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How to measure polymer degradation? An analysis of authors choices when calculating carbonyl index

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Abstract

The carbonyl index (CI) aims to measure the degradation level, and it is used in plastic degradation research as a proxy for the general degradation level of collected plastic pieces. According to the choices for CI calculation, comparison using this index is prevented, and it must be unveiled by the authors, which does not always happen. Herein, we systematically reviewed the methodologies used to determine CI for polypropylene as a case study. Based on 90 studies gathered from 2000 to 2023, two main methods were used to determine the CI: the ratio between the carbonyl band area and the reference band area (31.82%) and the ratio between the highest intensity of the carbonyl band and the reference band (68.18%). The reference band of choice and the type of the calculation method produce different values and mean different information, preventing the comparison among works with different conditions of CI calculation.

Keywords: Polymer degradation, Carbonyl index, Polypropylene

1 Introduction

The Anthropocene, defined by human-induced environmental transformations, presents a critical challenge: plastic pollution, one of recent decades' most widespread and enduring features. As proof of its pervasiveness, plastic waste and its adverse effects have been documented in every iconic environment, from mountain tops to the bottom of the sea, across cities, and even suspended in the atmosphere.[1] Additionally, one of this era's main features is investigating and understanding the changes that occur on the surface of these materials.[2] The perception of such modifications is significantly relevant in the integrity of their applicability and the estimation of their harmful effects on the environment.[2,3] Once plastic materials are exposed to ecosystems, they are subject to adverse weather conditions such as rain, solar radiation (ultraviolet), physical abrasion, and microbial effects. Such conditions can cause photodegradation, thermal degradation, wear, and abrasion on the surface of these materials and consequently cause embrittlement and fragmentation into smaller particles (micro and nanoplastics).[3] These processes cause chemical changes that degrade the surface of materials through a series of oxidative reactions in the polymer chain, modifying its composition, structure, and properties.[4,5]

One of the main techniques used to monitor chemical changes on the surface of plastic materials has been Fourier-transformed infrared spectroscopy (FTIR).[6–8] This approach allows the detection of functional groups of the substance through distinct absorption bands. [6–8] For this, it is customary to calculate the ratio between the area or intensity of a band that varies as a function of a stimulus to another not sensitive to the same stimulus, known as the reference band.[6] In plastics research, perhaps the most common example of this approach is the carbonyl index (hereafter called CI), which measures the intensity or the area of the carbonyl band compared to the intensity or the area of a reference band. From this perspective, the CI has been used for several purposes, such as the evaluation of resistance to degradation through extrusion processes[9], the assessment of the resistance of

recycled and reprocessed materials[10], the development of stabilizers and formulations[11] and the prediction of the useful life of a material[12].

Initially suggested by Mellor et al., (1973)[13], the CI specifically monitors the absorption band of carbonyl species as one of the main degradation products formed during the oxidative degradation processes of polymers. This region results from the convolution of at least three main bands[14], attributed to photoproducts that absorb in the same region, that is, carboxylic acids in dimer form (~1712 cm^{-1}), esters (~1735 cm^{-1}) and γ-lactones (~1780 cm^{-1}). Using this approach, Rouillon et al. (2016)[7] reinforced the evidence that the formation of different carboxylic species and maximum absorption peak vary according to the degradation time. After 40 h of degradation, the formation of bands with maximum absorption peak began, referring to dimeric acids (1712 cm^{-1}), which prevailed as a maximum until reaching 80 h of degradation. After 80 h, a progressive change in the maximum absorption of dimer acids to esters was observed, which prevailed until the full-time study (150 h). Although the γ-lactone species appeared within 40 h of degradation, at no point in the degradation experiment were these carbonyl species between the maximum absorption peaks. Furthermore, it was observed that the concentration of these degradation products is directly proportional to the degradation time when comparing similar formulations.[7,14]

