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.