Hydrogenated amorphous carbon film deposited by plasma on recycled polypropylene as a functional barrier to hazardous migrants

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ABSTRACT

Polypropylene (PP) is one of the most used polymers, especially in single-use packaging, as well as in the healthcare industry, which causes serious environmental problems. Its correct destination is essential, and in this sense, recycling is part of the solution. However, regulatory agencies, such as the Food and Drug Administration (FDA), restrict the use of recycled plastic due to the potential migration of contaminants from packaging to food. In this way, the hydrogenated amorphous carbon (a-C:H) films deposited by plasma are an alternative to reduce the contamination. Consequently, polypropylene was subjected to the forced contamination process recommended by the FDA and submitted to a recycling process. The a-C:H films were deposited by plasma as a possible functional barrier against harmful contaminants. The developed system (recycled polymer + a-C:H film) was characterized by FTIR-ATR, XPS, Raman spectroscopy and profilometry. The efficiency of the deposition of a-C:H films on recycled PP samples was evaluated by migration tests and target analysis of the contaminants. Moreover, the presence of microdefects determined by SEM micrographs were performed before and after migration tests. These defects play an important role to modify the migration once the detachment from the surface causes an increase in the migration. For the volatile contaminants (chloroform, heptane, and toluene), in most cases, no difference was observed with contaminant migration in the samples coated with a-C:H. On the other hand, a decrease in contaminant migration was observed for benzophenone (non-volatile), in both simulants and under the three established conditions. Although, the a-C:H films still represent an attractive strategy as a barrier to the migration of contaminants.

1. Introduction

In recent years, the consumption of plastics has grown exponentially, according to data from the WWF (World Wildlife Fund), cited by the Plastic Atlas (Böll, 2019). Projections show that in 2025, the plastic industry could exceed the historical market of 600 million tons/year, an increase of 50% over the current production in which the food packaging industry is the highest user (Associação Brasileira da Indústria do Plástico, 2018; Böll, 2019). The COVID-19 pandemic scenario created restrictions causing an increase in the production and consumption of single-use plastic packaging in the various delivery sectors. Also, the healthcare industry has had a significant increase in the demand for plastic materials such as masks and gloves, especially those made from thermoplastic resins such as poly (ethylene terephthalate), PET, and polypropylene, PP.

Incorrect and inappropriate disposal makes recycling of polymers more difficult due to eventual contamination, often hard to remove from the plastics and able to migrate to the packaged product after a migration process. The Brazilian Packaging Association (ABRE) reports that *in 2019* Brazil produced 80.2 *million* tons of plastic packaging and recycled only 2% of this amount, leading to environmental damage from incorrect disposal (Associação Brasileira de Embalagens, 2015). Furthermore, only 9% of all plastics generated worldwide are being recycled. In this context, the European Union regulation and all its amendments (Commission Regulation (EU) No 10/2011, 2011), US FDA directives (US Food and Drugs Administration (FDA), 2021) and Brazilian National Health Surveillance Agency (ANVISA) (ANVISA, 2004) authorized the use of recycled plastic in food contact material (FCM), as long as it does not present a risk to consumers, due to the migration processes of contaminants from the packaging to the food. Currently, the number of

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recycled plastic materials for direct food contact is increasing, a well-established example by regulatory agencies is PET and PEN (US Food and Drugs Administration (FDA), 2021). However, the Brazilian Association of the Plastic Industry (ABIPLAST) shows, in 2019, that PET represents only 5.9% of the consumption of the main resins. On the other hand, PP is holding the expressive 20.3% of the consumed resin, due to its great added value, low cost, high versatility, and easy processability, which makes it an outstanding material in the processing sector (Associação Brasileira da Indústria do Plástico, 2018). Therefore, the US FDA has approved the use of recycled PP for food packaging, increasing the possibility of insertion of this material into a circular economy. Furthermore, the EFSA *has* evaluated and published *several* positive opinions on the *use of recycling methods for PP and HDPE intended for application in agricultural products such as Schoeller Arca Systems, CO.N.I. P, CHEP, Petra and others (*Cef, 2013, 2014*;* Cef et al., 2013*)*.

Some studies report decontamination of PP packaging in the recycling process (Incarnato et al., 1998; Incarnato et al., 2003; Majumdar et al., 2004). Garcia et al. (2013, 2014) studied different types of mechanical recycling, such as single-screw, twin-screw and cascade extrusion to evaluate the efficiency of the decontamination of plastics. To this end, the extractability tests were done using different food simulants. The results showed that the twin-screw extruder with forced degassing provided the best results.

Another alternative to reduce the migration of contaminants present in food packaging is the deposition of barrier films from plasma-enhanced chemical vapor deposition (PECVD) (Abbas et al., 2005). One of the films studied as a functional barrier to decrease the migration of residual contaminants is the hydrogenated amorphous carbon film (a-C:H) (Boutroy et al., 2006; Tamor & Vassell, 1994). This material presents different types of hybridization of carbon (sp^3, sp^2 and sp^1) that affect their physical and chemical properties. Higher percentages of sp^3 carbon produced films with properties designating it as diamond-like carbon (DLC). Otherwise, films with a significant amount of sp^2 carbon show properties that designate it as polymer-like carbon (PLC). These sp^2/sp^3 bond characteristics influence the structural rigidity of these a-C:H films (Goswami et al., 2008; Stan et al., 2010) and the presence of microdefects. Some studies have reported the efficiency of the barrier properties of a-C:H films concerning the migration of contaminants (Cruz et al., 2010; Suzuki & Kodama, 2009). Oliveira et al. (2014)used diamond-like a-C:H films deposited on recycled PET to reduce the migration of contaminants present in recycled PET to food simulants. The content of surrogates that migrated to food simulants was analyzed by solid phase microextraction, while coupled to gas chromatography, which in turn was coupled to a mass spectrometer (SPME-GC-MS).

The technique of coating the recycled packaging with a-C:H films is a very interesting strategy for the reinsertion of recycled food-grade packaging by the following facts: (i) the production of the films does not generate toxic residues, and their base is only carbon and hydrogen that do not represent a health risk to the consumer; (ii) the recycling of the material coated with a-C:H films in nanoscale is not difficult, and (iii) the studies on PET show that there is a high rate of reduction of the migration process when a-C:H films are used as a functional barrier to contaminants and gases (Cruz et al., 2006; Nakaya et al., 2015; Zhang et al., 2013). Despite these advantages, a-C:H films showed high residual stress that may result in microdefects and microcracks, decreasing the efficiency of the barrier and this fact becomes more critical in the presence of food simulants. Although this topic is important, to the best of our knowledge, there is only study (Oliveira et al., 2014) in the literature on the influence of food simulants on functional barriers that correlate with the presence of defects, as proposed in this work.

Furthermore, the use of different types of functional barriers are viable for coating recycled packaging materials for direct contact, showing itself to be a promising alternative for the inclusion of other recycled materials in the food packaging industry (Aguiar et al., 2013; Zhao et al., 2020).

Therefore, this work aims to analyze the recycling process of post-consumer PP, followed by the deposition of a-C:H film as a functional barrier to reduce the migration of contaminants. To this end, migration tests and surrogates present in food simulants by SPME-GC-MS analysis were performed. Furthermore, the correlation between the surface defects caused by the contact with food simulants, in different conditions, and the efficiency of functional barrier against the migration of contaminants was analyzed by electron scanning microscopy.

2. Materials and methods

2.1. Materials

The high-purity gases, oxygen (99.9%), argon (99.9%) and acetylene (99.7%) from White Martins S. A., Brazil, were used for the treatment and plasma deposition. The surrogates used for the contamination process were *chloroform (Vetec, 99.8%, CAS No. 67–66–3*, P^o = 210 hPa), *toluene (Vetec, 99.5%, CAS No. 108–88–3*, P^o = 30.88 hPa), benzophenone (Acros Organics, 99%, No. CAS 119–61–9, P^o = 1.33 hPa), tetracosane (Merck, 99%, CAS No. 646–31–1, P^o = unspecified) and *heptane (Synth, 99%, CAS No. 142–82–5*, P^o = 111 hPa). Acetic acid (Sigma Aldrich, 99.8%, CAS No. 540–84–1), ethanol (HPLC grade No. CAS 64–27–5) were supplied by Scharlau Chemie S. A. (Sentmenat, Spain) and were used for food simulant preparation. Ultrapure water was from the Wasserlab Ultramatic GR system (Barbatáin, Spain).

