



Importance of profile of volatile and off-odors compounds from different recycled polypropylene used for food applications

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ABSTRACT

Nowadays, polypropylene is one of the most common polymers used in the food packaging industry due to its good functionality and relatively low cost. Nevertheless, usage of plastic disposable packaging can be a generator of plastic pollution having negative environmental effects. A feasible solution for this issue would be to recycle. The polypropylene samples were submitted to two processes, forced contamination, and recycling, and they were analyzed by solid-phase microextraction gas chromatograph-olfactometry-mass spectrometry. 45 different volatile compounds were identified and 9 of them presented distinct odoriferous activities. Among them, two important markers were detected: diethyl phthalate (probably coming from the catalyst of PP polymerization, intentionally added substance (IAS)), and glycerine (a marker of non-intentionally added substances (NIAS)).

1. Introduction

The production of thermoplastic resins was 7.2 million tons in 2017, according to the data from the Brazilian Packaging Association (ABRE). Whereas, the production in The European Union was 64.4 million tons, in the same year (Associação Brasileira de Embalagens – ABRE, 2018). Polypropylene (PP) consumption has shown the highest growth worldwide due to its versatility along with its good processability and relatively low cost. Polypropylene or poly(1-methylethylene) is a linear hydrocarbon polymer and a semi crystalline thermoplastic. The polymer chain consists of a backbone of two carbon atoms with attached hydrogen atoms, linked to every other carbon atom with a pendent methyl group. The methyl group can assume special arrangements about the carbon chain. However, the commercial PP presents the methyl group arranged along the same side of the chain assuming the isotactic form (Tice, 2002). Together with polyethylene terephthalate (PET), PP is also one of the most used polymers in the food packaging industry, for example, containers (pot noodles, margarine, cottage cheese, etc), orientated films bags to packaging pasta, rice, and sugar, films pouches for spices and sauces, dried and liquid soups, and others (Tice, 2002).

Nevertheless, its disposal might cause serious environmental issues.

Reusing, reducing and recycling are sustainable ways to partially solve this environmental problem.

However, the use of recycled materials for direct food contact has some restrictions regulated by international agencies such as the Food and Drugs Administration (FDA) (US Food and Drug Administration (FDA), 2006) in the United States, the European Regulations N° 1935/2004; 10/2011 (Union Europea, 2004, 2011) and 282/2008; the National Health Surveillance Agency (ANVISA) (ANVISA, 2010) in Brazil and Mercosur (Direto, 2004; MERCOSUR, 2005). In all of them, the restriction is directly related to possible contamination of food from the recycled material (e.g. pesticides, cleaning products, solvents).

Thus, the use of recycled materials for food contact requires the approval and permission of the competent health authorities. If new technologies can decontaminate and/or reduce the migration of contaminants, the use of recycled material for applications in the food packaging industry becomes feasible.

Over the lifecycle of the polymer, non-intentionally added substances (NIAS) may be formed, such as degradation products from both the polymer and its additives, impurities, or the reaction between them (Nerín, Alfaro, Aznar, & Domeño, 2013). Both Intentionally added substance (IAS) and NIAS can have odoriferous characteristics that

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interfere in the properties and quality of food in contact with packaging (Nerín & Wrona, 2018; PlasticsEurope, 2011). For a long time, the presence of NIAS was ignored, but since 2011 they are included in the EU Regulation (10/2011) (Union Europea, 2011).

Many studies on food-grade recycled material have been conducted (Demets et al., 2020; Sadler et al., 1996) and several technologies for recycling polymers, mainly PET, are nowadays available and currently applied at the industrial level. However, the case of polyolefins is different, as the efficient removal of contaminants is much more difficult, due to the high sorption capacity of polyolefins compared to that of PET. This means that some compounds, even at very low concentrations, could remain in the recycled PP, affecting its safety and quality. Among the potential compounds, IAS and NIAS, some of them odorous compounds, could be trapped in the recycled PP.

