetylene, and purification of benzene. In the first step, the cleaned metal reactor with a small hole, to minimize air access, was used for the carbonization of large mass of sample (~24g) in a muffle furnace at 700 °C under controlled pressure conditions. The process took 7 to 10 minutes to complete. The carbonized sample was ground into powder after cooling and directly treated with lithium metal with a proportion of 1:1 in the sealed metal reactor in the muffle oven at 700 °C. The obtained carbide product was treated with deionized water after cooling to produce acetylene. Acetylene was collected under liquid nitrogen after passing through a highly hygroscopic trap of a mixture of potassium dichromate and sulfuric acid. In the next step, acetylene was trimerized to benzene in the presence of preheated activated chromium catalyst at 600 °C for about half an hour. The obtained benzene was purified by keeping sodium metal in benzene overnight to absorb water and then stored in the freezer (at -15 °C) for approximately a month to make the sample radon-free (the half-life of radon is 3.8 days) [17, 19]. Quantulus 1220$^{\text{TM}}$ liquid scintillation β spectrometer was used for LSC measurements [22, 23].

1.2.2. δ13C measurements by Isotope Ratio Mass Spectrometry (IRMS)

The standardised isotope fractionation correction is calculated using the IRMS technique [24]. The relative ratio of stable carbon isotopes ($\delta^{13}C$ or $^{13}C/^{12}C$) is determined by IRMS measurements. Simax tubes were used for the combustion of samples with ~300 mg of CuO at 560 °C for ~12 hours with proper sealing. ANU-sucrose (IAEA-CH-6, ~3 mg), NBS-22 (oil, ~ 5 µL) and WZS (internal standard from lake sediment, ~2 µg) [25] were used as standards. The IsoPrime 100 spectrometer connected to the Gilson-271 autosampler MultiFlow was used for measurements of $\delta^{13}C$ [19, 26, 27].

1.2.3. Calculations of bio-based carbon and biomass content

Bio-based carbon content by dry mass was determined by European standard EN 16640 for measurements using the LSC and AMS techniques.

In Gliwice ^{14}C and Mass Spectrometry Laboratory, based on the measured sample activity by LSC technique, we determine percentage of modern carbon in the sample and calculate the bio-based carbon content ($BBCC$) by dry mass using measured total carbon content (TCC) in the sample and the same formula like for AMS technique:

$$BBCC = TCC \frac{percent\ of\ modern\ carbon\ in\ the\ sample}{reference\ value} \times 100\ (\%) \tag{1.1}$$

The bio-based carbon content by dry mass is expressed as a percentage, and the reference value, expressed in pMC, of 100% bio-based carbon of the biomass from which the sample is constituted.

The same standard also specifies how to calculate bio-based carbon content as a fraction of the total carbon content (X):

$$X = \frac{bio - based\ carbon\ content}{total\ carbon\ content} \times 100\ (\%) \tag{1.2}$$

In turn, the European standard EN 16785-1 uses the radiocarbon method and elemental analysis for bio-based content determination. In this way, the bio-based content is determined as the amount of bio-based elements (C, H, N, O) in the materials as a percent of the total mass of the material [21, 28] by the following formula:

$$Bio - based\ content = \frac{mass\ of\ bio - based\ content}{total\ mass\ of\ material} \times 100\ (\%) \qquad (1.3)$$

Regarding paper material, 90-99% of paper-based products typically composed of cellulose [29], with the empirical formula; $(C_6H_{10}O_5)_n$, where 'n' represents the degree of polymerization. Theoretically, the simplest paper contains 44.44% carbon, 6.17% hydrogen, and 49.38% of oxygen. These compositions depend on the type of material. By following Eq. 1.3, the bio-based content can be determined by chemical analysis of the elements presented in the bio-based product.

1.3. Results

The ^{14}C concentration in disposable packaging material samples is reported as percent modern carbon (pMC) [24] measured by LSC. The measured values of pMC, $\delta^{13}C$ and calculated bio-based carbon content according to EN 16640 [30] are listed in **Table 1.1**. $\delta^{13}C$ values were used for standardised isotope fractionation correction for LSC measurements and are expressed in per mil (‰) VPDB. A 100% reference value (REF) was used to determine the bio-based carbon content (see Eq. 1.2) [31, 32].