Regarding the studies of plastic pollution from varied sources subjected to distinct weather exposures, it is impossible to estimate this exposition time because there is no experimental control and no information about the type and concentration of stabilizers. In that case, CI can be a proxy of the degradation level but not any more of the degradation time. With the growing investigation on the impact of plastic materials in the environment and the related characterization, some studies still apply IC for this purpose.[15–17] For example, the CI PP from microplastics found in sediments was used to relate the level of degradation to the season. In addition, the CI of PP microplastics found in marine sediments near the port of Cartagena (southeast Spain) was used to relate the level of degradation with the different marine environments where the sampling was carried.[15] Celik et al. (2023)[16]

determined the CI of PP microplastic particles in several seas around Japan to correlate the level of degradation and the different regions. In this sense, to check the proper usage of CI to monitor polymer degradation and whether the CI can be used for comparison among studies, we performed a systematic review of the literature to follow how it is calculated and used.

2 Methodology

2.1 Literature Search

The literature search was performed on Web of Science with the word "polypropylene" in the title and the expression "carbonyl index" in the topics, which encompasses the title, the abstract, the author keywords, and the "keyword plus." According to the Web of Science Help section,[18] "KeyWords Plus" indexes terms automatically generated from the titles of cited articles. The outputs were limited for the Language "English" from 2000 to 2023, September 19th. The search yielded 107 records assessed for eligibility by reading the titles and abstracts; we also read the main text when necessary. The studies that did not calculate the carbonyl index were excluded. After the screening, 90 articles were gathered for analysis (**Fig. 1**). The degradation type categorization was done by gathering equivalent expressions to the pertinent categories (details shown in Supplementary Material **Table 1**).

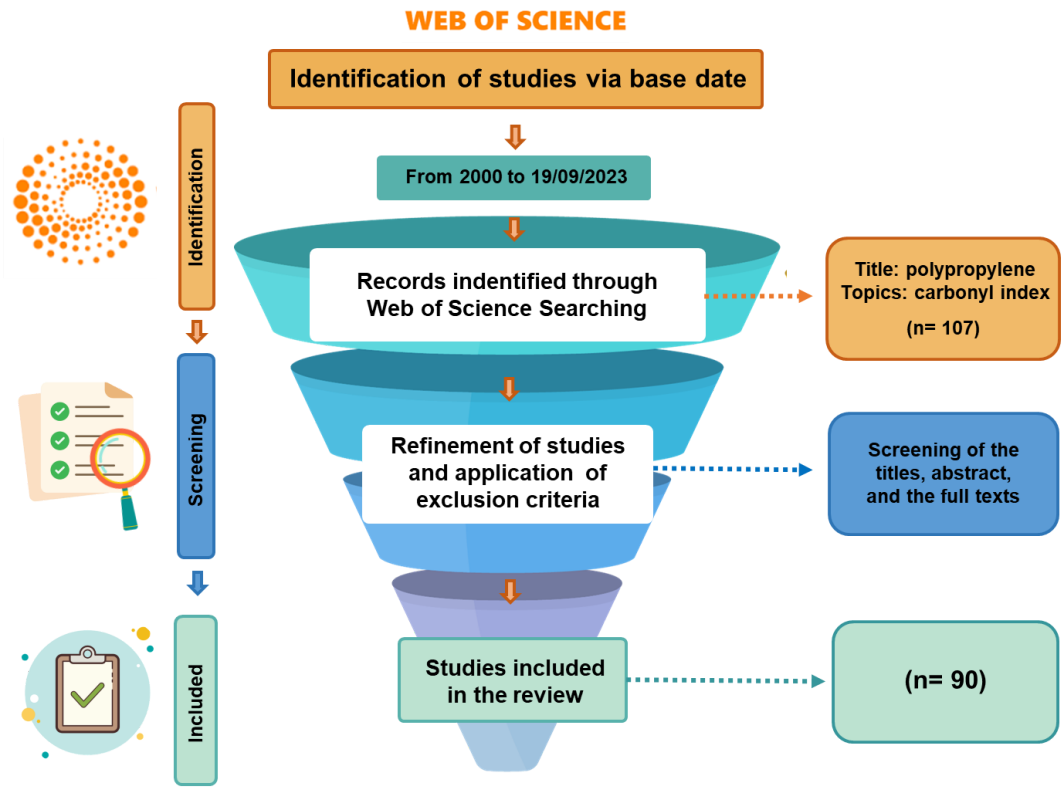

Fig. 1. The pipeline for the literature gathering to find and analyze studies using the carbonyl index in polypropylene materials.

