

Radiolabeling for polymers degradation studies: Opportunities and challenges ahead

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ABSTRACT

The production of bio-based polymers as replacements for fossil-based ones is becoming increasingly important to the human society due to the decreasing availability of fossil resources combined with rising fuel prices, and their potential to reduce greenhouse gas emissions that are the main cause of climate change. There is strong societal and regulatory pressure for the development of more sustainable biodegradable bioplastics. Viable recycling options are still lacking for many of these plastics. Due to the novelty of biodegradable bioplastics valuable chains, more research is required to reduce technical and economic uncertainties and demonstrate the feasibility and economic competitiveness of them. Therefore, there is an urgent need for technology development and the design of transition paths towards structural changes in polymers establishing local and regional circular production of bioplastics with potential impact on global economies.

It is essential to understand the factors that control the environmental behavior and fate of such bioplastics as well as their impact on ecosystem functioning. Extensive studies with accurate measurement tools and specialized analytical techniques are needed for this purpose. The radiolabeling technique (^{14}C) allows the quantification of the degradation process of biopolymers by easily being able to distinguish between CO_2 which is produced during degradation polymers and other carbon sources in natural environment.

This review provides an overview of the application of the ^{14}C -labeling technique in polymer degradation studies that is compared under various conditions. In following, standard methods for ^{14}C -labeling, as well as its potentials, obstacles, and deficiencies in usage, are also discussed.

1. Introduction

1.1. Circular economy and the emergence of bioplastics

The demand for plastic production reached an all-time high in 2020, mainly due to the COVID-19 pandemic, and this trend is still increasing [1–3]. While the annual production of plastics exceeds 390 million tonnes, bioplastics still account for less than one percent of this total. Various definitions have been provided to describe bioplastics [4]. According to the European Bioplastics definition, bioplastics are categorized into three groups: biobased, biodegradable or of both. Among these three categories of bioplastics, two of them are considered as biodegradable [5]. Biodegradability is defined by the American society

for testing and materials (ASTM) as the degradation or decomposition of polymers through chemical, physical, and biological interactions with microorganisms into water, carbon dioxide. Under anaerobic conditions, methane can also be produced [6]. Between two types of biodegradable bioplastics, biobased biodegradable polymers which are made from renewable sources such as corn, sugar beet, cassava, and sugar cane, appear to be superior to fossil based biodegradable polymers [7]. Since, these resources are expected to become much more expensive and scarce very soon (Fig. 1) [5].

Atmospheric carbon dioxide absorbed by plants during photosynthesis is used to create bioplastics, which can help reduce greenhouse gas emissions and potentially contribute to carbon neutrality. This is achieved by converting CO_2 into plant biomass, which is then processed

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into bioplastics. The carbon can remain sequestered for extended periods through effective upcycling or recycling of the final products, minimizing the release of CO₂ back into the atmosphere [5,8]. On the other hand, if these bioplastics are incinerated for use as a renewable energy source, the released carbon dioxide can contribute to atmospheric pollution. If bioplastics do not degrade in the receiving environment to create valuable biomass (humus or compost), their accumulation can lead to significant problems. Fig. 2 illustrates the fate of bioplastics after production. Plastic pollution has severe impacts on both the environment and living beings, altering the carbon balance in soil and disrupting water ecosystems. Plastics contain toxins and carcinogenic chemicals that leach into the environment, contaminating soil and water sources and causing health problems for animals and humans [9]. Animals often mistake plastic waste for food, which can lead to starvation, suffocation or death [10]. Meanwhile, floating plastics transport invasive species that threaten biodiversity [11].

The European bioplastics organization, in cooperation with the nova-Institute, has predicted that global bioplastics production capacities will increase from about 2.18 million tonnes in 2023 to approximately 7.4 million tonnes by 2028 (Fig. 3) [5].

The linear economy of plastics, which follows the produce-use-dispose model, leads to issues such as material leakage into the environment with detrimental effects on e.g. marine ecosystems and CO₂ pollution through incineration. To maintain materials within the cycle, it is suggested to transform raw material and waste management and reduce the consumption of fossil resources by transitioning to a circular economy model [7,12]. Traceability is a prerequisite for a circular economy. In closed-loop systems, having knowledge about the origin and history of used materials and their destination can provide a competitive advantage [13]. In the European Commission action plan [13], implementing measurements in various sectors is considered a solution along the entire life cycle of products. This plan includes a hierarchy of waste in four parts: dispose, recycle, reuse and reduce (S1).

Managing polymers waste is one of the challenging issues at the global level [14–16]. Mechanical recycling is recognized as the most common strategy for the reuse of polymers and thus partially closing the loop. It consists of collection, sorting, grinding, washing, and extrusion of waste materials [17]. There are many obstacles in establishing an efficient recycling process, such as the lack of information about the composition of mixed plastics with different recycling processes, and multi-layer plastics that consist of layers of different materials (for example aluminum, and paper). Additionally, the use of colors and non-recyclable additives, for instance flame retardants, plasticizers, and stabilizers pose significant challenges [18]. The presence of labels, adhesives, and residues from food or other products can contaminate the recycling process and affect the quality of the recycled material [19,20]. Despite current improvements in waste management systems polymers are still accumulating in natural environments. Plastics discarded in the

nature affect the global carbon cycle and have a direct impact on climate change [21]. Moreover, using plastics in daily applications is unavoidable as they are part of many products that we need in different industries, such as packaging, construction, automotive, electronics, agriculture, textiles, and medical applications [22,23].