To maintain food quality, changes in its organoleptic properties must be avoided and nutritional compounds must be preserved. These changes may be related to the interaction between the substances present in packaging and food. The presence of off-odors is critical concerning recycled polymers. The presence of degradation products and contaminants results in an increase in NIAS due to high temperatures and shear rates employed in the recycling process, and the possibility of the interaction between the compounds formed (Vera, Canellas, & Nerín, 2019). Besides, literature shows that these odoriferous compounds may come from the exposure of the packaged food to high temperatures, which produces a significant loss of quality of the food (Úbeda et al., 2017).

The importance of analyzing and quantifying NIAS and IAS in food packages, especially in recycled polymers has been described in the scientific literature (Bach et al., 2013; Cincotta, Verzera, Tripodi, & Conduro, 2018; Skjevraak et al., 2005). Song et al. used analytical techniques such as GC-MS and statistics methods to characterize and map the profile of 17 compounds that caused degradation in recycled expanded polystyrene resins used in the production of food packaging. They noted that these compounds are classified as NIAS and IAS (Song, Wrona, Nerin, Lin, & Zhong, 2019). Su et al. listed a long series of compounds identified in the migration of recycled polyolefins using direct immersion solid-phase microextraction- atmospheric pressure-gas chromatography-mass spectrometry (Su, Vera, & Nerín, 2020). Osorio et al. determined volatile NIAS by applying different chromatographic techniques from starch-based biopolymers employed in food contact (Osorio, Aznar, & Nerín, 2019). Headspace solid-phase microextraction (HS-SPME) technique and gas chromatography coupled to both mass spectrometry and a sniffing port (GC-MS-O) were used and 35 odorant compounds were detected.

NIAS has been long ignored in safety assessments of materials in contact with food. After they were included in the EU regulation (10/2011) (Union Europea, 2011) many studies have been done to assess the possible interferences they may bring to both materials and food that will be consumed, as S. Koster et al. demonstrated in their work on strategies for determining NIAS in carton food contact materials (Koster et al., 2014).

However, literature is scarce when it comes to exploring the odoriferous characteristics of NIAS. Resolution N/228, November 2010 published by ANVISA clarifies that materials in contact with food should not transfer any odors and taste to the food for which it is intended (ANVISA, 2010). It reinforces the importance of studying the types of NIAS that are formed during the recycling processes, as well as establish a better technique to determine them. One of the major challenges is related to their low concentrations. Usually, the sensory analysis of quality control of odors is carried out by a group of trained panelists that can determine the presence or absence of off-odors in materials. Although this technique is widely used in the food industry, it is not valid to determine individual odors coming from individual compounds. GC-O-MS technique that combines the MS detector with the human nose is a good technique to determine the individual odor compounds, even as defined by its chemical structure with very low concentration as

Table 1
Concentration and properties of contaminants used in the cocktail.

Contaminants	Concentration	Properties
Chloroform	10% (v/v)	Volatile Polar
Toluene	10% (v/v)	Volatile Non-Polar
Benzophenone	1% (v/v)	Non-Volatile Polar
Tetracosane	1% (m/v)	Non-Volatile and Non-Polar
Heptane	78% (v/v)	Volatile and Non-Polar

described by Vera et al. (Vera et al., 2019). This is an important tool, as sensory perception is much more sensitive for many substances than the chemical detectors, even being MS.

Therefore, this work aims to study the aroma profile of polypropylene after it goes through forced contamination, according to USFDA directives, and submitted to the recycling process. Additionally, polymeric degraded compounds and the NIAS were evaluated. For this purpose, the profile of volatile compounds from the PP samples submitted to the different processes was analyzed. The analysis was performed by headspace solid-phase microextraction (HS-SPME) coupled to gas chromatography with a mass spectrometer and a sniffer port (GC-O-MS). Kovats Index (KI), mass spectrum, modified frequency (MF), and odors description were used to identify the compounds.

2. Material and methods

2.1. Chemicals

The surrogates used for the contamination process were chloroform (Vetec, 99.8%, CAS No. 67663), toluene (Vetec, 99.5%, CAS No. 108883), benzophenone (Acros Organics, 99%, CAS No. 119619), tetracosane (Merck, 99%, CAS No. 646311) and heptane (Synth, 99%, CAS No. 142825).