Table 1.1

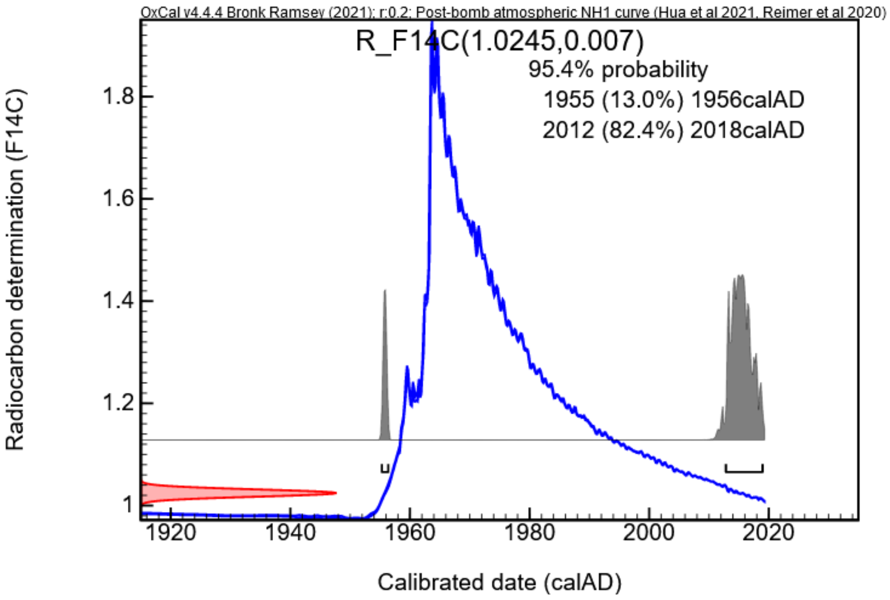
Results of the ^{14}C concentration and $\delta^{13}C$ measurements and calculated bio-based carbon content for DPMs

Wyniki pomiarów koncentracji izotopu ^{14}C i $\delta^{13}C$ oraz obliczonej zawartości węgla bio-bazowego.

No.	***Sample***	***Lab code***	***^{14}C conc. (pMC)***	***$\delta^{13}C_{VPDB}$ (‰)***	***Bio-based carbon content (%)***
1	QSCP-1 Sugarcane plates	GdS-4610	103.20 ± 0.74	-24.156 ± 0.059	103.20 ± 0.74
2	QPC-2 Paper cups	GdS-4611	114.65 ± 0.80	-29.465 ± 0.037	114.65 ± 0.80
3	QBP-3 Baking paper	GdS-4616	109.99 ± 0.78	-27.43 ± 0.23	109.99 ± 0.78
4	QPS-4	GdS-4617	110.36 ± 0.78	-26.97 ± 0.36	110.36 ± 0.78

	Paper straws				
5	QPP-5 Paper plates	GdS-4620	108.30 ± 0.72	-26.14 ± 0.21	108.30 ± 0.72
6	QWC-6 Wooden cutlery	GdS-4618	125.51 ± 0.87	-30.02 ± 0.16	125.51 ± 0.87
7	QBPP-7 Brown paper plates	GdS-4621	111.36 ± 0.74	-27.78 ± 0.24	111.36 ± 0.74
8	VWBP-8 Wheat plates	GdS-4622	103.56 ± 0.71	-14.24 ± 0.74	103.56 ± 0.71
9	BSCB-9 Sugar cane boxes	GdS-4623	102.45 ± 0.70	-15.84 ± 0.42	102.45 ± 0.70
10	BPP-10 Paper plates	GdS-4624	114.92 ± 0.76	-29.68 ± 0.16	114.92 ± 0.76

Results of the ^{14}C measurement can be converted to calendar age using the post-bomb atmospheric NH1 calibration curve [32, 33] and the OxCal v.4.4.4 calibration program [34]. Example calibration results for the sample with the highest and lowest measured ^{14}C concentration are shown in **Fig. 1.1**.