The production of degradable alternative materials appears to be one of the most promising approaches at present. The steady development of degradable polymers such as polyhydroxyalkanoates (PHA), poly(lactic acid) (PLA), polyamides (PAs) and poly(butylene succinate) (PBS) has made bioplastic alternatives applicable for almost every conventional plastic material derived from fossil fuels. It is also expected that a wider range of products will be produced to meet newly emerging needs in the future [5,13]. In the context of waste management processes, plastics become part of the circular economy when they can be reused or recycled. Moreover, if the CO₂ released during the degradation of plastics enters the photosynthesis cycle in plants, they can also be considered parts of this system [24].

Unfortunately, with the invention of plastics, the end-of-life of these materials was not considered for many years [25]. The significant amounts of plastics, especially the small-sized micro and nanoplastics will invariably end up in water, soil, compost, landfills, sewage, and mud environment through material wear, industrial discharge, and littering. So, increasing concerns are being raised regarding their potential environmental and health risks [26–29].

1.2. The complex path of bioplastic degradation in environment

Ideally, bioplastics are expected to naturally break down irrespective of their surrounding environment in shorter period compared to conventional plastics [30–32] and only produce carbon dioxide, water, and biomass. This means that the degradation or decomposition of these materials should not cause environmental damages in theory, but the degradation process is not as simple as it may seem. This process is influenced by macroscopic and microscopic changes, which manifest not only on the surface of the polymer but also in terms of molar mass, weight, and even microstructures [33–36].

Laboratory degradation studies often overestimate the biodegradability of plastics, as they simulate optimal conditions that differ significantly from the complex and variable conditions found in natural environments [37]. In the lab, stable temperatures, controlled light exposure, and isolated microbial populations create a best-case scenario for biodegradation, leading to accelerated rates that may not reflect real-world scenarios. In contrast, natural environments experience fluctuating temperatures [38], variable sunlight and UV exposure [39, 40], and diverse microbial communities, all of which can slow down the degradation process. Additional factors, such as mechanical stress, the physical shape [41,42], and co-substrates like food residues [43,44], further complicate biodegradation in nature may cause partial

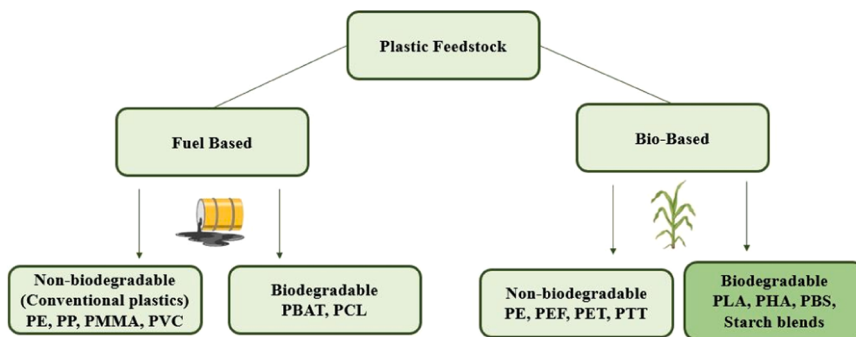


Fig. 1. Feed stocks for different kinds of plastics.

Polyethylene (PE), polypropylene (PP), poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC), poly(butylene adipate terephthalate) (PBAT), poly(ϵ -caprolactone) (PCL), poly(ethylene 2,5-furandicarboxylate) (PEF), poly(ethylene terephthalate) (PET), poly(trimethylene terephthalate) (PTT), poly(lactic acid) (PLA), polyhydroxyalkanoates (PHA), poly(butylene succinate) (PBS).

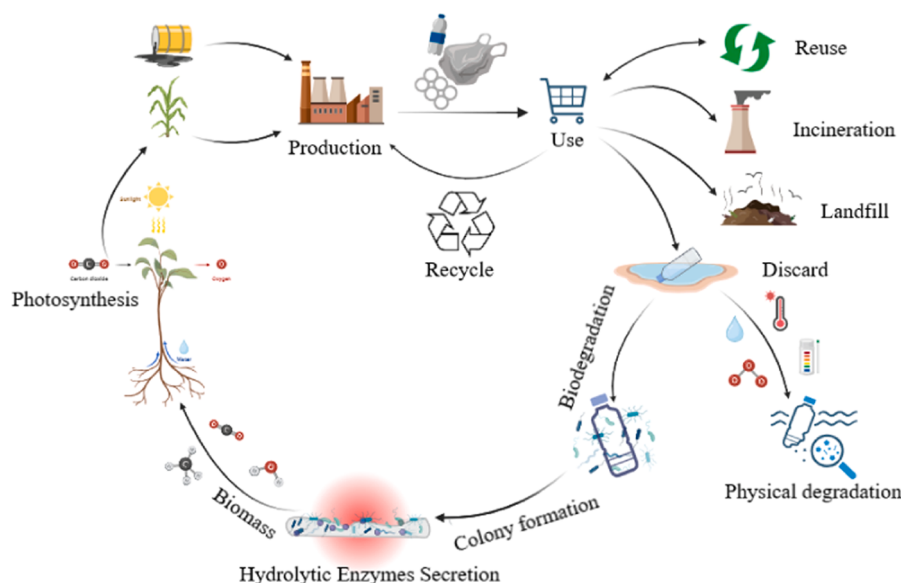


Fig. 2. Bioplastics production and fate.