2.2. Samples

The commercial polymer used in this project was polypropylene (Prisma 2400) supplied in pellets by Braskem S.A, Brazil. The polymer presents a melt flow index (MFI) of 20 g/10 min (ASTM 1238, 230 °C, 2.16 kg) and density of 0,902 g/cm³ (ASTM D 792). It is used for food packaging, such as transparent bottles for mineral water, teas, juices, and isotonic.

2.3. Samples preparation

2.3.1. Process of contamination of polypropylene pellets

Pristine PP pellets (PPp) have been subjected to contamination using the procedure described in the USFDA (2006) protocol (US Food and Drug Administration (FDA), (2006)). The contamination cocktail of surrogates represents the worst post-consumer conditions a polymer can be exposed to. Initially, the pristine PP pellets were added to the cocktail of surrogates. Then, they were hermetically sealed for 14 days in constant agitation and under the controlled temperature of 40 °C (US Food and Drug Administration (FDA) (2006)). Table 1 describes the surrogates used, their concentrations, and physicochemical properties.

2.3.2. Recycling and washing process

The process of washing contaminated PP (PPc) samples were divided into three steps. In the first step, the pellets were washed with distilled water for 10 min. Then, they were washed with 1L of 1% sodium hydroxide solution for 5 min, and finally, they were washed with distilled water for 10 min. At the end of these three washing steps, the samples (PPcw) were dried at room temperature for 24 h (Garcia, Scuracchio, & Cruz, 2013).

To study the influence of the contaminants during polymer processing, the contaminated PP samples were recycled in the single-screw

Table 2
Nomenclature of the PP samples.

Samples	Nomenclature	Sample #
PP pure	PPp	1
PPp recycled	PPpr	2
PP contaminated	PPc	3
PP contaminated, washed, and recycled	PPcwr	4
PP contaminated washed	PPcw	5
PP contaminated and recycled	PPcr	6

extruder (AX Plastic) under temperatures of 180, 190, and 210 °C at a screw speed of 30 rpm. Afterward, the pelletizing process was carried out.

Table 2 presents the nomenclature employed in this work, as well as, the steps that the samples are submitted to (contamination, washing, and recycling).

2.3.3. Preparation of the samples for extraction and analysis

PP samples were cut and 1 g (± 0.015 g) of it was added to the SPME vials with a capacity of 20 mL and heated at 120 °C for 30 min. The volatile compounds were analyzed by headspace solid-phase micro-extraction technique (SPME) coupled to gas chromatography coupled with mass spectrometry and olfactometry port (GC-O-MS). All samples were prepared in triplicate.

2.4. GC-O-MS conditions

For the analysis of volatile compounds, the GC 7890 N coupled to the MS detector 5977D (Agilent Technologies, Santa Clara, CA) with a sniffer port (Phaser, GL Sciences, Germany) were used. HP-5MS column (30 m \times 25 mm \times 0.25 μ m film thickness) from Agilent Technologies was used in scan mode detector (45–350 m/z). The oven temperature program was as follows; the initial temperature was 40 °C for 5 min, with a heating rate of 10 °C min^{-1} to 300 °C, then held at 300 °C for 2 min. Analytes were adsorbed in the SPME fiber. Then, they were manually transferred to the GC injection port, where desorption of the compounds occurred at a temperature of 250 °C for 2 min.

The determination of odors was performed through the olfactometric line heated to 170 °C and coupled to the sniffing port. Three trained panelists performed the olfactometric analysis. The approximate time for analysis was 30 min of sniffing. Each panelist determined the retention time of the detected smell, its type, and intensity.

2.5. Fiber selection and optimization for HS-SPME

For the selection of the best fiber for HS-SPME-GC-O-MS analysis, the total area of all extracted compounds by three different fibers was compared. The tested fibers were polyacrylate (PA 85 μ m), Polydimethylsiloxane (PDMS 100 μ m), and divinylbenzene/carboxen/ polydimethylsiloxane (DVB/CAR/PDMS 50/30 μ m). For the analysis and selection of the fiber suitable for extraction by HS-SPME, the PPcr sample was used. This was since it was the sample with the highest number of peaks and possible odorous compounds during the optimization process.