2.2. Samples

The commercial polymer used in this project was polypropylene (Prisma 2400) supplied in pellet form by Braskem S.A., Brazil. *The characteristics and properties of the polymer are described in the ASTM 1238 and ASTM D 792 standards.*

2.3. Sample preparation

Pristine PP pellets (PPp) were subjected to the forced contamination process as described in the US FDA (2006) protocol (Center for Food Safety and Applied Nutrition, 2006). This contamination process represents the worst post-consumer conditions that the intended food contact materials (FCMs) can be exposed to, as described in some studies (Cruz et al., 2006; Garcia et al., 2013, 2014; Paiva et al., 2021). A 800 mL solution was prepared to employ the concentrations of the contaminants listed in Table 1. After the forced contamination protocol, the PP pellets were submitted to the washing process developed by Garcia et al. (2013) consisting of first washing with water for 10 min, followed by washing with a 1% NaOH solution for 5 min and finishing with a washing with water for 5 min (Garcia et al., 2013), followed by reprocessing in a single-screw extruder (AX Plastic) with different temperatures, 180, 190 and 210 °C with a screw speed of 30 rpm followed by the pelletization process (Garcia et al., 2014; Paiva et al., 2021). After this, PP pellets were submitted to a thermoforming procedure to obtain the PP films with approximately 168 μm (± 0.026 μm) of thickness at 190 °C and 2.7 mbar of pressure.

2.3.1. Oxygen plasma treatment and a-C:H film deposition

The surface of PP films was exposed to oxygen gas plasma to increase

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

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

its adhesive property, as reported in some papers (Cruz et al., 2009, 2010; Oliveira et al., 2012). For the plasma oxygen treatment, as well as the a-C:H film, a 13.56 MHz radio frequency-generated plasma reactor (Cruz et al., 2009; Goswami et al., 2008; Stan et al., 2010), located at the Institute of Physics Gleb Wataghin of the University of Campinas, Brazil, was used. Details regarding the apparatus can be found in the article by Cruz et al. (2006).

Initially, the thermopressed PP films were treated with an oxygen plasma using a 50 sccm flux rate, 70 W power, and 9.33 mbar for 2.5 min. Next, without opening the reactor, the step of deposition of the a-C: H film was used with a mixture of argon/acetylene with a flow rate of 65/55 sccm, respectively. The reactor was operated under the same conditions of oxygen plasma treatment (70 W, 9.33 mbar) and the time was a change of 2.5–30 min to determine the deposition rate and to obtain a-C:H films with different thicknesses. Fig. 1 represents the flowchart of the process of surface modification by oxygen plasma and deposition of the a-C:H films on the PP substrate.

The nomenclature used in this work is described in Table 2. In this way, the different samples of the PP films were submitted to migration tests in contact with the different simulants and conditions described. The tests were made in triplicate.

2.4. Food simulants and migration test

PP coated with a-C:H films was submitted for the analysis of surrogate migration using 3% acetic acid (3% HAc, representing acidic foods) and 10% ethanol (10% EtOH, representing alcoholic and low-fat foods) according to the European Union Directive (Commission Regulation (EU) No 10/2011, 2011). The migration cells were designed to allow just one face to remain in contact with food simulants (a-C:H face- Fig. 2) and with a surface/area of contact with a food ratio equal to $6 \, dm^2$ kg^{-1} (Commission Regulation (EU) No 10/2011, 2011). Three different conditions stipulated by the US FDA were employed (a) 10 days at 40 °C, (b) 10 days at 60 °C and (c) 2 h at 70 °C (US Food and Drugs Administration (FDA), 2021). Fig. 2 shows the procedure from sample preparation to migration tests.

2.4.1. SPME-GC-MS conditions

Contaminants present in the simulants were analyzed using SPME. The chosen fiber was DVB/CAR/PDMS (50/30 μm) due to its porous structure that assists in the extraction of both high and low molar mass compounds, as described by Vera, et al. (2012) and Osorio et al. (2019) in their works on the identification of compounds from FCMs. The contaminants (benzophenone, tetracosane, toluene, chloroform, and heptane) present in the post-migration simulants (acetic acid 3% and ethanol 10%) were quantified by SPME-GC-MS.

A CTC Analytics CombiPal from CTC Analytics AG (Zwingen, Switzerland) coupled to GC-MS equipment GC 6890 N gas chromatograph from Agilent (Palo Alto, CA, USA) was used for the analysis of volatile compounds. Separation of analytes was performed on an HP-5 MS column from Agilent (30 cm × 0.25 cm, 0.25 μm film thicknesses). The applied temperature program started at 40 °C for 5 min and increased by 10 °C min⁻¹ up to a 300 °C hold for 1 min. The injector had a temperature of 250 °C, and helium was the carrier gas used with a flow of 1 mL min⁻¹. Temperature and time of adsorption were 60 °C and 15 min, respectively. An Agilent 5975 Mass Spectrometer was used as

Table 2
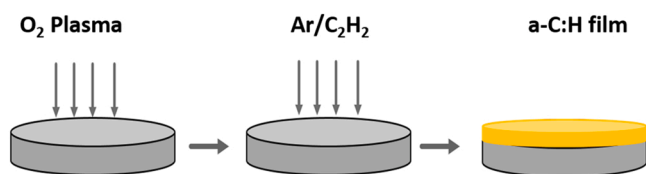Description of the PP film samples for migration testing.

Sample Description	Terminology
PP non-contaminated	PP$_{nc}$
PP contaminated, washed and reprocessed	PP$_c$
PP$_c$ coated with a-C:H film of 100 nm	PP$_{100}$
PP$_c$ coated with a-C:H film of 300 nm	PP$_{300}$
PP$_c$ coated with a-C:H film of 500 nm	PP$_{500}$

the detector of temperatures at the MS source and the quadrupoles 230 °C and 250 °C, respectively. SIM mode was applied, and target analysis of migrants was performed. The compounds were detected and identified from the chromatograms using the mass spectra library (US National Institute of Standards and Technology, NIST) and the retention times of previously injected standards of contaminants (NIST (National Institue of Standards and Technology), n.d.).

Standard solutions were prepared in 3% acetic acid and 10% ethanol for quantitative analysis. The analytical parameters of the applied method were determined: linearity, linear range, limits of detection (LOD) and quantification (LOQ). LOD and LOQ were established by application of SPME-GC-MS to pure standards of the compounds, under the same analytical conditions as those applied to the samples. Then, they are based on the SPME-GC-MS method. The Table S1 shown in the Supplemental Material lists the LOD and LOQ for each compound in the two food simulants, using the SPME-GC-MS methodology.

After the migration tests, the surface films of the PP samples were analyzed by scanning electron microscopy (SEM) to check the structure and morphology of the films before and after contact with the simulants through migration assays.

3. Characterization of plasma modification

3.1. Characterization of plasma treatment

Samples of polypropylene film were analyzed before and after the oxygen gas plasma treatment by Fourier Transform Infrared Spectroscopy (FTIR) with Attenuated Total Reflection (ATR) using the Varian 640-IR model. The samples were scanned at a wave number ranging from 4000 to 800 cm⁻¹ and 4 cm⁻¹ resolutions at 32 scans.

For X-ray photoelectron spectroscopy (XPS), the acquisition of the spectra was performed in a Scienta Omicron ESCA+ model equipment with hemispherical analyzer EA125 and a monochrome Xm 1000 A (kA = 1486.7 eV). The X-ray source was used with a power of 280 W and a constant-pass power mode of 50 eV. The measurement of the spectrum survey was performed with a power step of 0.1 eV. In comparison, the high-resolution spectra of 0.05 eV and high-resolution spectra were calculated by the Shirley function, and the load effects were corrected using the carbon 1 s peak at 2684.9 eV.