3 Results and Discussion

Since studies on plastic pollution usually cite or learn the calculation protocols from the polymer degradation research, we based our review on the general literature calculating the carbonyl index without limiting our search to words like microplastic or pollution. Doing so, we gathered all the literature that calculated the CI and could assemble the discussion about the choices of the authors.

3.1 Framework characterization of the gathered literature

The distribution of the papers using CI to track the degradation level in polypropylene-based materials was 53.3% for polypropylene alone and 46.7% for multicomponent materials: 36.7% for composites and 10% for blends (**Fig. 2a**). **Fig. 2b** is representative of the degradation types encompassing formation of carbonyl as part of the mechanistic evolution, with more than 40% of the studies in the context of indoor photodegradation, and only 20% of the experiments performed in outdoor environment. Notably, some studies performed more than one type of degradation, so the percentage will exceed 100% (**Fig. 2b**).

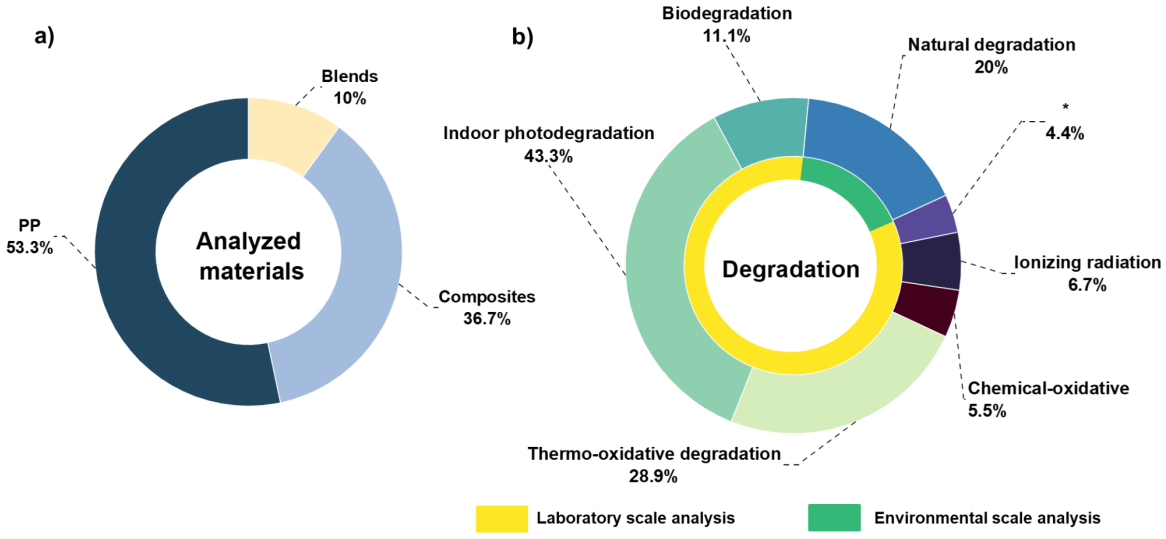

Fig. 2. Percentage of publications distributed according to a) material type and b) degradation type.