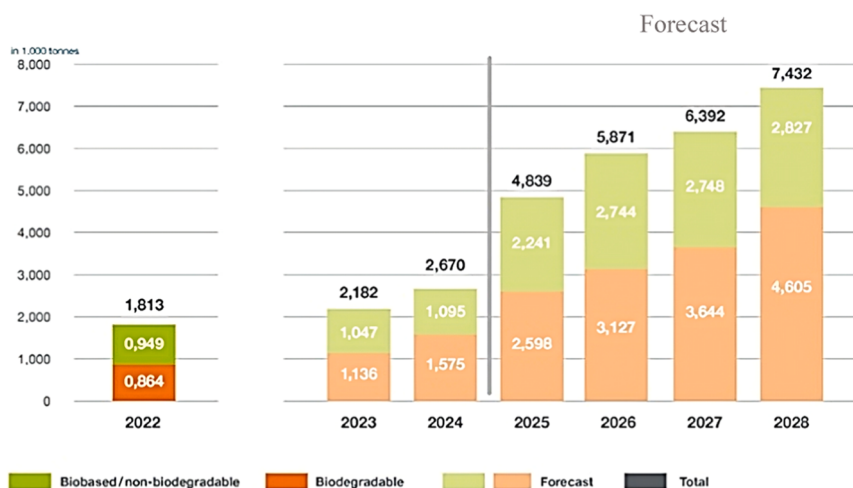


Fig. 3. Global production capacities of bioplastics 2022–2028 [5].

degradation which leads to microplastics formation [24]. While it appears that biodegradable microplastics have fewer ecological effects compared to fossil-based ones, they still cause environmental contamination that affects the lives of creatures. Therefore, it is essential to revise biodegradation test procedure to better represent natural conditions by adjusting variables for more accurate assessments.

1.3. Factors affecting polymer degradation

Influencing factors control the rate and procedure of degradation, stemming not only from characteristics of materials (such as the chemical composition and structure of polymers) but also from environmental conditions (temperature, humidity, pH value, radiation, microbial population and environmental composition) under which the polymer is expected to biodegrade [7].

1.3.1. Chemical structures

The polymeric compositions and structures are important factors in biodegradation reactions. Polymers with unsaturated backbones are more susceptible to oxidative degradation due to the presence of double bonds that readily react with oxygen and free radicals [45]. In contrast,

aromatic polymers, like polystyrene, exhibit greater resistance to thermal and UV degradation because the stable aromatic rings require more energy to break. The presence of heteroatoms, such as oxygen and nitrogen, in the backbone also influences degradation [46]. Additionally, the side groups and branching patterns of polymers affect degradation in various ways. Bulky side groups, can hinder degradation by sterically protecting the backbone, while polar side groups can enhance degradation by attracting water molecules and facilitating hydrolytic or oxidative degradation [7,47,48]. Highly branched or cross-linked polymers tend to be more resistant to degradation due to their three-dimensional network, which hinders the penetration of degradative agents, but this can also lead to incomplete degradation and the formation of microplastics [49]. Crystallinity and morphology significantly impact polymer degradation, with amorphous regions generally being more susceptible due to their higher free volume and accessibility. In contrast, crystalline regions are tightly packed and resist penetration [50,51]. Lastly, the composition of copolymers affects their degradation, with random copolymers degrading more uniformly than block copolymers, where different blocks may have varying degradation rates, leading to complex behavior [45].

1.3.2. Environmental conditions

Regarding environmental conditions, temperature is the primary factor. Higher temperatures often enhance the metabolic processes of mesophilic microorganisms. However, there are exceptions for which the dependence on temperature is the opposite [7].

Water availability in the matrix is a vital factor for living organisms, as their activities significantly facilitate the degradation process. The pH level of the environment also affects the rate of plastic degradation. Most microorganisms that contribute to biodegradation thrive in environments with a pH range of 5 to 9. This optimal pH range supports microbial growth and activity, enabling efficient degradation of plastics. Deviations from this pH range can inhibit microbial activity and slow down the degradation process. Exposure to UV radiation, or photo-oxidation, is another factor that can accelerate the degradation of certain plastics. UV light can create free radicals within the polymer structure, breaking down chemical bonds and making the plastic more susceptible to microbial attack. This process can initiate the degradation of plastics that might otherwise be resistant to microbial activity alone. Lastly, the diversity of the microbial community is a significant factor influencing plastic decomposition. A diverse microbial ecosystem increases the likelihood of having organisms with the specific enzymes needed to break down various types of plastics [7].

1.4. Understanding microbial biodegradation

Long-duration polymer degradation studies face several challenges in determining the role of microorganisms in the mineralization process. Microbial populations are dynamic and can change due to environmental fluctuations, making it difficult to maintain specific populations over time. Microbes may adapt or struggle to survive, altering their effectiveness in degradation. Stable environmental conditions, such as pH and temperature, are hard to maintain, and nutrient availability may decline, further impacting microbial activity. Unintended microbes or chemical contamination risks and difficulties in accurately quantifying mineralization also complicate the analysis. Additionally, the structural complexity of polymers can affect microbial access and degradation rates [52–56].