Microscopy images were taken on a Carl Zeiss MERLIN™ field emission scanning electron microscope (FESEM) with the HKL EBSD detector (Electron Back Scatter Diffraction), at 200 and 3000x magnification, and the images were compared before and after the migration tests.

The Raman spectra of the a-C:H films were obtained with a Horina Jobin-Yvon LabRAM micro spectrometer with excitement through an Olympus TM BX41 microscope. A profilometry model Dekatak 150-Veeco with superficial measurements of topography, roughness, and step height in nanometric scales was used for the analysis of the a-C:H films' thicknesses. To analyze the influence of a-C:H film thickness on the increase of barrier property for contaminant migration, 3 types of thicknesses were obtained; 100, 300 and 500 nm (low, medium, and high thickness).
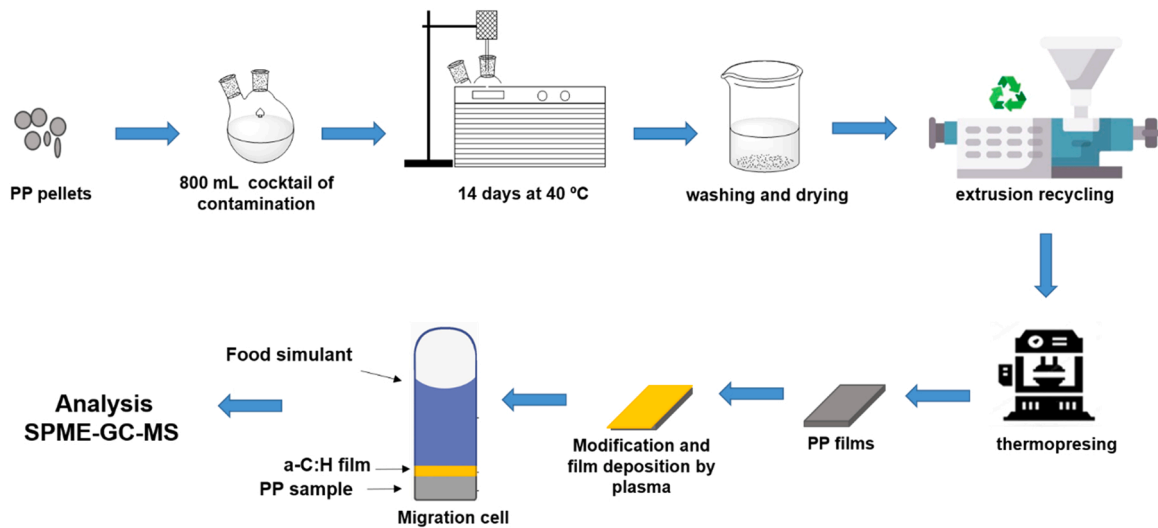

Fig. 1. : Flowchart of PP films treated with oxygen gas plasma followed by the deposition of a-C:H films using PECVD.

Fig. 2. : Diagram of the PP sample preparation procedure until migration tests.
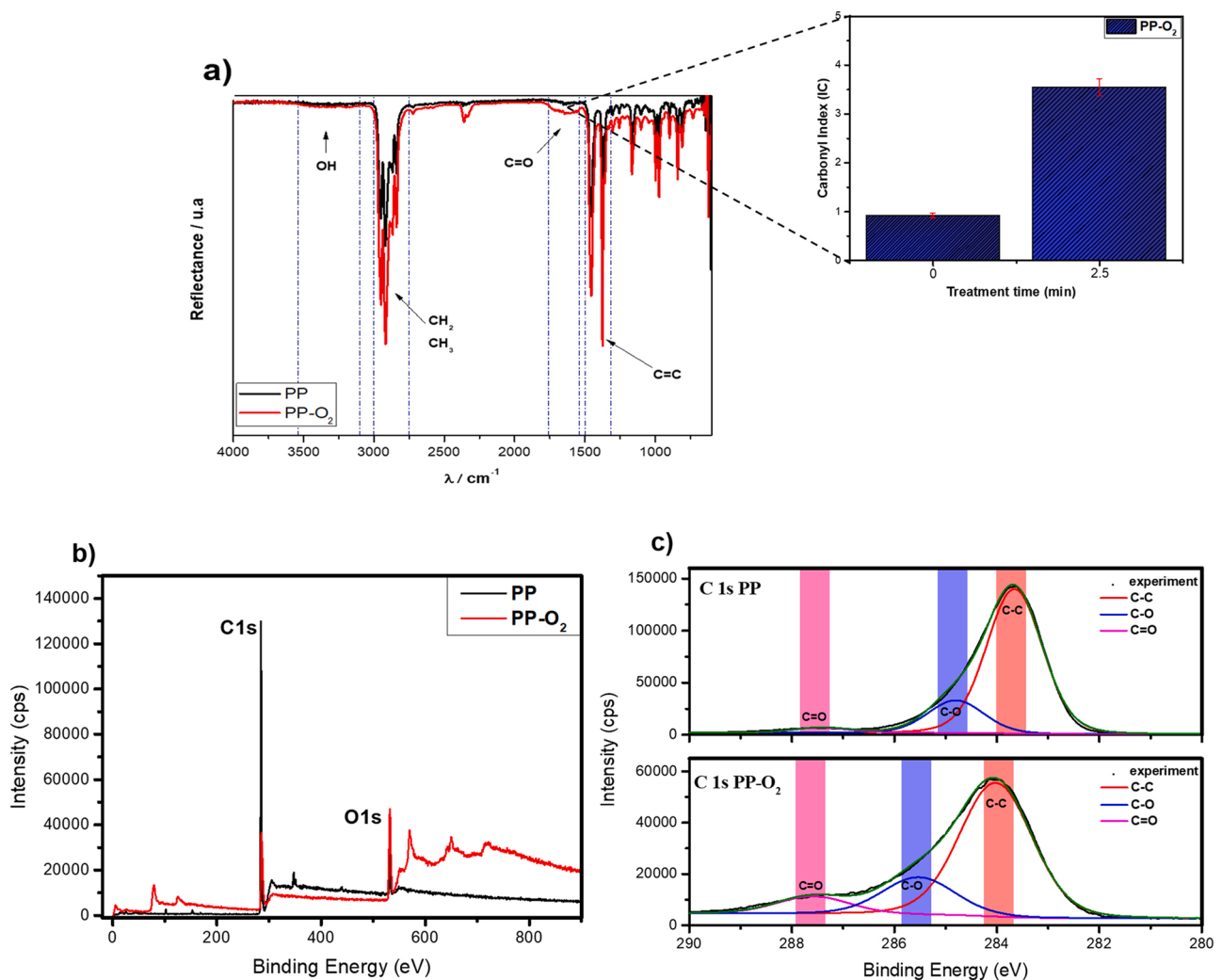

Fig. 3. : a) FTIR-ATR for PP and PP samples treated with oxygen plasma for 2.5 min of plasma exposure and b) XPS survey of the 1 s carbon and 1 s oxygen levels for PP and PP-O₂ as well as c) deconvolution of the reference peak C1s and proof of the new bond formation of oxygen-based functional groups.

4. Results and discussion

4.1. Surface modification of PP films

Plasma oxygen treatment generates a lot of reactive oxygen-based species once oxygen reacts with the PP surface. The chemical modification with plasma treatment was analyzed by FTIR-ATR and XPS. Fig. 3 (a) shows the spectra of FTIR-ATR for the untreated PP sample and treated for 2.5 min with oxygen plasma PP-O$_2$. The region in the 2800–3000 cm^{-1} is associated with the vibration modes of the CH$_2$ and CH$_3$ groups present in the molecular structure of PP. The peaks around ~3350, ~1680–1730 and ~1500 cm^{-1} correspond to O-H stretching, C=O and C=C, respectively (Bhat & Upadhyay, 2002; Dorai & Kushner, 2003). The plasma treatment promotes an increase in the incorporation of oxygen-based species proved by the increase in 72% in the carbonyl index, as shown in Fig. 3(a). The same results are described by Bhat & Upadhyay (2002); Sanbhal et al. (2018). Previous results indicated that the chemical modification of PP due to oxygen plasma treatment increase the adhesion of a-C:H films to the substrate (Aguiar et al., 2013). Additionally, Fig. 3(b) illustrates the survey XPS spectra and Fig. 3(c) presents the deconvolution of carbon 1 s level for the untreated PP and the oxygen plasma-treated sample (PP-O$_2$). In the survey spectrum, C 1 s and O1s were fitted in 285.0 eV and 532.5 eV, respectively, where three components were used for C 1 s

The C1s peak in the spectrum of the PP when deconvoluted, Fig. 3(c), presents binding energy at 284.6 eV, corresponding to the C-C, at 286.4 eV for the C-O bonds and 287.9 eV for C=O. Table 3 presents the elemental composition and ratios of treated and untreated samples based on XPS spectra.