The predominance of indoor degradation experiments (**Fig. 2b**) is due to the need for better and more reliable assessment under accelerated and controlled conditions in a shorter period.[11,12,19–42] These experiments provide experimental data to indicate optimal parameters for the best adjustment of products and processes that delay degradation and increase lifespan, improving recycling conditions and formulation.[11,12,19–42] On the other hand, exposition to the weather in outdoor degradation experiments allows better prediction of how properties change as a function of degradation time in realistic conditions, although the experiments take longer. While indoor experimental conditions provide essential information and predictions regarding the behavior of materials under such controlled experimental conditions, laboratory experimental tests do not encompass all conditions of a true-to-life environment. For instance, Rajakumar et al. (2009)[43] determined the CI of PP films that were directly exposed to the natural environment where they were exposed to the weather and the related conditions such as the entire solar spectrum radiation, not only the UV-A range, beyond rain, wind, and temperature variation as a function of the time, which influence the degradation.

According to the articles assessed, CI was the method employed to determine the degree of degradation of plastic materials. In these studies, the materials were exposed to mechanical forces, saline environments, solar radiation, rain, wind, and various temperatures. The environment where the material is exposed to degradation is a significant factor when evaluating CI, as the stressors to which plastics are subjected can directly influence the result. Photodegradation, for example, typically occurs on the surface of plastic materials, so the degree of deterioration can be higher on the surface of the plastic and lower in the inner regions of the material.[7,16] Then, a single material tends to have a deterioration gradient and, consequently, a CI gradient. Additionally, since photodegradation promotes the breaking of chemical bonds and the increase of crystallinity, the materials change, enabling cracks and peeling of the surface, which leads to fragmentation into smaller particles (micro and nanoplastics). This fragmentation can cause an underestimated CI value of the polymer matrix since the most degraded region undergoes fragmentation, leaving the matrix and being remained the former inner layer, which is less degraded.[16]

3.2 Determination of carbonyl index

Several sample features can interfere with the final spectra obtained by FTIR, like roughness, scattering radiation, or thickness, for increasing the optical path. Since the entire spectrum will be homogeneously affected by those features, one approach to overcome this difficulty is the calculation of ratios between a band that changes as a function of a treatment one wants to measure and another band, called the “reference band,” which does not change as a function of this given treatment.

Fig. 3 shows the characteristic spectrum of pristine and degraded PP with bands analyzed in the spectral range from 4000 to 500 cm^{-1} and band assignments. In the pristine material, all the characteristic bands of PP are observed; however, bands are absent in the carbonyl region. On the other hand, in the degraded material, in addition to the characteristic bands, there is the convolution of carbonyl species

bands that result from degradation products formed during the material degradation process. To calculate CI, the evolution of the absorption band of carbonyl species in the range of 1850-1650 cm^{-1} is precisely monitored (highlighted in orange in **Fig. 3**).