2.6. Qualitative analysis

2.6.1. Identification of odorous compounds

Over the olfactometric analyses, the three trained panelists described the odors and intensity of detected compounds, classifying them on a scale from 1 (low intensity) to 3 (high intensity), and their fractionated values. After the analyses, the modified frequency MF (%) was calculated for the odorous compounds identified by the panelists. Equation (1) describes the calculation for the modified frequency (Vera, Uliaque, Canellas, Escudero, & Nerín, 2012);

Table 3
Compounds from different PP samples detected by HS-SPME-GC-MS.

No	tR (min)	Compound	KI	Sample
1	3.184	2,2-Dimethylpentane	616	3 and 6
2	3.851	3-Methylhexane	645	1, 3 and 6
3	4.063	1,3-Dimethylcyclopentane	654	4 and 5
4	4.849	Methylcyclohexane	688	1, 4 and 5
5	4.953	1,1,3-Trimethylcyclopentane	692	3 and 6
6	6.019	2,5-Dione-1 h-pyrrole	738	6
7	6.112	3-Ethyl-2-methyl-pentane	742	3
8	6.374	Toluene	754	1
9	7.472	3-Ethylhexane	801	1
10	7.673	2,4-Dimethylheptane	810	1
11	7.720	Norbornene	812	6
12	7.731	Thujone	813	6
13	10.716	2-methyl-2,3-hexadiene	950	6
14	11.947	4,4-Methyldecane	1014	1
15	12.568	Undecane	1051	1, 3 and 6
16	12.586	3,6-Dimethyldecane	1052	1, 2 and 6
17	12.665	5-Methylundecane	1056	5
18	12.963	Glycerin	1074	2, 4 and 6
19	13.307	4,7-Dimethylundecane	1094	1
20	13.842	2-phenyl-1,3-dioxolane	1128	2
21	14.452	Tetradecane	1168	1, 6
22	14.893	Pentadecane	1197	1, 2 and 6
23	15.019	2,5-Dimethylundecane	1206	6
24	15.134	4-Methyldecane	1214	6
25	15.231	3,5-Dimethylbenzaldehyde	1221	6
26	15.460	Hexadecane	1238	1, 2 and 6
27	15.780	6,6-Dimethylundecane	1261	4
28	16.002	2-Methyltridecane	1277	4
29	16.056	2-Chlorophenylloxirane	1280	3
30	17.825	Heptadecane	1416	6
31	17.858	2,7,10-Trimethyldodecane	1418	2
32	18.737	Heptacosane	1490	6
33	18.776	Octadecane	1493	1, 2 and 4
34	18.952	2,4-Di- <i>tert</i> -butylphenol	1508	6
35	19.243	Nonadecane	1532	1,3
36	19.264	Heneicosane	1534	4, 5 and 6
37	19.307	4,7-dimethylundecane	1538	2
38	20.047	diethyl phthalate	1600	all sample
39	20.535	Benzophenone	1644	all sample
40	21.177	2-Methyleicosane	1704	1 and 6
41	23.384	2-Methyl-nonadecane	1920	1, 4 and 6
42	23.786	dibutylphthalate	1962	6
43	25.351	Docosane	2200	2 and 6
44	27.159	Pentacosane	2345	6
45	27.529	Tetracosane	2390	4, 5 and 6

$$MF(\%) = [F(\%) \times I(\%)]^{0.5} \quad (1)$$

where F (%) represents the percentage of panelists who had detected the odorous compound and I (%) was the percentage of intensity calculated by the average of the values of intensity given by all the panelists divided by three (Vera et al., 2012). Some works show that the odoriferous stimuli of compounds detected by panelists have an MF (%) greater than 50% (Koster et al., 2014). These compounds were classified as the most important in the samples, as in the case of the study made by P. Vera et al. on odors detected in different commercial adhesives (Vera et al., 2012).