XPS results proved that, after the plasma treatment, an increase in the oxygenated species was observed (C-O and C=O). The increase in O/C ratio implied that the modified PP had an active surface from a chemical point of view after plasma exposure and the chemical reactions may happen between the plasma modification and atmospheric air exposure. These data corroborate those of FTIR-ATR.

4.2. Deposition and characterization of a-C:H films

The structure of the a-C:H film was evaluated by the Raman spectroscopy technique, which is widely used in literature for the chemical characterization of this type of film (Yu et al., 2008; Zhang et al., 2013). The deconvolution of the spectrum of a-C:H film results in two bands, G (1474 cm^{-1}) and D (1288 cm^{-1}), as shown in Fig. 4(a), and are derived from the sp^3 and sp^2 hybridization, respectively (Cruz et al., 2006; Maheswaran et al., 2011).

Based on the intensities of bands D (361.99) and G (607.53), it is possible to calculate the ratio index of intensity of the bands (I$_D$/I$_G$). Therefore, the greater the I$_D$/I$_G$, the higher similarity to DLC films, and the lower this ratio, the higher the structural PLC characteristic. In this case and due to the limitations of the reactor system, the structures obtained from a-C:H films are of type PLC, with an I$_D$/I$_G$ (362/607) of 0.59. The predominance of sp^3 bonds was also found by Li et al. (2009); Oliveira et al. (2012) when studying the properties of a-C:H films deposited on PET bottles and how increasing the RF power interferes with the structure of the films, leading to I$_D$/I$_G$ values less than 1.

Fig. 4(b) shows the deposition rate of the a-C:H films determined by the profilometry technique. As expected, an increase in the deposition time increases the thickness of the films. However, after 20 min of

Table 3
Concentration (%) of carbon and oxygen present and the ratio of the species' concentration on the surface of pristine PP and PP treated by 2.5 min.

Sample	C (%)	O (%)	O/C (%)
PP	92.3	7.0	0.075
PP-O$_2$	67.9	24.2	0.358

deposition time, this relationship was not so clear and a change in the slope of the curve was modified. Os (2000); Yasuda & Hsu (1977) studied the relationship between time and thickness of films deposited by plasma polymerization. They reported that the instability in the deposition of a-C:H films is related to the high reactivity of the radicals and active species formed in the process. This fact leads directly to saturation and non-homogeneity throughout the films, as observed in this case. Cheng et al. (2000) proposed a study of an adsorbed layer, it is possible to elucidate the reaction mechanism between the Ar/C$_2$H$_2$ gas mixture in plasma to the a-C:H film deposition by the PECVD schematized in Fig. 4(b). The film growth occurs by incorporating ions and neutral molecules, following the hydrogenation of films by hydrogen diffusing from the plasma sheath and impinging on the surface. The deposition rate depends on the adsorption of ethyl radicals and the etching process caused by ions and active argon species.

4.3. Contaminants migration

After the a-C:H films were deposited on contaminated PP, they were tested to evaluate their barrier property, with the variation of contaminants concentration present in the food simulants being the determining factor of the tests. This step was performed analyzing the migration of contaminants present in the samples submitted to a forced contamination protocol (US Food and Drug Administration (FDA), n.d.). The analytical parameters of the contaminant calibration curves are presented in the Supplementary material (Table S1). The linear ranges were from 0.0002 mg kg^{-1} to 4.92 mg kg^{-1} with regression coefficients r in the range of 0.9937–0.9997. The lowest values of LOD, indicating the sensitivity of the method, were obtained for toluene in both simulants, 3% acetic acid (LOD=0.00005 mg kg^{-1}) and 10% ethanol (LOD=0.00006 mg kg^{-1}). However, the highest LOD was obtained for tetracosane, 3% HAc *(LOD=0.0009 mg kg^{-1}))* and 10% EtOH (LOD=0.0012 mg kg^{-1}) and heptane, 3% HAc (LOD=0.0004 mg kg^{-1}) and 10% EtOH (LOD=0.00032 mg kg^{-1}). In addition, the same trend was observed for LOQ values.

Unfortunately, it is not possible to determine the exact concentration of the input of the contaminants in this system. One possibility for total contaminant determination employed is the dissolution of the pellets at high temperatures using the solvent toluene. However, one of the limitations of this technique for our process is the interference of the toluene solvent in the concentration of the toluene analyte used in the contamination process; the actual concentration would not be possible to extract from the pellets. In addition, the dissolution process has a high temperature that can cause loss by volatilization of the analytes. Furthermore, the cooling and consequent precipitation of the sample after the dissolution process can carry part of the analytes into the sample, which can also interfere with the actual concentration of the contaminants. However, in the migration analyses, after sample preparation, we analyzed the direct comparison with the control, standard sample (PPc), and the efficiency of the a-C:H films on the substrates. In addition, the 6:1 correction factor was used.

Fig. 5(a and b) shows the results of the migration tests comparing the concentration of contaminants under the test conditions for 3% acetic acid and 10% ethanol. To facilitate interpretation and visualization more accurately, Table S2 (Supplementary Material) shows the same data. In general, the data indicate that the migration of surrogates is influenced by (i) migration conditions, (ii) the physicochemical properties of the contaminants, and (iii) the presence of the functional barrier.