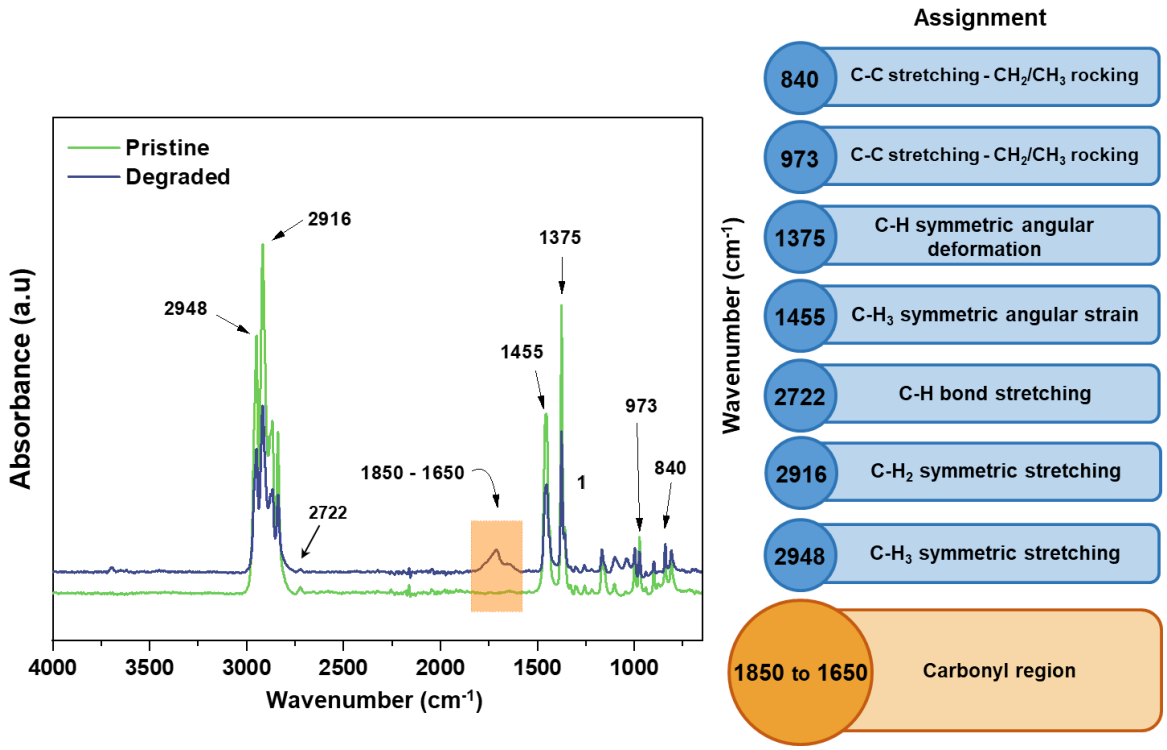

Figure 3. FTIR spectra of PP with the band's assignment.

Fig. 4a presents the results gathered from the 90 papers using CI as a measurement to monitor oxidative degradation. Here, 98.88% of the collected studies did inform the methods used to obtain the CI, and two main methods were identified. The first method is the ratio between the highest intensity of the carbonyl band and the intensity at the peak of a reference band, with 68.8% of the occurrences (**Fig. 4b**); the second method is the ratio between the carbonyl band area and the reference band area, which accounted for 31.1% of the studies (**Fig. 4c**). Noteworthy that some studies performed more than one method used to obtain the CI so that the percentage will exceed 100%. Both methods have

advantages and disadvantages. Using the peak intensity is simple, as it only uses the intensity recorded at the maximum wavenumber of the band, whereas using the area of the whole band can be complicated due to the baseline inclinations.

Regarding the calculation step, the usage of the peak intensity decreases the chance of overlapping with other bands attributed to contaminations like other polymer components, as in blends or composites, additives in higher concentrations, or organic matter adhered to the microplastic surface, like humic substances or biofilms. In contrast, because it occupies a broader range of the x-axis, the band area has a higher chance of overlapping with such contaminants, making it harder to accurately calculate. Regarding the variety of carbonyl types, since we know several carbonyl types are due to polymer degradation, choosing only one peak intensity to measure the photodegradation does not capture the diversity and complexity of the degradation products. For that purpose, the band area is a better choice if the contamination presence, as mentioned above, allows it.