The Kovats index (KI) of compounds detected by GC-O-MS from PP samples was calculated using a series of *n*-alkanes (C7-C40) prepared in hexane and injected under the same chromatographic conditions (Wrona, Vera, Pezo, & Nerín, 2017). The KI and characteristics of the analyzed compounds were compared to those described in the literature (Mahajan, Goddik, & Qian, 2004). Additionally, combinations of the PP samples mass spectra for the identification of unknown peaks were based on the NIST mass spectra library (NIST (National Institute of Standards and Technology), 2018).

Finally, the odorous compounds identified were compared to those described in the literature (García et al., 2013; Wrona et al., 2017) and databases such as Flavornet, Pherobase (database of pheromones) (El-

Table 4
Identification of odor compounds in different PP samples and their classification to odor groups.

No	Compound	CAS	KI	Odor description	Odor group (OG)	Sample	(%) MF
1	2,2-Dimethylpentane	108-08-7	616	Apple vinegar	Sweet, pungent, chemical, apple, pineapple, sharp, bitter, fruity (A)	3	71
						6	72
2	1,1,3-Trimethyl-cyclopentane	4516-69-2	692	Apple vinegar	Sweet, pungent, chemical, apple, pineapple, sharp, bitter, fruity (A)	3	73
						6	72
3	2-Methyl-2,3-hexadiene	29212-09-7	950	Scented smell	Alkene, waxy (B)	6	64
4	3,6-Dimethyldecane	17312-53-7	1052	Scented smell	Alkene, waxy (B)	6	71
5	Glycerin	59-81-5	1074	Hot oil	Oily, odorless, sweet, fatty (C)	2	71
						6	53
6	2-Chlorophenylloxirane	62717-50-4	1280	Vinegar steam	Sweet, pungent, chemical, apple, pineapple, sharp, bitter, fruity (A)	3	74
						7	73
7	Diethyl phthalate	84-66-2	1600	Burnt synthetic	Aromatic odor, burnt (D)	4	68
						5	59
						6	84
						8	81
						9	96
8	Benzophenone	119-61-9	1644	Plastic	Peach, powdery, apricot, rose, balsam, geranium, metallic, plastic (E)	1	81
						2	96
						3	96
						4	99
						5	91
9	Docosane	629-97-0	2200	Plastic	Alkene, waxy (B)	6	99
						3	96

Sayed, 2019), VCF online (Volatile Compounds in Food) (Dongen et al., 2000) and FlavorDB (Garg et al., 2018).

3. Results and discussion

3.1. Fiber selection for HS-SPME

The PPcr sample was used because during the optimization process it was shown to be the sample with the highest number of peaks and possible odorous compounds. The results of the PPcr related to the total area of all extracted compounds using three different fibers (PA, PDMS, and DVB/CAR/PDMS) are presented in the appendix (Fig. A1). It can be noticed that DVB/CAR/PDMS present the major total extraction area (approx. 6.8×10^9) when compare to PA and PDMS fiber. This behavior is related to its structure that contains micropores facilitating the extraction of high and low molar mass compounds (da Oliveira et al., 2020; Souza Silva et al., 2017). For this reason, DVB/CAR/PDMS fiber was chosen for this study.

3.2. Identification of volatile compounds

A chromatogram of the PPcr sample analyzed by the HS-SPME-GC-MS is shown as additional information in the appendix (Fig. A2). Besides, Table 3 shows the 45 compounds identified in all analyzed PP samples and it is important to emphasize that part of them were not odorous.

Part of the compounds detected (Table 3) comes from the cocktail of spiked contaminants (surrogates) and they were considered as IAS (toluene, benzophenone, and tetracosane). On the other hand, many NIAS were detected, such as glycerin that could be attributed either to degradation of the polymer, or the interaction between other compounds present in the material (cocktail molecules, catalyst residue, antioxidants additives, and plasticizers). The PPcr sample presents the highest amount of detected and identified compounds (26 compounds). Many of these compounds are linear or branched alkanes and alkenes that may be produced from the degradation of the PP chain.