By the analyzing the results present in Fig. 5 and Table S2, it may be observed that for non-contaminated polypropylene (PPnc), only benzophenone and, tetracosane were detected. Benzophenone is present at a concentration below the limits established by legislation (0.6 mg kg^{-1}) (Silano, Bolognesi, & Castle, 2017), in 3% HAc and 10% EtOH simulant, and all conditions of the migration tests. This compound is widely used as a photoinitiator in catalytic polymerization reactions of
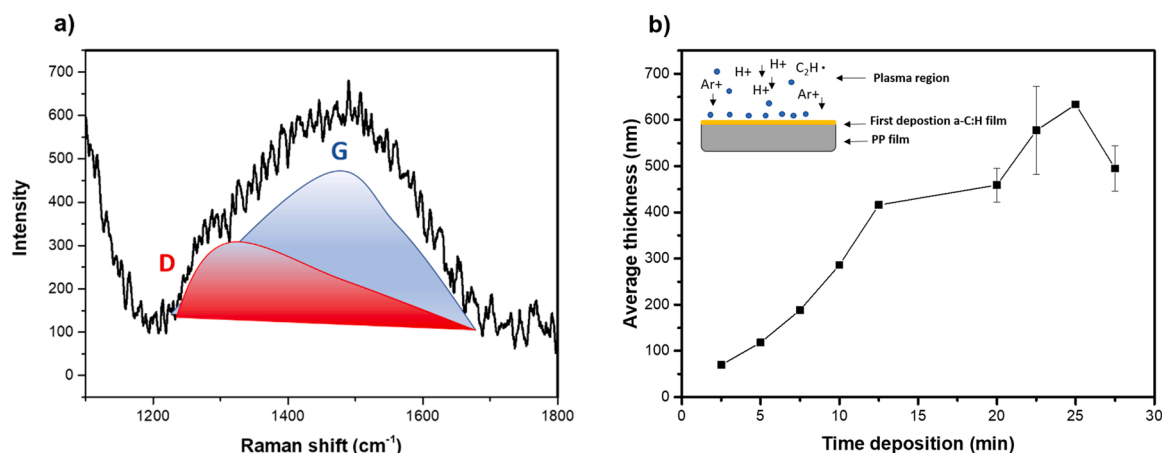
Fig. 4. : a) Raman spectrum of the a-C:H film and the deconvolution and characterization of the D and G bands referring to the type of a-C:H obtained from the band intensity ratio calculation I_D/I_G and b) determination of the deposition rate of a-C:H films and the schematization of the polymerization mechanism and PECVD-assisted deposition of a-C:H films.
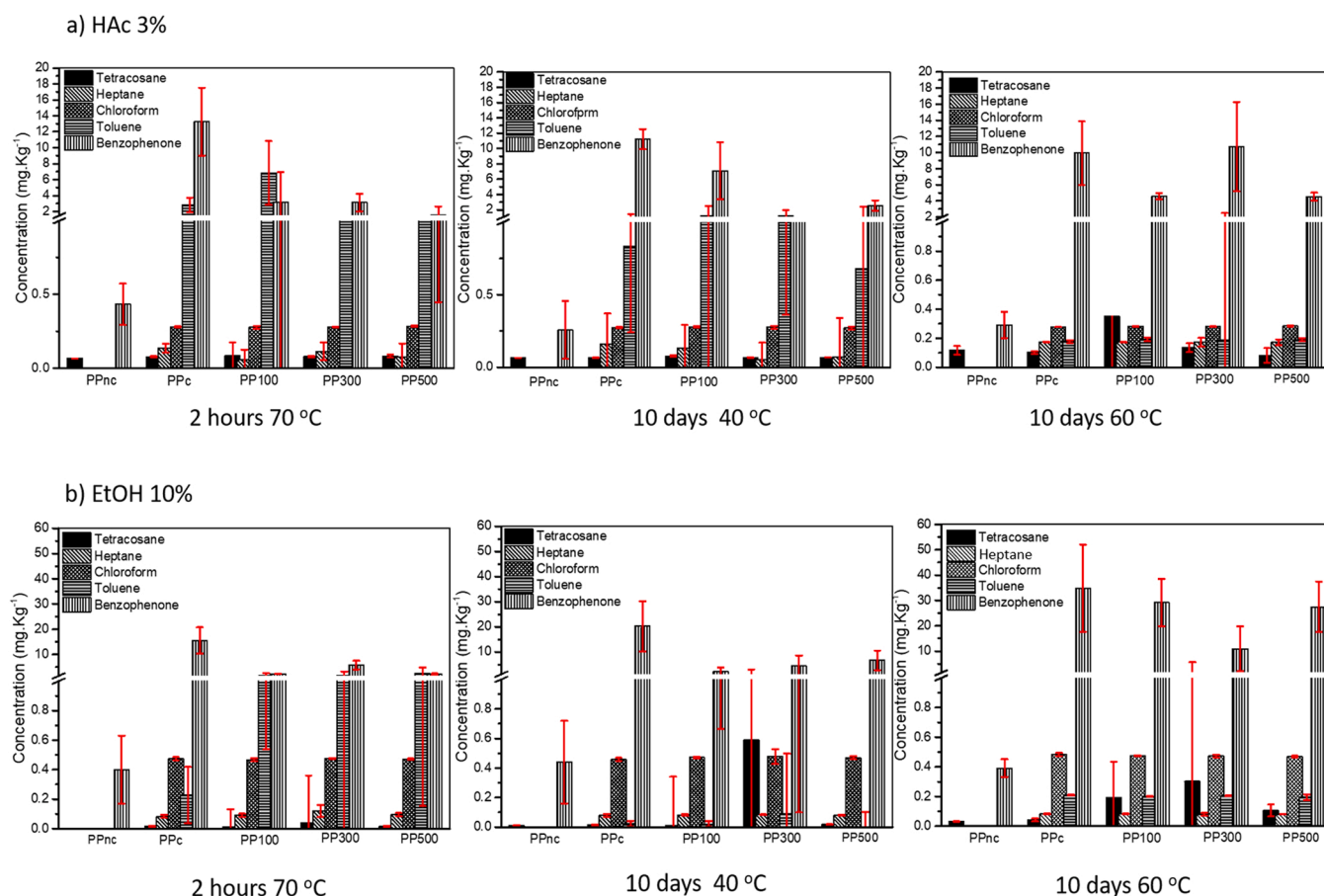

Fig. 5. : Concentration of contaminants that migrated from non-contaminated, contaminated and a-C:H films samples with different thicknesses to the food simulants a) acetic acid 3% and b) ethanol 10% after 2 h at 70 °C, 10 days at 40 °C and 10 days at 60 °C.

thermoplastic resins, adhesives, varnishes and printing inks, and is classified as an intentionally added additive (Silano et al., 2017). On the other hand, tetracosane probably comes from the processing step, as it is composed of long-chain hydrocarbons that are usually used as lubricants (motor oil) according to the Food Standards Agency (Food Standards Agency, 2006). Furthermore, according to the US FDA and the EU, which rely on "the dose makes the poison" principle to regulate substances that migrate from food packaging and processing equipment into

food, tetracosane is classified as an unlisted substance and for this type substance, according to the CEPE code of practice, it cannot migrate at a detection limit great than 0.01 mg kg^{-1} of food (Birgit, 2018; PlasticsEurope, 2011a). The tetracosane concentration is present at low levels, according to Table S2. Similar results were observed in another study by Paiva et. al. about the profile of odoriferous compounds in recycled PP samples when compared to pristine PP.

4.3.1. Influence of physicochemical properties of contaminants

The migration of surrogates is a process that depends mainly on diffusion, which is related to the physiochemical properties of the surrogate and the molecular structure of the polymer. Thus, many factors can change the process of migration of contaminants, among which molar mass, volatility (vapor pressure), and chemical affinity with food simulants are included (Incarnato et al., 1998). Additionally, it is important to emphasize that *migration of surrogates* in the contaminated samples depends on the input of contaminants during the contamination process, as well as the loss during the recycling steps and the preparation/manipulation of the samples, and subsequent output, which means migration to the food during the analyses. Consequently, in this work, the migration of contaminants from PPc (control) film samples was considered as the standard for comparison versus the a-C:H film, to later evaluate the influence of migration conditions and the presence of the a-C:H film.

As described by Paiva et al., the diffusion process has a close relationship with the molar mass of the surrogates (tetracosane – 338.65 g mol^{-1}, benzophenone – 182.2 g mol^{-1}, chloroform – 119.38 g mol^{-1}, toluene – 92.14 g mol^{-1}) (Paiva et al., 2022). However, there is no relationship between the molar mass and the *migration of contaminants*, which means that the molar mass is not the main factor in this case. Benzophenone, a polar and non-volatile compound, presents a higher concentration when compared to other surrogates, Fig. 5 and Table S1. The importance of volatility of the surrogate, and consequently its vapor pressure, on the migration, have been reported in the literature (Paiva et al., 2022). The low vapor pressure of benzophenone associated with higher affinity with aqueous liquids justifies this behavior. However, despite tetracosane being non-volatile, it has a low affinity for polar compounds, such as the food simulants employed.

As chloroform is a very volatile compound, it appears in concentrations below 0.5 mg kg^{-1}, even for the contaminated sample (PPc), which is related to its high vapor pressure (210 hPa) and its vaporization could occur during the contamination, sample preparation, and recycling steps as reported by Garcia et al. (2014). The same behavior was observed for toluene and heptane, which again was associated to their volatility and high vapor pressure, 30.88 hPa and 111 hPa, respectively, especially when compared to benzophenone (1.33 hPa).