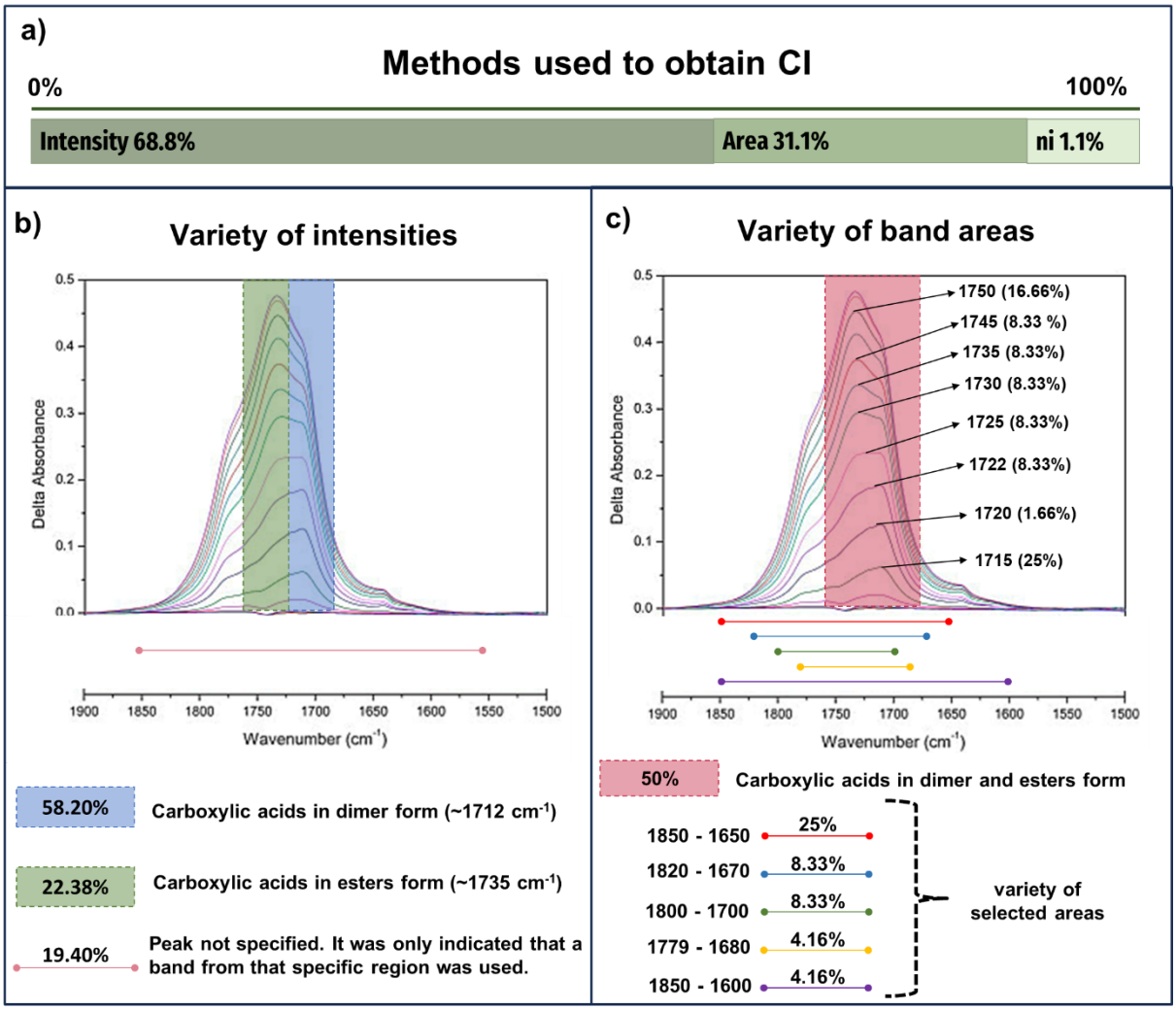

Figure 4.(a) Distribution of studies that used area or intensity. The value exceeds 100% because one of the studies used both methods, (b) variety of intensities used, and (c) variety of areas used. Reprinted from *Polymer Degradation and Stability*, 128, C. Rouillon,P.-O. Bussière, E. Desnoux, S. Collin, C.Vial, S. Therias, J.-L. Gardette, T. Is carbonyl index a quantitative probe to monitor polypropylene photodegradation?, Pages 200-208., Copyright (2023), with permission from Elsevier (Order number: 5693730725023). Publisher tax ID: GB 494 627212. https://myaccount.copyright.com