Garcia et al. in a study regarding the effect of residual contaminants in post-consumer PP recycling found that the surrogates act as a catalyst and accelerate the degradation process (Garcia et al., 2013).

Phenols hindered sterically are used on a massive scale as a primary antioxidant in polyolefin. During its entire life cycle, PP and its additives may suffer modifications that can change these molecules (Jaworek & Czapllicka, 2014). Phthalates identified in all PP samples probably come from the catalyst used in the PP polymerization.

The samples submitted to contamination and reprocessing present the highest content of these compounds. As previously described, these processes accelerate the thermal or/and oxidation degradation caused by contaminants, as reported by S. P. Garcia et al. (Garcia et al., 2013).

3.3. Identification of odorous compounds

Félix et al. (Félix, Domeño, & Nerín, 2013) found that natural fiber-reinforced polypropylene composite degradation generates characteristic odors of low molecular weight compounds that are associated with aldehydes, ketones, and carboxylic acids. Nine compounds extracted from the PP samples by HS-SPME and analyzed by GC-O-MS had odoriferous activity. The panelists classified the type of odors and intensity and obtained the MF (%) factor of each compound with odors listed in Table 4. Only three compounds had an MF (%) factor below 60%. Compounds with MF (%) higher than 60% were considered as the basis of the odors analyzed for each sample and the odors identified by the panelists were the following: apple vinegar, scented smell, hot oil, burnt synthetic, plastic, fermented apple, and vinegar steam.

The odor groups were identified based on FlavorDB (Garg et al., 2018), Pherobase, and Flavornet (El-Sayed, 2019). Each odorous compound was matched according to an odor analysis provided by the panelists. Then the odor groups (OG) were created and listed in Table 4 correlating the type of detected odors. The OG was divided into A (sweet, pungent, chemical, apple, pineapple, sharp, bitter, fruity), B (alkene, waxy), C (oily, odorless, sweet, fatty), D (aromatic odor, burnt), and E (peach, powdery, apricot, rose, balsam, geranium, metallic, plastic), according to each odor class listed in the databases (El-Sayed, 2019; Garg et al., 2018).

Benzophenone was detected in all PP samples and it presents the highest average MF (%) factor of all samples and it was the base aroma for PP samples. The Food Standard Agency (FSA) (Food Standards Agency, 2006) reports that benzophenone is considered a contaminant associated with ink and coatings on food packaging and can migrate into the food. The PP employed was not previously used. However, benzophenone was widely used as a photoinitiator and may be added as an additive. The six panelists judged its odor as very intense, on a scale of 1 (low intensity) to 3 (high intensity). Moreover, its characteristic aroma varied between plastic and metallic and was classified in odor group (OG) D according to FlavorDB (Garg et al., 2018).

Diethyl phthalate was also identified in all PP samples. However, only in samples 3, 4, 5, and 6 its odor was perceived and identified as burnt synthetic. The mentioned samples were previously submitted to the contamination process, using the USFDA directives (US Food and

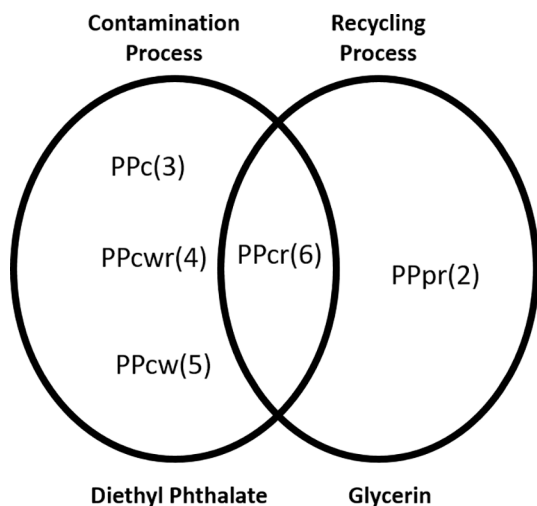


Fig. 1. Relationship between odorous compounds and two processes, contamination and recycling.