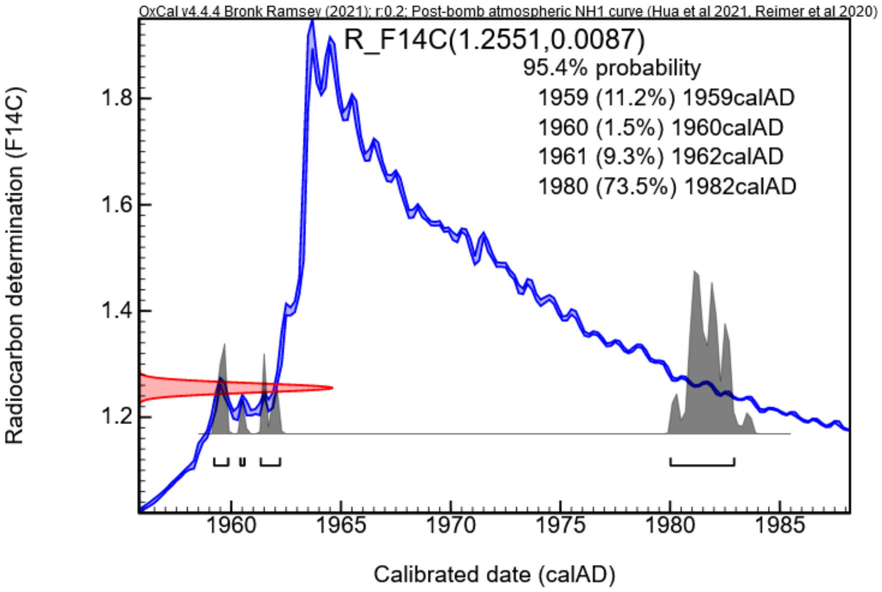


Fig. 1.1. Conversion of the ^{14}C isotope concentration (here expressed as F^{14}C = pMC/100) to calendar age given as 95.4% confidence intervals, using the OxCal v.4.4.4 calibration program [34] and NH1 calibration curve [32, 33]. The blue curve is the calibration curve, the red distribution on the vertical axis is the measurement result, and the resulting probability distributions of calendar ages are shown in gray

Rys. 1.1. Przeliczenie stężenia izotopu ^{14}C (tutaj wyrażonego jako F^{14}C = pMC/100) na wiek kalendarzowy podany jako przedziały 95,4% ufności, przy użyciu programu kalibracyjnego OxCal v.4.4.4 [34] i krzywej kalibracyjnej NH1 [32, 33]. Niebieska krzywa to krzywa kalibracyjna, czerwony rozkład na osi pionowej to wynik pomiaru, a powstałe rozkłady prawdopodobieństwa wieków kalendarzowych pokazano w kolorze szarym

1.4. Discussion

Ten disposable packaging material samples were measured for bio-based carbon content analysis by the LSC technique. All samples presented ^{14}C concentration values higher than 100% bio-based carbon content, so the samples are considered as biomass produced between AD 1955 and 2018.The obtained concentrations of the isotope ^{14}C above 100% are related to the fact that after nuclear weapons tests between 1955 and 1965, the concentration of this isotope in the atmosphere (and thus in the biosphere) increased above the 100% level assumed for the year 1950. The changes in the concentration of the isotope ^{14}C after nuclear weapons tests are presented by the calibration curve in **Fig. 1.1**. **Table 1.1** represents the ^{14}C concentration in pMC, δ^{13}C values in ‰ and bio-based carbon content in pMC of each sample. Bio-based carbon content was calculated using 100 REF value according to EN 16640 [30]. The concentration values of ^{14}C and the corresponding uncertainty values are graphically explained in **Fig. 1.2**. For standardised isotope fractionation correction, the $\delta^{13}C$ value was used. **Fig. 1.3** presents $\delta^{13}C$ values with uncertainty according to the type of material.