4.3.2. Influence of migration conditions

In this study, different migration conditions (10 days at 40 °C, 10 days at 60 °C and, 2 h at 70 °C) were used as described by the EU (Commission Regulation (EU) No 10/2011, 2011) and the FDA (US Food and Drug Administration (FDA), n.d.), to submit the material under the most severe temperatures and time conditions anticipated for the proposed use. Voultzatis et al. (2007) showed that the key to understanding the diffusion process lies on the time and temperature at which the samples are exposed to migration test, i.e., the diffusion process should be faster at 70 °C for 2 h when compared to tests done at 40 and 60 °C for 10 days. However, this behavior was not found when the results shown in Fig. 5 are observed, for most samples, especially for the PP coated with a-C:H film. The glass transition temperature of the PP is relatively low (Tg −20 °C), which means that at the temperature of the migration tests, the PP films are in the rubber state, having a liquid structure with high segmented movements that increase the free volume that support the input and output of the surrogates. *The influence of time and temperature is clearly observed on the migration behavior of non-volatile compounds, such as benzophenone and tetracosane. Under most of the conditions analyzed, an increase in time leads to an increase in the concentration of these surrogates. Especially for the 10% ethanol food simulant, a significant increase in benzophenone migration is observed with increasing temperature. As previously described, an increase in temperature results in an increase in the free volume, which, in association with very long times, can favor the migration process of these contaminants. In addition to this parameter, it is observed that the chemical affinity between the contaminant and the food simulant is highlighted. 10% ethanol is a simulant with a*

stronger polarity than 3% acetic acid, causing benzophenone to migrate more in this type of contaminant. The presence of microcracks observed in Fig. 6 due to contact with food simulants may contribute to an increase in the migration process once the barrier is damaged.

As indicated, the migration process is a phenomenon that depends on several aspects that can have an isolated effect, such as temperature, or even overlap, such as time, temperature, chemical affinity, and vapor pressure, among others. For the other contaminants, a migration pattern is not observed, probably due to the lower concentration observed for these contaminants that do not allow a significant differentiation and their higher vapor pressure, and therefore, high volatility that allows their loss during the sample preparation step.

As described by Palkopoulou et al. (2016), polyolefins, such as polypropylene, present a greater diffusivity when compared to PET (Tg ≅ 69 °C) due to its lower Tg values. Additionally, the increase in temperature could also influence the adhesivity of the a-C:H film on the PP substrate, increasing the presence of microcracks and microdefects (Supplementary Materials, Fig. S1), and influencing the migration of contaminants.

4.3.3. Influence od barrier property of a-C:H films

For the PP coated with a-C:H films, two different behaviors were observed analyzing Table S2/Fig. 5. For the volatile contaminants (chloroform, heptane, and toluene), the a-C:H films did not seem to act as a barrier at all. In most cases, no difference was observed with contaminant migration. On the other hand, a decrease in contaminant migration was observed for benzophenone (non-volatile), in both simulants and under the three established conditions. For example, in 2 h at 70 °C, an 88% reduction in the concentration of these contaminants in 3% acetic acid as a food simulant was observed.

The *migration* of tetracosane is not influenced by the presence of a-C:H films. Its low volatility associated with the non-polar characteristic of this contaminant means that its migration, even under extreme conditions, will not occur. An increase in film thickness was expected to result in a reduction of the *migration* of the contaminants (Siracusa, 2012). *However, when analyzing Fig. 5, there is no relationship between an increase in the thickness of the deposited films and a decrease in the migration of contaminants. The results regarding the migration tests are related to a complex system and its interrelationships, such as (i) the affinity between contaminants and simulant, considering the worst contamination conditions, that is, 100% of post-consumer packaging is contaminated, (ii) the influence of time and temperature that affect not only the migration of contaminants but also the physicochemical properties of the PP films, and (iii) the presence of microdefects in the a-C:H films due to residual tension characteristic of the plasma deposition. The plasma surface treatment showed an effective increase in adhesion properties, as described in previous work (Aguiar et al., 2013). However, direct surface contact with the liquid simulants under migration test conditions directly interferes with the adhesion of the a-C:H films and the plasma-treated PP surface. Then, the a-C:H films could present stress on the film, leading to detachment and poor adhesion of the films to the surface (Pandiyaraj et al., 2015; Yang et al., 2009). Despite the importance of evaluating the presence of microdefects in the structure of plasma deposited films in the presence of food simulants, this important issue is a scarce topic in literature. Fig. 6 shows the SEM images before and after the migration test of the a-C:H films for the tests carried out at 40 °C for 10 days for both simulants, HAc 3% and EtOH 10%.*

It is clearly observed that in contact with the food simulant there is a detachment of the a-C:H films and the presence of microcracks. This behavior makes the migration process unpredictable and loses its correlation with thickness.

The results regarding the migration tests are related to a complex system and its interrelationships, such as (i) the affinity between contaminants and simulant, considering the worst contamination conditions, that is, 100% of post-consumer packaging is contaminated, (ii) the influence of time and temperature that affect not only the migration of contaminants but also the physicochemical properties of PP films, and
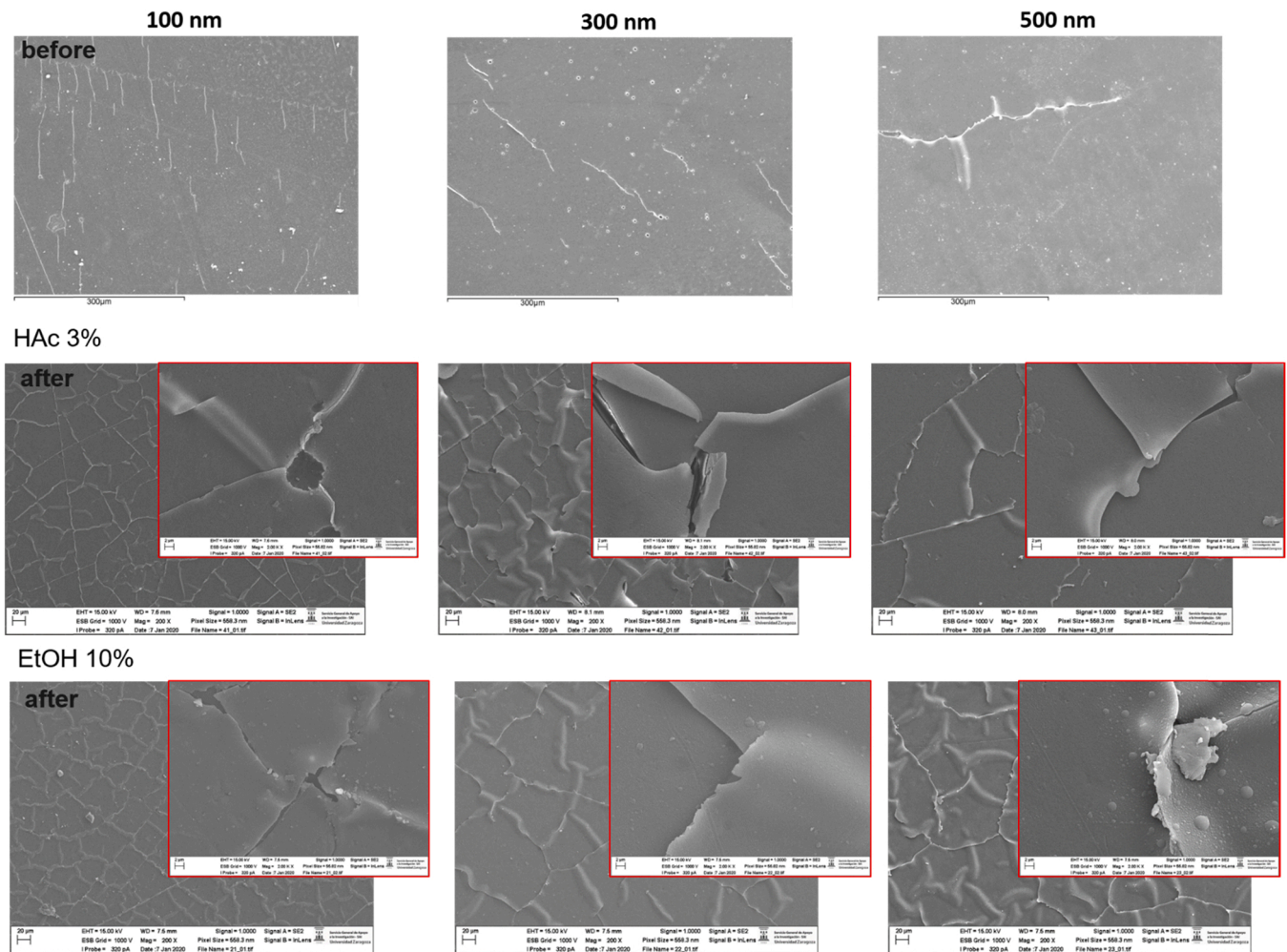
Fig. 6. : Microscopy images of the a-C:H films deposited by PECVD on the PP substrate before and after the contaminants migration tests for the HAc 3% and EtOH 10% simulants at 40 °C for 10 days.