Biodegradation by microorganisms is recognized as a complex process involving physical, chemical, and biological changes [39]. This process can be divided into three general stages. First, microorganisms attack the surface of the polymer and form a colony to destroy its surface structures. Then, they secrete hydrolytic enzymes, such as depolymerase, lipase, cutinase, hydrolase, protease, and lignin-modifying enzymes, onto the surface [57]. As a result of hydrolysis and redox reactions, long-chain polymers are converted into low molecular weight compounds which they can pass through the microorganisms interior cell wall where they can be metabolized [58]. Under natural environmental conditions, degradation can occur by any of the above mechanisms alone or in combination with one another. This process continues until the entire biodegradation reaction stops. Finally, microorganisms absorb and digest short chains and low molecular weight compounds such as oligomers, dimers, and easily metabolizable monomers as a food source [54]. The outcome of compounds digestion is their conversion into energy, carbon dioxide in aerobic conditions, and/or methane in anaerobic conditions, along with water and biomass. These end products are eventually released back into the natural environment (Fig. 3) [7, 59]. The most favorable degradation conditions are typically found in composting environments [58], but studies have demonstrated that the environmental impacts of anaerobic biodegradation and composting are greater than the benefits of energy recovery through incinerating plastics [60].

2. Advantage of ^{14}C -radiolabeling in degradation studies

Plastic degradation studies in natural environment are a challenging field, as they depend on various factors, including polymer properties, and the characteristics and conditions of complex receiving environments [24]. Reliable evaluation of a material's degradability and the ability to compare degradation processes can only be achieved when all the relevant conditions are measured and controlled [58]. Different conventional methods have been used to track changes in polymeric structures during degradation. For instance, optical detection [61], Gravimetric analysis [62], Differential scanning calorimetry (DSC) [63], Atomic force microscopy (AFM) [64,65], Dynamic method of thermal analysis (DMA) [66], Gel permeation chromatography (GPC) [67], mass spectrometry (MS) [68,69], and spectroscopy methods like nuclear magnetic resonance (NMR) [70], Infrared absorption (IR) [62,71], and X-ray diffraction analysis (XRD) [62]. These most available analytical methods cannot directly detect the degradation of biodegradable plastics or their constituent polymers at environmentally realistic concentrations in complex matrices such as soil. Therefore the results obtained from them have limitations for quantitative measurement of changes over time, especially when the degradation process is slow [72–75]. For example, visual detection and assessments of physical characteristics that provide information about alterations in appearance, hardness and tensile strength, may not be indicative of shifts in conformation, changes in functional groups, or bond breakage at susceptible polymer regions. Additionally, gravimetry has low sensitivity, making it impractical for slow degradation processes with insufficient decomposition products. Gravimetric analysis can also produce misleading results if a polymer fragments into small particles that are lost during handling but not fully degraded. This may falsely suggest complete degradation, leading to an overestimation of biodegradability and false positive results. FTIR and X-ray photoelectron spectroscopy (XPS) are qualification tools, primarily indicating shifts in functional groups subsequent to degradation. So, due to their inherent limitations, these techniques cannot be used in isolation [76]. This is precisely where scientists can benefit of the sensitive radiolabeling technique as the only reliable method to directly find out what will happen when plastics are discarded into the natural environment, and enable the determination of the actual degradation [77,78]. The Table 1 summarize advantages and limitations for different analytical methods in polymers degradation studies.

The application of ^{14}C is stands out as a distinctive tool for fate studies, due to its capacity for facile substitution with non-radioactive carbon in the exact location of desired molecules without making any changes in the structure and physico-chemical properties of polymer [79]. This isotope possesses a half-life of 5730 years. So, it is sufficiently stable for prolonged-term investigations with sensitivity exceeding 0.001 % [80]. Therefore, adjustment for decay is not necessary when employing it for long-term fate studies, and a small amount of sample is enough for analysis. Notably, this atom emits low-energy β -particle radiation (specifically, electrons with an average energy of 56 keV) [81]. These characteristics not only make this method safe for laboratory analysis, but also enabled to measure very slow degradation rates over short time intervals. Considering the experiment's objectives, the position of the radiolabel is a critical factor and should be chosen thoughtfully. In general, it is advisable to place the labeled carbon atom within the most resistant portion of the molecular structure. This ensures that, following degradation analysis, it can be presumed that the entire molecule undergoes mineralization [82]. So, the interpretation of results will be simplified [83].

The products of polymer degradation can be categorized into three groups: mineralized carbon in the form of CO_2 , biomass resulting from microbial activity, and residual polymers in the environment [73,84,

Table 1
Comparison of analytical methods for polymer degradation studies: advantages and limitations.