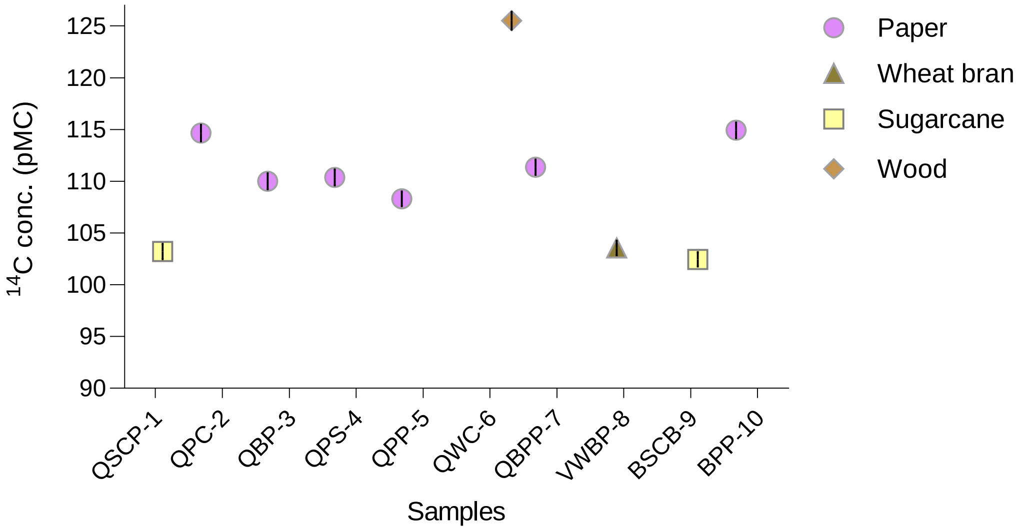


Fig. 1.2. Results for the ^{14}C concentration measurements in different DPMs
Rys. 1.2. Wyniki pomiarów stężenia ^{14}C w różnych opakowaniach jednorazowych

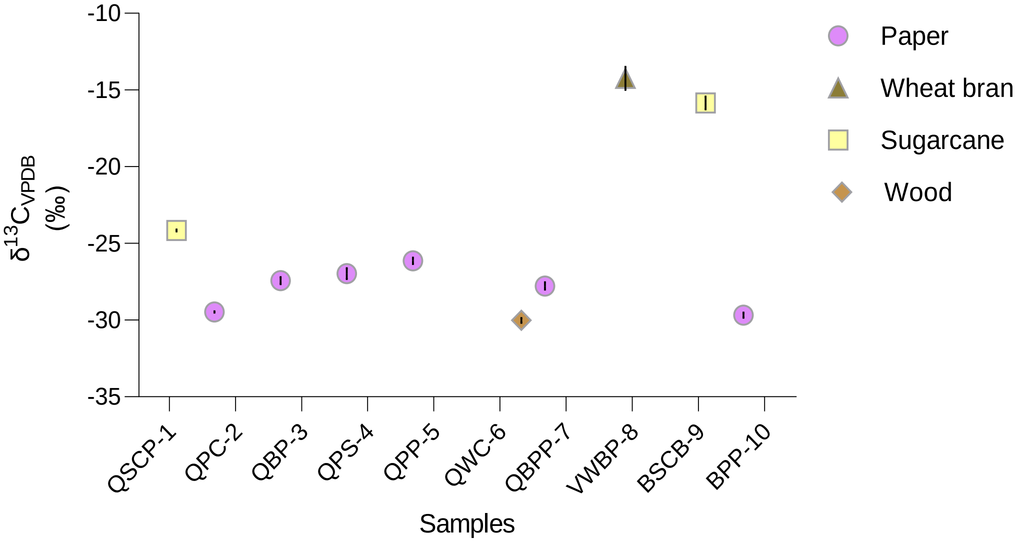


Fig. 1.3. Comparison of the $\delta^{13}C$ values with uncertainty across different DPM material categories
Rys. 1.3. Porównanie wartości $\delta^{13}C$ z niepewnością dla różnych kategorii opakowań jednorazowych

Nine samples out of ten show the ^{14}C content between 102.45 ± 0.7 pMC to 114.92 ± 0.76 pMC. Six samples of paper materials – paper cups (QPC-2), baking paper (QBP-3), paper straws (QPS-4), paper plates (QPP-5), brown paper plates (QBPP-7) and paper plates (BPP-10) – show ^{14}C concentrations between 108.30 ± 0.72 to 114.92 ± 0.76 pMC, corresponding to the modern carbon concentration of packaging material reported in [6, 35, 36]. The $\delta^{13}C$ values for the paper materials are in range of -29.68 ± 0.16 ‰ to -26.14 ‰, corresponding to the range reported in [6, 11].

A sample of wheat, wheat bran plates (VWBP-8), shows a ^{14}C concentration of 103.56 ± 0.71 pMC corresponding to the reported ^{14}C concentration values of recent years in [6, 36]. The $\delta^{13}C$ value for the wheat bran sample is the highest, -14.24 ± 0.74 ‰, corresponding to the $\delta^{13}C$ value of C4 plants reported in [15].