Drug Administration (FDA) (2006)), which leads us to the idea that the contamination cocktail influenced the degradation process of the PP and thus, the concentration of diethyl phthalate increased, leaving its odors more noticeable with a high average value of MF (%) equal to 91%. Phthalates are intentionally added substances (IAS) used to alter the properties of the polymers described in the EU regulation (10/2011) (Union Europea, 2011). But some phthalates are also used as catalysts for PP polymerization. In this work, pellets of PP were used and the

phthalates may be used in their polymerization. Nevertheless, many phthalates are not linked to the polymer chains and they can migrate to food (ANVISA, 2010).

Glycerin was detected in samples 2 and 6 and its odor was identified as burnt oil, classified into the group (OG) C. Even though it is one of the compounds with an MF (%) factor lower than 60%, it has high importance because it can be a non-intentionally added substance (NIAS). Some NIAS include impurities in the prime matters for polymerization, reagents used in reactions, reaction intermediates, decomposition products, and substances that arise due to the production process (Union Europea, 2011). In this case, samples 2 and 6 were recycled pellets, which classify glycerin as a production process NIAS as described by the International Life Sciences Institute (ILSI Europe) (Koster et al., 2015).

2,2-dimethylpentane, 1,1,3-trimethyl-cyclopentane, and 2-chlorophenylloxirane were detected with MF (%) between 54% and 70%, and with very similar aroma descriptions (apple vinegar and vinegar steam), which classifies them as part of the OG A. Moreover, they have been also reported in the literature (da Oliveira et al., 2020).

As above described, the processes of forced contamination and recycling step increase the rate of PP degradation. Furthermore, the degradation intensifies the presence of these odors, as demonstrated by the GC-O-MS results. Sample 6 (PPcr) was submitted to both processes, contamination, and recycling, and the two odoriferous compounds glycerin and diethyl phthalate were identified, that represent NIAS and IAS, respectively. Both compounds were confirmed by injecting the pure standards under the same experimental conditions. Fig. 1 illustrates the correlations between analyzed samples, showing the relationship between the two odoriferous compounds, glycerin, and diethyl phthalate, and the two processes that the samples had undergone. These results prove that different types of processing along with previous