Analytical method	Advantages	Limitations
Optical Detection	Simple, non-destructive, low-cost.	Provides limited chemical or structural information; cannot detect molecular-level changes.
Gravimetric Analysis	Simple, direct method for mass loss measurement.	Low sensitivity: can be misleading if polymer fragments but does not degrade completely; may result in false positives.
Differential Scanning Calorimetry (DSC)	Provides insights into polymer stability, crystallinity, and thermal transitions.	Cannot directly track chemical changes; limited to thermal properties.
Atomic Force Microscopy (AFM)	High-resolution imaging of surface changes.	Only provides surface information; does not reveal bulk degradation.
Dynamic Mechanical Analysis (DMA)	Tracks changes in mechanical properties over time.	Limited to mechanical changes; no direct information on chemical degradation.
Gel Permeation Chromatography (GPC)	Effective for tracking changes in polymer molecular weight and chain scission.	Requires complex instrumentation; does not provide detailed chemical information.
Mass Spectrometry (MS)	Highly sensitive; can identify small degradation products.	Requires complex sample preparation and analysis; may not detect large fragments.
Nuclear Magnetic Resonance (NMR)	Provides detailed molecular-level information.	Limited to soluble degradation products; requires specialized equipment.
Infrared Spectroscopy (IR)	Sensitive to chemical changes in functional groups.	Qualitative; may not quantify the extent of degradation accurately.
X-ray Diffraction (XRD)	Identifies structural changes in crystalline regions.	Not useful for amorphous polymers; requires crystalline materials for analysis.
X-ray Photoelectron Spectroscopy (XPS)	Provides surface-level chemical information.	Limited to surface analysis; doesn't reveal bulk degradation or structural changes.
Radiolabelling (C-13 and C-14)	Provides direct insight into degradation mechanisms and pathways; allows for tracking over time.	Requires specialized handling and safety precautions; can be costly; may not reflect behavior in non-labelled materials.

85]. Unfortunately, all polymers degradation literatures and even contemporary standard methods do not provide comprehensive insights into these three parts, albeit the following simple formula is generally used to calculate the decomposition percentage.

$$\text{Biodegradation degree \%} = \frac{\text{Evolved CO}_2 \text{ in the sample chamber} - \text{Evolved CO}_2 \text{ in the blank chamber}}{\text{Theoretical CO}_2 \text{ value from the sample}} \times 100$$

Through this formula, only the evolved CO₂ is measured, and the obtained results are attributed to the degradability or non-degradability of the polymers. While we do not know how much polymers had remained at the end of an incubation period or whether these remaining carbons were present still in the original forms or whether microorganisms had already incorporated them into biomass.

If we just track the released carbon in the form of ¹⁴CO₂ from their

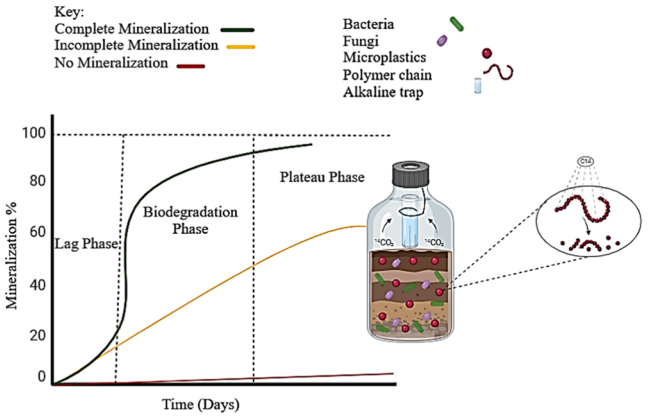


Fig. 4. Three different biodegradation trends in a schematic incubation chamber.

carbon chains, it can be graphed over time, revealing variations in three distinct phases (Fig. 4). The initial part represents a lag phase, demonstrating the time required for microbial colonization. The subsequent portion corresponds to degradation phase, while the third segment, the plateau phase, signifies the ultimate stage of this process. The configuration of the diagram can be different depending on the nature of the polymers and the environmental matrices [86,87].

Typically, degradation studies in soil are conducted within sealed incubation chambers with CO₂ free air flow, and detection systems (Fig. 4). Specifically designed instruments are commonly employed for radiolabelling techniques. The most widely utilized instrument in this field is liquid scintillation counting (LSC) [88], recognized as an indirect technique. In this approach, ¹⁴C in polymer chains through decomposition converts into carbon dioxide (¹⁴CO₂) and subsequently traps in a carbonate form within alkaline trap solutions, such as (NaOH, KOH, Ba (OH)₂ or ethanolamine). This solution needs to be combined with an organic solvent that is known as cocktails [89], creating the final solution that is introduced into the LSC device for analysis. During LSC analysis, the emitted beta particles interact with cocktail, resulting in the emission of photons. Then, these emissions can be quantified using photomultiplier tube (PMT) detectors. Given the inherently low concentrations of ¹⁴C in the atmosphere, the LS counter must adhere to specific technical criteria to effectively mitigate the impact of background effects [90].

Accelerator mass spectrometry (AMS) directly measures the presence of ¹⁴C isotopes. Once the sample is converted into graphite, its atoms are transformed into high-energy ions, and accelerated within an electric field to precisely quantify ¹⁴C counts. Despite its high sensitivity, the complexity of AMS technology, along with its associated cost, limits its application [90].

Beta-ionization (BI) is an alternative indirect method for detecting

beta particles. Unlike LSC, BI counting takes place in a gas counter, where beta particles are measured as electrical pulses generated between high-voltage electrodes. However, this approach is less commonly used for analysis of bio-based products due to a counting time of several days, and limited accessibility of BI instruments [91].