(iii) the presence of microdefects in the a-C:H films due to residual tension characteristic of the plasma deposition. The plasma surface treatment showed an effective increase in adhesion properties, as described in previous work (Aguiar et al., 2013). However, direct surface contact with the liquid simulants under migration test conditions directly interferes with the adhesion of a-C:H films and the plasma-treated PP surface. Then, the a-C:H films could present stress on the film, leading to detachment and poor adhesion of films to the surface (Pandiyaraj et al., 2015; Yang et al., 2009). Although the presence of microdefects together with other factors affects the behavior of the migrants, this important issue is a scarce topic in literature. Fig. 6 shows the SEM images before and after the migration test of the a-C:H films for the tests done at 40 °C for 10 days for both simulants, HAc 3% and EtOH 10%.

The use of a-C:H films for increasing the contaminant barrier property in recycled food packaging and the plasma vapor deposition technique, PECVD, is a very interesting strategy to decrease the environmental impact because there is no waste generation and the a-C:H films are non-toxic as reported in some works (Aguiar et al., 2013; Boutroy et al., 2006; Stan et al., 2010). As described previously, the US FDA considers that the migrated concentration must be less than 0.6 mg kg^{-1} and 0.01 mg kg^{-1} for a substance listed and unlisted, respectively (US Food and Drugs Administration (FDA), 2021). For volatile contaminants, all recycling processes employed in this work are effective in decontaminating the material once levels of contamination below the stipulated amount by the US FDA were observed. Instead, for

benzophenone, the barrier is effective, although their concentration is present at a higher level than allowed by the regulatory agencies. Tetracosane has non-volatile and non-polar properties that result in lower migration to aqueous simulants. Nevertheless, the concentration of tetracosane is not influenced by the presence of a-C:H films. However, it is important to emphasize that the present study was conducted using extreme conditions (worst-case scenarios), which means that a higher concentration of surrogates will be found when compared to realistic conditions (Beneventi et al., 2020; Munoz et al., 2018; Palkopoulou et al., 2016).

The microscopy images (Fig. 6) show a crucial aspect regarding the migration of contaminants and the functional barriers. Before the material was submitted to the migration test, the a-C:H film seems to be intact with few points of detachment and wrinkles. These wrinkles did not present a great depth and were without expressive plate detachment, which can be a positive factor for the oxygen plasma treatment that increases the surface adhesiveness of the substrate through the incorporation of functional groups. However, these points increase the risk of surface stress when exposed to high-energy/temperature systems for a prolonged time and, when in contact with food simulants. As described previously, the migration testing was performed by employing the most severe conditions of temperature and time anticipated for the proposed use.

Then, after it is submitted to the migration test, there is a detachment of the films and the presence of microcracks, and microdefects can be observed. This behavior was observed in both food simulants and all

conditions (10 days with 60 °C and 2 h with 70 °C). The results can be seen in the Supplementary Material, Fig. S1. This factor was caused by the interaction of internal factors, such as the stress and reactivity of intramolecular active species and external factors, such as the temperature of the tests and the diffusion of contaminants that force stress points and increases the tendency of detachment and defects on the surface. However, even with the defects observed in the microscopy images, Fig. 6, the a-C:H films still represent an attractive strategy as a barrier to the migration of contaminants.

Additionally, according to Regulation (EC) No. 2023/2006, the definition of Good Manufacturing Practice (GMP), establishes quality assurance aspects of materials and articles that are consistently produced for food contact. Furthermore, GMP ensures that these materials do not represent a hazard to human health or cause an unacceptable risk of altering the composition of the food or its organoleptic properties (Commission Regulation EC, 2008; PlasticsEurope, 2011b)*.*

In this sense, the production and application of the functional barrier of the a-C:H film fits within the GMP because studies described in the literature (Rodil , 2006) *indicated that a-C:H does not induce any toxic effect. Therefore, the a-C:H films are a very promising strategy for use as a functional barrier, since they have applicability for recycled food packaging and comply with the GMP regulations for food contact materials.*

5. Conclusions

This work addresses the viability of the use of post-consumer recycled PP coated with a-C:H film as a functional barrier to reduce the migration of contaminants. The study was carried out to demonstrate that the PECVD surface treatment of recycled PP can be a good alternative for decreasing the migration of substances from the recycled material to the food in contact with them. This specially for benzophenone (non-volatile), in both simulants and under the three established conditions. On the other hand, for the volatile contaminants (chloroform, heptane, and toluene), the a-C:H films did not seem to act as a barrier at all. *That means, two different behaviors regarding the migration of contaminants were observed for the PP samples coated with a-C:H: (1) the barrier efficiency was not observed for volatile contaminants, such as chloroform, heptane, and toluene, and (2) a decrease in contaminant migration was observed for benzophenone (non-volatile), in both simulants and under the three established conditions.*

Although the integrity of the functional barrier is an important issue to the migration of contaminants, few works address the effect of contact with food simulating the real conditions. After the system is submitted to the migration test, it was observed a detachment of a-C:H films and, the presence of microcracks and microdefects can be observed. Even with the defects observed in the microscopy images, the a-C:H films still represent an attractive strategy as a barrier to the migration of contaminants. However, study strategies to avoid these defects may be the key to further improving its performance as a functional barrier.

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. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.fpsl.2022.100864.

References

Abbas, G. A., Roy, S. S., Papakonstantinou, P., & McLaughlin, J. A. (2005). Structural investigation and gas barrier performance of diamond-like carbon based films on polymer substrates. *Carbon, 43*(2), 303–309. https://doi.org/10.1016/j.carbon.2004.09.016

Aguiar, P. H. L., Vidotti, S. E., & Cruz, S. A. (2013). The effects of accelerated aging and contact with food simulants on the adhesion of amorphous hydrogenated carbon films deposited on clarified polypropylene. *Journal of Adhesion, 89*(8), 611–628. https://doi.org/10.1080/00218464.2013.781467

ANVISA, A.N. de V.S. (2004). *RDC N° 216_ ANVISA - Agência Nacional de Vigilância Sanitária.*

Associação Brasileira da Indústria do Plástico, A. (2018). Indústria brasileira de transformação e reciclagem de material plástico - perfil 2017. *Abiplast*, 45. ⟨http://www.abiplast.org.br/wp-content/uploads/2019/03/Perfil-2017.pdf⟩.

Associação Brasileira de Embalagens, A. (2015). O valor das embalagens flexíveis no aumento da vida útil e na redução do desperdício de alimentos. *ABRE- Associação Brasilera de Embalagens, 1*, 1–47. ⟨https://www.abre.org.br/wp-content/uploads/2021/11/cartilha-embalagens-fexiveis.pdf⟩.

Beneventi, E., Tietz, T., & Merkel, S. (2020). Risk assessment of food contact materials. *EFSA Journal, 18*(S1), 1–11. https://doi.org/10.2903/j.efsa.2020.e181109

Bhat, N. V., & Upadhyay, D.J. (2002). *Plasma-Induced Surface Modification and Adhesion Enhancement of Polypropylene Surface. June 2001.* https://doi.org/10.1002/app.11024.

Birgit, G. (2018). Dossier - Non-intentionally added substances (NIAS). *Food Packaging Forum, June,* 7. https://doi.org/10.5281/zenodo.1265331

Böll, H. (2019). Plastic Atlas. In L. Fuhr, H. Böll Fundation, & M. Franklin (Eds.), *Taiwan Review* (Second edi, Vol. 69, Issue 4). https://www.boell.de/sites/default/files/2020–01/PlasticAtlas 2019 2nd Edition.pdf.