It is noteworthy that for the peak intensity approach, 19.4% of the works did not disclose the peak wavenumber (**Fig. 4b**). As discussed before, because of the

diversity of carbonyls formed as a function of the exposition time[14] the same piece of plastic can have different predominance of carbonyls after other times of degradation. That is the reason behind the variety of carbonyl wavenumbers chosen for the calculation of CI. For microplastic research, it is essential to disclose this information to enable further meta-analysis on the variety of carbonyls and advance the knowledge about polymer degradation in various weathering conditions outdoors. The use of the carbonyl band area (31.8%) considers the integration of the entire area of the wavenumber, and a wide variety of ranges were observed (**Fig. 4c**). Although this approach finds a large part of the degradation products formed to calculate the CI, the comparison between the results becomes inconsistent or imprecise given the variety of ranges in different regions used in the works. Additionally, 50% of the studies that mentioned using the carbonyl band area did not use a range of wavenumbers but only the area of a single wavenumber of interest (**Fig. 4c**).

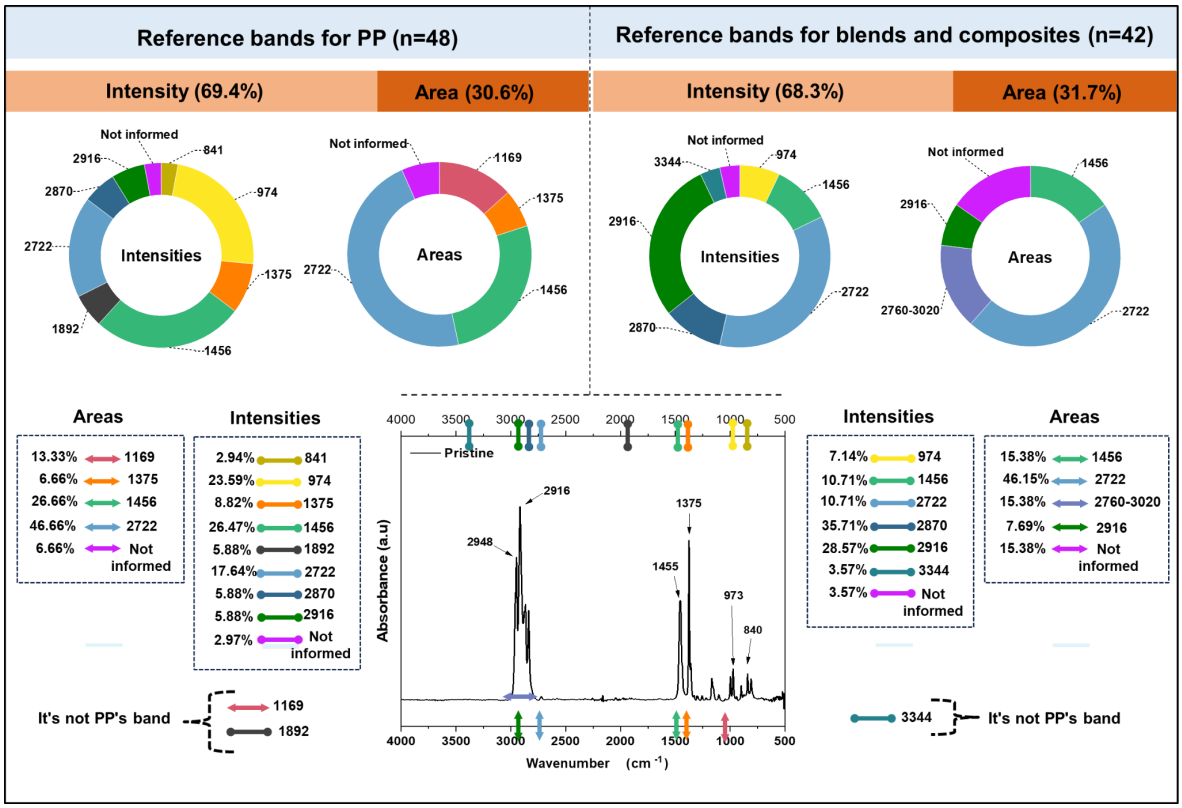

Figure 5. Distribution of the main reference bands used for PP and blend/composites according to CI calculation methods. At the top of the PP spectrum, the shapes with circular ends represent studies that used the band intensities. At the bottom of the PP spectrum, the shapes with triangular ends represent studies that used the band areas. The horizontally arranged shapes represent a strip of bands.