3. ¹⁴C labeling studies limitations

Despite all advantages of ¹⁴C-labelling, its use is limited and often impractical for various reasons. In many countries, there are concerns about handling and disposal and management of radioactive waste. So, new efforts to focus on creative ways for recyclability of radioactive waste is crucial [81]. Moreover, accessibility of the measurement device (LSC) is restricted, because it is specifically designed for radioactive radiation measurements and not universally available in all laboratories [22,92]. Soluble radioactive residue during the synthesis stage poses another issue, potentially leading to positive errors or overestimations during measurement [79]. Furthermore, the inherent electron emission of the ¹⁴C isotope, when compared with the stable ¹²C and ¹³C isotopes may induce covalent bond cleavage, giving rise to the formation of by-products. This phenomenon is termed radiolysis in the literature [81, 93]. On the other hand, it is still difficult or expensive to access to a large number of radiolabeled monomers to make desired polymers [81]. These challenges are mainly related to the fundamental source of the ¹⁴C-radioisotopes is generated in nuclear reactors as Ba(¹⁴C)CO₃ and through a series of consecutive reactions, it is transformed into the desired molecule [94]. This production route is not without drawbacks; it demands rigorous waste management, synthesis process is time-consuming and quiet expensive and needs safety regulations.

4. Standard methods for ¹⁴C determination

Radiolabeling tended to be used for degradation studies when standard methods are insufficient [83], but Organization for Economic Co-operation and Development (OECD) has provided guidelines for aerobic and anaerobic transformation [95,96], leaching [97], photo-transformation [98,99], and chemical degradation of substances in various matrices that they also can be used for radiolabeled materials [100-104]. For example, ISO 14855-2:2018 introduces a method for determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions [105]. Unfortunately, there are standard methods for investigating the degradation evaluation for ¹⁴C-labeled plastic materials over time in different matrixes that now are withdrawn, such as ASTM D6340-98(2007) [106] for aqueous or compost environment, ASTM D6692-01 [107] for Seawater, D6776 [108] for a laboratory-scale simulated landfill [109]. The crucial aspect concerning these methods and standards is that the criterion for determining whether a polymer is degradable revolves around the environment rather than the substance. Therefore, each of the existing standard methods pertains to the polymer's decomposition in general within a specific environment [110].

5. An overview of degradation studies for ¹⁴C-labeled polymers

The first individual to recognize the significance of employing radiolabelling for studying polymer fate in complex environments was Nykvist [111]. His report on the biodegradation of low-density polyethylene gained considerable attention when it was presented at the 'Degradability of polymers and plastics' conference in 1973 [111]. Prior to this, he had dedicated over five years to study polyethylene degradation both in and on the soil surface, without yielding any reportable results. Consequently, he opted to employ radiolabelling as a technique to differentiate between CO₂ produced by polyethylene degradation and that originating from other carbon sources in the soil. Relevant papers about carbon radio labelling for synthetic and natural polymers are summarized in Table 2 and the mineralization of various polymers using the ¹⁴C-labeling technique is compared in Fig. 5. These box plots describe the total degradation of polymers using minimums, maximums, and mean values without considering degradation time scale and other influencing factors.

Analysis of all polymers was performed using LSC, except for poly (ε-caprolactone) (PCL) [130] and poly(butylene succinate) (PBS) [130] which were analyzed using the Accelerator Mass Spectrometry (AMS) method. Sadly, the results from Nykvist's research on the degradation study of low-density polyethylene were disregarded due to the use of beta radiation to describe degradation levels instead of the percentage of ¹⁴CO₂.

Studies have been conducted under effects of various physical, chemical, and biological factors, including environmental conditions (UV light exposure, ozonation, heat, fungi, invertebrates and variety of matrices) as well as polymer compositions (chemical structures, different molecular weights, shapes, sizes and additives). The highest mean level of decomposition is reported for high density poly(tetramethylene adipate) (H-PTMA), followed by PCL, L-PTMA, and PBS. The rate of mineralization for different types of polystyrene (PS) and high-density polyethylene (HDPE) is very low. The mean values for mineralization of low density polyethylene (LDPE), LDPE with starch and poly (ethylene-co-vinyl alcohol) (EVOH) [122] are nearly identical, while this number is twice as high for ecolyte LDPE. This ratio also applies to polystyrene and ecolyte polystyrene low-density polymers are more branched, making them more flexible and less dense. They have lower crystallinity, tensile strength, and melting points compared to high-density polymers, so they typically degrade more easily than the latter [134]. Low density polyethylene (LDPE) exhibited its highest level of decomposition after exposure to UV radiation for 27 days with a 5 % UV sensitizer, followed by a subsequent 10-year decomposition period [118]. Additionally, polystyrene in nanoparticle form, when subjected to UV radiation at a wavelength of 254 nm, exhibited a high decomposition rate in both water and air [128]. This is also shown in the case

Table 2
¹⁴C-labelled plastics degradation studies

Polymers	References
Polyethylene	Nykvist [111], Albertsson. [112], Albertsson. [113], Albertsson and Ranby [114], Albertsson; Ranby . [115], Albertsson. [116], Albertsson. [117], Kaelsson, et al. [118], Albertsson & Karlsson. [119], Albertsson, et al. [120], Albertsson & Karlsson. [121], Erlandsson, et al. [122], Guillet, et al. [123]
Polystyrene	Guillet, et al. [124], Sielicki, et al. [125], Kaplan, et al. [126], Tian, et al. [127], Tian, et al. [128], Tian, et al. [74], Guillet. [123]
Poly(methyl methacrylate)	Kaplan, et al. [126]
Poly(tetramethylene adipate)	Albertsson and Ljungquist [129]
Ethylene-vinyl alcohol (copolymer)	Erlandsson, et al. [122]
Poly(ε-caprolactone)	Kunioka,et al. [130], Federle, et al. [131]
Poly(butylene succinate)	Kunioka, et al. [109]
Cationic polyacrylamide copolymers	Hennecke, et al. [132]
Polyhydroxybutyrate- polyhydroxyvalerate	Luzier [133]
Poly(3-hydroxybutyrate-co-3- hydroxyoctanoate)	Federle, et al. [131]