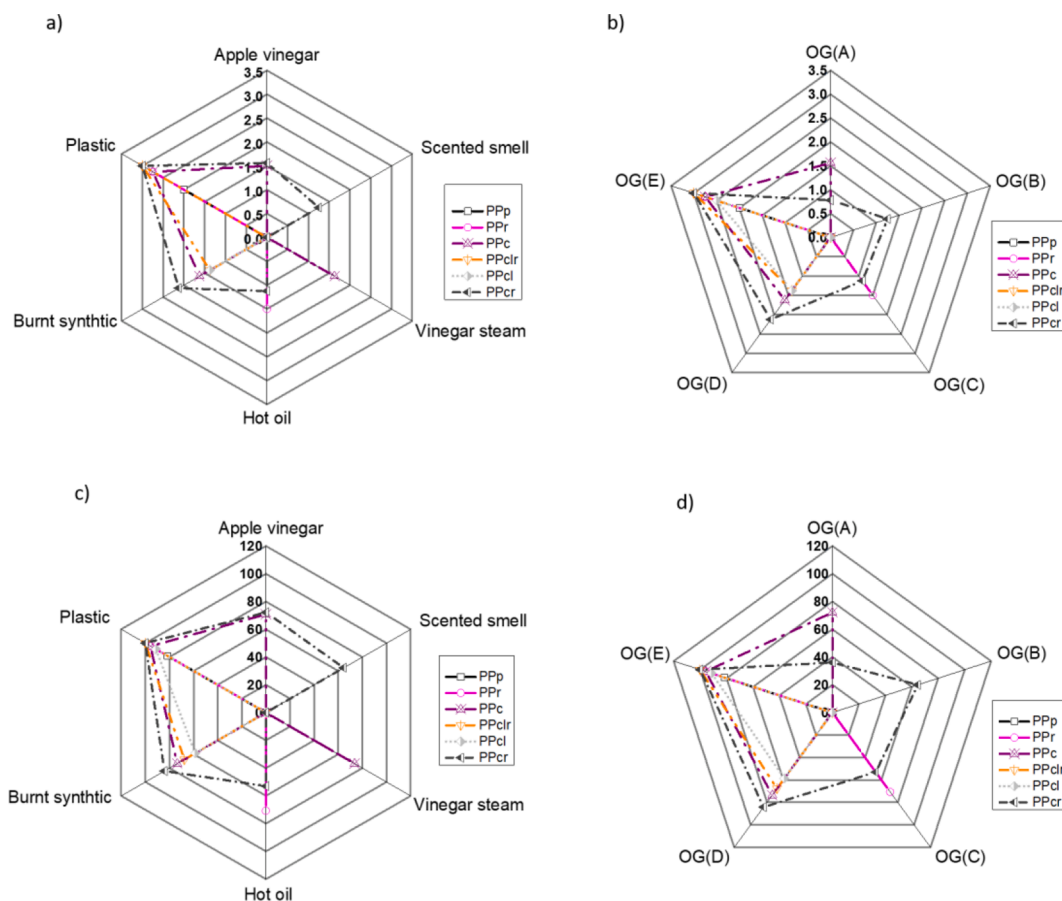


Fig. 2. Analysis of the intensity of the odors of the PP samples represented by radar graphs to compare the similarities of (a) panelist evaluations of odors; (b) panelist evaluations of odor groups (OG); (c) MF(%) correlation with odor impact (c) and (d) MF(%) correlation with odor groups (OG).

characteristics, as well as their combinations, can result in the appearance of new compounds such as glycerin.

3.4. Sensory evaluation

The identified odors were divided into 5 groups according to the sensory characteristics described by the panelists described in Table 4 as OG(A), OG(B), OG(C), OG(D), and OG(E). Fig. 2 shows the radar graphs describing the odors noticed by the panelists and their relationship with the OG in which the odorous compounds were classified. The graphs were arranged by comparing the intensity of the aroma (0 to 3) and MF (%). The graphs indicate (both in intensity and MF (%)) that plastic odor derived from benzophenone is predominant in the samples, and that some samples have minor traces of burnt synthetic, characteristic of diethyl phthalate.

4. Conclusion

The qualitative analysis of the 6 polypropylene samples submitted to the different processes, forced contamination, and recycling, allowed the identification of 45 compounds extracted by HS-SPME and analyzed by GC-MS and GC-O-MS.

Among the detected compounds, 9 had odoriferous characteristics verified by the panelists, which allowed the mapping of the characteristic odors of each compound present in the samples, such as apple vinegar, scented smell, hot oil, vinegar steam, burnt synthetic, and plastic. This fact reinforces the idea of the importance of using the olfactometric method (GC-O) to detect odorous compounds in plastic for food packaging applications. Furthermore, the proposed method allows studying the impact of the two processes, contamination, and recycling that the PP samples were subjected to.

Compounds with MF (%) higher than 60% were detected. It was proven that the predominant odors in the samples were plastic scents derived from benzophenone. This compound was present both in the samples that were forcibly contaminated and in those that were not subjected to that process.

In conclusion, this study showed the extreme importance of identifying the compounds responsible for the different odors present in the samples. Moreover, the presence of contaminants together with the high shear rates and temperatures, typically used in the extrusion recycling process, may result in new degradation compounds with odoriferous characteristics. This should lead the current legislation authorities and companies to develop process methodologies that reduce the impact of these contaminants from food-grade packaging that eventually reach the consumers.

CRedit authorship contribution statement

Robert Paiva: Writing - original draft, Methodology, Validation, Investigation, Data curation. **Magdalena Wrona:** Conceptualization, Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing, Supervision. **Cristina Nerin:** Conceptualization, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition. **Isabelly Bertochi Veroneze:** Methodology, Validation, Investigation, Data curation. **Georgiana-Luminita Gavril:** Conceptualization, Methodology, Validation, Investigation, Data curation. **Sandra Andrea Cruz:** Conceptualization, Writing - review & editing, Resources, Supervision, Project administration, Funding acquisition.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.foodchem.2021.129250>.

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