Two samples of sugarcane, sugarcane plates (QSCP-1) and sugarcane boxes (BSCB-9), show the ^{14}C concentration of 102.45 ± 0.70 pMC and 103.20 ± 0.74 pMC, respectively. The values are close to the ^{14}C concentration values reported in [6]. The $\delta^{13}C$ values for the QSCP-1 and BSCB-9 are -24.156 ± 0.059‰ and -15.84 ± 0.42 ‰, respectively. The $\delta^{13}C$ value of BSCB-9 corresponds to the $\delta^{13}C$ value of wheat bran samples in [15], whereas QSCP-1 represents unexpected results probably because of the presence of a plastic coating layer.

A sample from wood, wooden cutlery (QWC-6), shows ^{14}C concentration of 125.51 ± 0.87 pMC, corresponding to the reported range of ^{14}C content in wood samples by [6, 37]. The wood sample gives $\delta^{13}C$ value of -30.02 ± 0.16 ‰.

1.5. Conclusion

The liquid scintillation method was used to determine the bio-based carbon content in ten different disposable packaging samples. Disposable samples were composed of paper, wheat bran, sugarcane, and wood samples. Isotope ratio mass spectrometry was used for the standardised isotope fractionation correction for LSC measurements. Samples QSCP-1 and BSCB-9 from sugarcane, and sample VWBP-8 from wheat bran, represent the lowest bio-based carbon content between 102.45 - 103.56 pMC and the highest $\delta^{13}C$ value except

QSCP-1. The bio-based carbon content of all samples is greater than 100 pMC, indicating that modern biomass was used to produce the disposable packaging samples. QWC-6 from wood represents the highest, whereas the six paper material samples (QPC-2, QBP-3, QPS-4, QPP-5, QBPP-7 and BPP-10) represents the intermediate bio-based carbon content concentration.

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Streszczenie:

W rozdziale przedstawiono analizę oznaczania zawartości biowęgla w próbkach opakowań jednorazowych techniką spektrometrii ciekłoscyntylacyjnej (LSC). Dla skorygowania wartości koncentracji izotopu ^{14}C ze względu na frakcjonowanie izotopowe wykorzystano spektrometrię masową stosunków izotopowych (IRMS). Zawartości biowęgla określono dla dziesięciu typów próbek opakowań jednorazowych. Były one wykonane z papieru, otrębów pszennych, , trzciny cukrowej i drewna. Wszystkie próbki wykazały koncentrację izotopu ^{14}C większą niż 100 pMC, co wskazuje, że próbki są współczesne i do ich produkcji użyto biomasy. Największą zawartość biowęgla wykazała próbka drewna, natomiast najmniejszą mają próbki trzciny cukrowej i otrębów pszennych.

Summary:

The chapter presents an analysis of the determination of bio-carbon content in disposable packaging samples using liquid scintillation spectrometry (LSC). To correct the ^{14}C isotope concentration values for isotopic fractionation, isotope ratio mass spectrometry (IRMS) was used. Bio-carbon content was determined for ten types of disposable packaging samples. They were made of paper, wheat bran, sugarcane, and wood. All samples showed a ^{14}C isotope concentration greater than 100 pMC, indicating that the samples are contemporary and biomass was used in their production. The highest bio-carbon content was found in the wood sample, while the lowest in the sugarcane and wheat bran samples.

Gliwice, 19th Feb 2024

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Co-authorship statement

I hereby declare that my contribution to the paper:

‘Bio-carbon content determination in disposable packaging by liquid scintillation counting’, [in:] POB6 Monograph “Climate and environmental protection, modern energy - selected issues”, SUT (in press).
Authors: Komal Aziz Gill, Danuta J. Michczyńska.
My participation consisted of;

- Carbonization of samples in a metal reactor at 700 °C.
- Synthesis of benzene for LSC measurements at the Gliwice ^{14}C and Mass Spectrometry Laboratory.
- Preparation of samples for IRMS measurements at the Gliwice ^{14}C and Mass Spectrometry Laboratory
- Data analysis and interpretation of results.
- Preparation of figures, graphs, and tables of the manuscript.
- Manuscript writing.

My participation in the work was 70%.

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Gliwice, 30th July 2024

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I covered data analysis and manuscript review.

My participation in the work was 25%.

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I covered LSC measurement analysis and minor text addition.

My participation in the work was 5%.

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