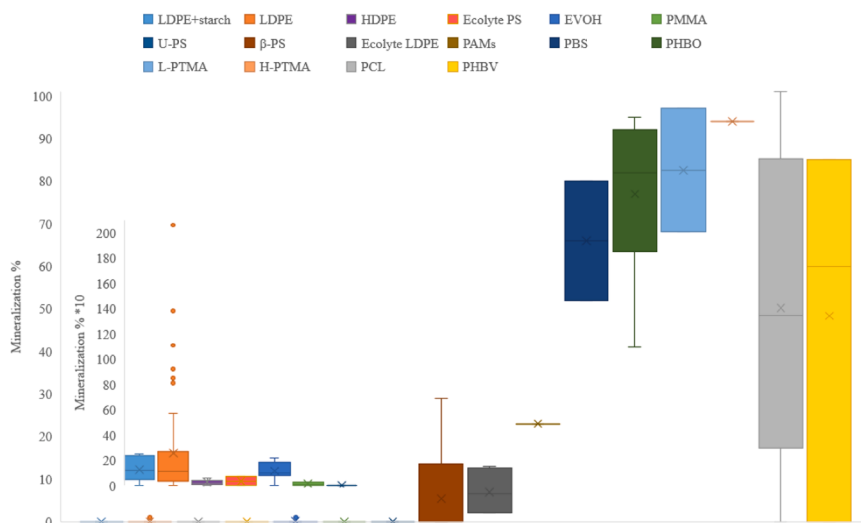


Fig. 5. The percentages of mineralization for low density polyethylene (LDPE), high density polyethylene (HDPE), polystyrene (PS), ethylene vinyl alcohol (EVOH), poly(methyl methacrylate)(PMMA), cationic polyacrylamide copolymers (PAMs), poly(butylene succinate)(PBS), poly(3-hydroxybutyrate-co-3-hydroxyoctanoate) (PHBO), low density Poly(tetramethylene adipate) (L-PTMA), high density Poly(tetramethylene adipate) (H-PTMA), poly(ϵ -caprolactone) (PCL), and polyhydroxybutyrate-polyhydroxyvalerate (PHBV). The percentage of mineralization for polymers with low decomposition rates was multiplied by ten in a separate graph to provide a more accurate representation.

of the polyhydroxybutyrate-polyhydroxyvalerate (PHBV) copolymer film, which was buried in two types of soil for eight months. This polymer is biodegradable in microbially active environments and stable in humid air [133]. The degradation study of cationic polyacrylamide copolymers (PAMs) in loamy sand soil in an outdoor lysimeter shows a slow degradation rate, with no vertical movement in the column for the top 10 cm soil layer after 3 years [132]. It is evident that in the absence of physical and chemical factors facilitating polymer decomposition, negligible or minimal decomposition is observed. The estimated average annual degradation rate, in percentage, for non-degradable or slowly degradable polymers from previous studies is shown in the graph (S2).

6. Critical considerations in long-term polymer degradation studies

The half-life of ^{14}C is a key factor to conduct mineralization studies for an extended duration, ranging from days [128] to more than 10 years [118,121], without a significant loss in the intensity of received signals. Therefore, the duration of the test can be determined based on the objectives of projects and factors influencing degradation. It is suggested to continue studies as long as the degradation process reaches its conclusion, as indicated by the plateau phase (Fig. 4), fully observing the entire degradation process [129].

The influence of the synthetic process and the use of catalysts and additives during the production process of the labeled polymer have received less attention, and there have been fewer attempts to compare the active or weak points of the polymer during the degradation process through selective labeling [74,124,127]. Some polymers react to pH changes due to their structures and also some microorganisms behave differently in pH range [135–137]. With this understanding, pH in the environment can be monitored and controlled to achieve the desired results.

Any agent used to degrade plastics must be fully explained. For example, if plastics are exposed to UV radiation before the degradation process, the duration and intensity become important factors. Alternatively, the types and number of microorganisms must be defined in advance. The biodegradation process with a mixed population of microorganisms is generally more effective than pure cultures of single strains [112,113]. When microorganisms are used in the test, their effects should be compared with sterile systems to account for aging

effects.

To make a realistic comparison between the degradation rate of synthesized plastics in the lab and commercial products, determination of molecular weight is necessary. Apart from this factor, the size of the polymer particles and the ratio of the amount of polymer to the environment must be clearly defined. The higher the amount of plastics in the environment, the lower the degradation rate [112]. It is necessary to have positive and negative blanks, measuring the background radiation and monitoring samples without matrix, to show the effect of oxygen and isotope radiations. In some research, to calculate the amount of CO_2 before preparing a sample for LSC analysis, titration with acids or weighing the alkaline trap solution, which converts CO_2 to carbonate precipitation to relate the increase in weight to the amount of CO_2 , had been conducted [109].