In addition to the choices regarding the carbonyl band, there are also various choices regarding the reference bands (**Fig. 5**). For an overview of the type of reference bands; we group them according to band similarity (details shown in **Table 2** of the Supplementary Material). The most used bands as reference were the bands at 974, 1456 and 2722 cm^{-1} for the PP and those at 1456, 2722 and 2916 cm^{-1} for the blends/composites.

CI obtained using different reference bands cannot be compared since they use other chemical groups as denominators with varying coefficients of molar absorptivity. Given the mathematical operation, the values obtained can be greater

or lesser in the CI calculation stage with an invariable numerator and variable denominator. Consequently, there will be a difference in CI values to underestimate or overestimate the degradation states of the materials. Considering this premise, the reference band used must not vary with the degradative processes to which the materials are subjected. However, it can be anticipated that the reference bands are not necessarily inert or insensitive to context change, as is the case of the CH_3 band at ~1454 cm^{-1},[2] which decreases in intensity due to the formation of volatiles containing the pendant CH_3 groups, from PP. The degradation mechanism reported by Rouillon et al. (2016)[2] and Delprat et al. (1995)[1] indicate that the main volatile products are acetic acid and acetone, which carry the CH_3 portion in which a large part of these products migrate from the polymer phase to the gas phase, causing the IR absorption of CH_3 to decrease with exposure.

There is an increasing attempt to establish standards for CI use, application, and acceptable values. Consequently, the PAS 2019:2020 specification emerged to provide methods, deadlines, and criteria demonstrating that polyolefins containing biodegradable additives can decompose in outdoor terrestrial environments without forming microplastics. To this end, PAS 2019:2020 uses CIs as one of the main parameters determining whether this specific type of plastic decomposes and meets soil biodegradability requirements. According to the guideline, values greater than 1.0 in CIs after artificial or outdoor weathering indicate that the material will biodegrade in the soil without forming microplastic particles. However, although PAS 2019:2020 uses the second method identified in this study (area under the band) to monitor the carbonyl region, there needs to be a specification as to which reference band should be used. The lack of this information directly compromises the validity of this statement since, as previously discussed, the CI mathematical calculation is influenced by the reference band used. Furthermore, it was also discussed previously that several factors can influence the determination of CI, and many materials can exhibit a gradient of CIs. Therefore, it is necessary to consider several factors when standardizing the use of CI.

Additionally, it can be anticipated that the reference bands are not necessarily inert or insensitive to context change, as is the case of the CH_3 band at ~1454 cm^{-1} [2] which decreases in intensity due to the formation of volatiles containing the pendent CH_3 groups of PP.[2] The degradation mechanism reported by Rouillon et al., (2016)[2] and Delprat et al., (1995)[1] indicates that the main volatile products are acetic acid and acetone, which carry the CH_3 moiety in which a large part of these products migrate from the polymeric phase to the gas phase, causing the IR absorption of CH_3 to decrease with exposure.

4 Conclusions

The method using the area for the CI calculation takes into consideration the carbonyl diversity, whereas the intensity method takes into consideration the predominant form of carbonyl at the time of the measurement, which might change as a function of time. Additionally, the choices for the reference band influence the CI value, preventing comparison among different works. Finally, due to the lack of standards, some works are using bands not assigned to the polypropylene structure as reference bands, which is inadequate and biases the results.

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Authors Contributions

Raimara de S. Gomes: Conceptualization, Methodology, Investigation, Writing - original draft. Walter R. Waldman: Conceptualization, Methodology, Investigation, Writing - original draft. Andreia N. Fernandes: Investigation, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Statements and Declarations

- Conflict of interests

The authors declare that they have no conflict of interest.

- Data availability

The datasets generated and/or analyzed during the current study are available from the supplementary material **Table 3**.

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