To prevent overestimation or underestimation of the results, a comparison between lab and natural conditions is needed. In soil studies, a point that has not received much attention is the effect of the ratio of nitrogen to carbon in the soil matrix on the polymer degradation process, which can indicate the activity of microorganisms. This factor can be controlled by adding fertilizer [138]. The displacement and transmission of polymer particles through leaching in the environment and their impact on the growth of plants or other living organisms have not been thoroughly investigated [87,92,139,140]. In biodegradation studies, the challenge lies in establishing a reliable biological system that can operate under controlled conditions for extended periods [114]. An anaerobic environment could develop inside the flask during incubation, leading to a lower decomposition rate [125]. Therefore, it is crucial to continuously aerate the system. After the termination of the experiment, the fungal and bacterial life present in all vessels should be measured and compared to the beginning [112].

Plastics can be converted into smaller particles when placed in the environment, even if there are no microorganisms present. Therefore, experiments showing the effect of particle size on autoxidative processes, due to increased access to oxygen, for polymer powder with varying mesh sizes under abiotic aging conditions are suggested. Additionally, to better understand the environmental fate of nanosized plastic particles, long-term experiments under natural or simulated solar radiation are needed. The influence of inorganic ions and natural organic matter on the photodegradation of nanoplastics should also be considered [92,128].

Most of the tests were conducted on homopolymers, and less attention was paid to copolymers [122]. The application of this technique can also be used to investigate the fate of polymer additives, including plasticizers and photostabilizers, as well as water-soluble synthetic polymers [18,113,122]. Polymers with different concentrations of the ^{14}C -isotope should also be compared to study radiation-induced reactions [112,114].

In laboratories degradation studies, alkaline liquids such as NaOH, KOH, and $\text{Ba}(\text{OH})_2$ are chosen as trap solutions, but the reason for this choice or the advantage of each over the other, based on their concentration and adsorption capabilities, was not compared. Generally, if the degradation experiments based on radiolabeling are designed correctly, it means that the complete synthesis route is described, and an attempt is made to identify the factors affecting degradation based on the type of polymers. To check the reproducibility of reactions, it is necessary to have at least 3 to 5 repetitions for measurements. In order to obtain a more accurate picture of degradation, it is very important to benefit from qualification examinations alongside LSC, such as IR, GPS, SEM, and XPS, to trace structural changes during the test [127]. Details make it possible to repeat the experiment and achieve consistent results for further research. Extensive and comprehensive studies may alter our perception of the harmlessness of certain bioplastics in the future.

7. Stable isotope vs radioactive isotope

^{13}C is recognized as a stable alternative to ^{14}C . The degradation studies of polymers using ^{13}C is almost a new topic [141]. The utilization of stable isotopes eliminates the risk of radioactive contamination, so restrictive regulations is not needed anymore. In polymer synthesis, ^{13}C -labelled monomers or precursors are readily accessible at reasonable prices. The application of stable isotopes is not only limited to the degradation studies in polymers, they also are used for characterization of real amount of polymer additives [142], reaction mechanisms of polymer stabilizers [143], transfer and transform nanopolymers in the environment [92], and the abundance of $\delta^{13}\text{C}$ can function as an indicator for identifying the source of raw materials, so classification of polymers to bio based or non-bio based become easy to distinguish [86, 144–146].

Quantification of stable radioisotopes involves coupling chromatography techniques with isotope ratio mass spectrometry (IRMS) or $^{13}\text{CO}_2$ -sensitive cavity ring-down spectroscopy, as demonstrated by studies [87,92]. Nowadays, the application of this isotope in transfer and transformation processes is well-established, particularly for naturally occurring biopolymers. However, studies involving ^{13}C -labeled plastics are not as extensive as they should be, primarily due to the unresolved issue of the availability of specialized and expensive measurement equipment in this field [92].

8. Conclusion

The selective partial or whole molecule labelled of carbon atoms within the polymer backbone, available as both ^{14}C (radio isotope) or ^{13}C (stable isotope), has simplified the interpretation of polymer degradation studies. Previous studies have shown that high molecular weight poly tetramethylene adipate (H-PTMA) exhibited the highest average decomposition level. Conversely, the mineralization rate for polystyrene (PS) and high-density polyethylene (HDPE) variants was notably low. It is clear that without physical and chemical factors aiding polymer decomposition, very little to no breakdown occurs.

There is a need to extend carbon radiolabeling application to a wider range of polymers by making more ^{14}C (or ^{13}C) labelled precursors available at a fair price for improving more synthesis routes. Furthermore, combining ^{14}C based technique with a variety of complementary analytical methods would enable more accurate assessment especially for biodegradable plastics. This would further clarify the final fate of plastics and their impact on the receiving environment and facilitate

more informed decisions for future risk management.

CRediT authorship contribution statement

Sara Adeleh: Writing – original draft, Visualization, Methodology, Formal analysis, Conceptualization. **Roland Bol:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization. **Tabea Becker:** Writing – review & editing. **Sonja Herres-Pawlis:** Writing – review & editing, Supervision. **Harry Ver-ecken:** Writing – review & editing. **Thomas Pütz:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.polymdegradstab.2024.111053](https://doi.org/10.1016/j.polymdegradstab.2024.111053).

Data availability

No data was used for the research described in the article.

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