Boutroy, N., Pernel, Y., Rius, J. M., Auger, F., Bardeleben, H. J. vo, Cantin, J. L., … Robertson, J. (2006). Hydrogenated amorphous carbon film coating of PET bottles for gas diffusion barriers. *Diamond and Related Materials, 15*(4–8), 921–927. https://doi.org/10.1016/j.diamond.2005.10.049

Cef, P. A. (2013). Scientific Opinion on the safety evaluation of the process "Schoeller Arca Systems", used to recycle polypropylene and high-density polyethylene crates for use as food contact material. *EFSA Journal, 11*(4), 1–10. https://doi.org/10.2903/j.efsa.2013.3187

Cef, P. A. (2014). Scientific Opinion on the safety assessment of the process "Petra Polimeri" used to recycle polypropylene trays and insert trays for use as food contact material. *EFSA Journal, 12*(7), 1–11. https://doi.org/10.2903/j.efsa.2014.3780

Cef, P. A., Beckman, U., Binderup, M., Bolognesi, C., Brimer, L., Castle, L., … Pratt, I. (2013). Scientific Opinion on the safety evaluation of the process "CO.N.I.P." used to recycle polypropylene and polyethylene crates for use as food contact material. *EFSA Journal, 11*(4), 1–9. https://doi.org/10.2903/j.efsa.2013.3157

Center for Food Safety and Applied Nutrition. (2006). *Guidance for Industry: Use of Recycled Plastics in Food Packaging (Chemistry Considerations) .* ⟨https://www.fda.gov/regulatory-information/search-fda-guidance-documents/guidance-industry-use-recycled-plastics-food-packaging-chemistry-considerations⟩.

Cheng, Y. H., Wu, Y. P., Chen, J. G., Qiao, X. L., Xie, C. S., Tay, B. K., … Shi, X. (2000). On the deposition mechanism of a-C:H films by plasma enhanced chemical vapor deposition. *Surface and Coatings Technology, 135*(1), 27–33. https://doi.org/10.1016/S0257-8972(00)00736-2

Commission Regulation (EC). (2008). Consolidated text: Commission Regulation (EC) No 2023/2006 of 22 December 2006 on good manufacturing practice for materials and articles intended to come into contact with food (Text with EEA relevance). Oj L 384, 75. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:02006R2023–20080417&from=EN.

Commission Regulation (EU) No 10/2011. (2011). COmmission Regulation (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food. *Offical Journal of the European Union, 21*, 1–136. ⟨https://www.legislation.gov.uk/eur/2011/10/contents⟩.

Cruz, S. A., Zanin, M., & de Moraes, M. A. B. (2009). Accelerated aging and contact with food simulants in adhesion of amorphous hydrogenated carbon films obtained by the PECVD process from recycled PET from packaging. *Journal of Applied Polymer Science, 111*(1), 281–290. https://doi.org/10.1002/app.29037

Cruz, S. A., Zanin, M., Nascente, P. A. P., & Bica de Moraes, M. A. (2010). Superficial modification in recycled PET by plasma etching for food packaging. *Journal of Applied Polymer Science, 115*(5), 2728–2733. https://doi.org/10.1002/app.29958

Cruz, S. A., Zanin, M., Nerin, C., & De Moraes, M. A. B. (2006). Study of barrier properties and chemical resistance of recycled PET coated with amorphous carbon through a plasma enhanced chemical vapour deposition (PECVD) process. *Food Additives and Contaminants, 23*(1), 100–106. https://doi.org/10.1080/02652030500384064

Dorai, R., & Kushner, M. J. (2003). A model for plasma modification of polypropylene using atmospheric pressure discharges. *Journal of Physics D: Applied Physics, 36*(6), 666–685. https://doi.org/10.1088/0022-3727/36/6/309

Food Standards Agency. (2006). *Guidance on Allergen Management and Consumer Information Best Practice Guidance on Managing Food Allergens with Particular Reference to Avoiding Cross-Contamination and Using Appropriate Advisory Labelling.* ⟨https://www.food.gov.uk/sites/default/files/multimedia/pdfs/maycontainguide.pdf⟩.

Garcia, P. S., Cruz, S. A., & Nerín, C. (2014). Comparison of different extrusion processes for cleaning the recycled polypropylene removing volatile and non-volatile

contaminants. *Progress in Rubber, Plastics and Recycling Technology, 30*(1), 37–54. https://doi.org/10.1177/147776061403000103

Garcia, P. S., Scuracchio, C. H., & Cruz, S. A. (2013). Effect of residual contaminants and of different types of extrusion processes on the rheological properties of the post-consumer polypropylene. *Polymer Testing, 32*(7), 1237–1243. https://doi.org/10.1016/j.polymertesting.2013.08.002

Goswami, R., Jana, T., & Ray, S. (2008). Transparent polymer and diamond-like hydrogenated amorphous carbon thin films by PECVD technique. *Journal of Physics D: Applied Physics, 41*(15). https://doi.org/10.1088/0022-3727/41/15/155413

Incarnato, L., Di Maio, L., Aciernot, D., Denaro, M., & Arrivabene, L. (1998). Relationships between processing-structure-migration properties for recycled polypropylene in food packaging*. *Food Additives and Contaminants, 15*(2), 195–202. https://doi.org/10.1080/02652039809374630

Incarnato, L., Scarfato, P., Acierno, D., Milana, M. R., & Feliciani, R. (2003). Influence of recycling and contamination on structure and transport properties of polypropylene. *Journal of Applied Polymer Science, 89*(7), 1768–1778. https://doi.org/10.1002/app.12168

Li, J., Gong, C., Tian, X., Yang, S., Fu, R. K. Y., & Chu, P. K. (2009). Structure and gas-barrier properties of amorphous hydrogenated carbon films deposited on inner walls of cylindrical polyethylene terephthalate by plasma-enhanced chemical vapor deposition. *Applied Surface Science, 255*(7), 3983–3988. https://doi.org/10.1016/j.apsusc.2008.10.064

Maheswaran, R., Ramaswamy, S., Thiruvadigal, D. J., & Gopalakrishnan, C. (2011). Systematic study of various stages during the growth process of diamond-like carbon film by atomic force microscopy. *Journal of Non-Crystalline Solids, 357*(7), 1710–1715. https://doi.org/10.1016/j.jnoncrysol.2011.02.012

Majumdar, J., Cser, F., Jollands, M. C., & Shanks, R. A. (2004). Thermal properties of polypropylene post-consumer waste (pp pcw). *Journal of Thermal Analysis and Calorimetry, 78*(3), 849–863. https://doi.org/10.1007/s10973-005-0453-0

Munoz, C., Eicher, A., Biedermann, M., & Grob, K. (2018). Recycled paperboard with a barrier layer for food contact: set-off during stacking or reeling. Analytical method and preliminary results. *Food Additives and Contaminants - Part A Chemistry, AnalysisControl, Exposure and Risk Assessment, 35*(3), 577–582. https://doi.org/10.1080/19440049.2017.1411618

Nakaya, M., Uedono, A., & Hotta, A. (2015). Recent progress in gas barrier thin film coatings on PET bottles in food and beverage applications. *Coatings, 5*(4), 987–1001. https://doi.org/10.3390/coatings5040987

NIST (National Institue of Science and Technology). (n.d.). Libro del Web de Química del NIST, SRD 69. *Retrieved March 26,* 2020, from ⟨Https://Webbook.Nist.Gov/⟩.

Oliveira, É. C., Cruz, S. A., & Aguiar, P. H. L. (2012). Effect of PECVD deposition parameters on the DLC/PLC composition of a-C:H thin films. *Journal of the Brazilian Chemical Society, 23*(9), 1657–1662. https://doi.org/10.1590/S0103-50532012005000027

Oliveira, É. C., Echegoyen, Y., Nerin, C., & Cruz, S. A. (2014). Barrier properties to surrogates of hydrogenated carbon nano-films deposited on PET by plasma-enhanced chemical vapour deposition. *Food Additives and Contaminants - Part A Chemistry, Analysis, Control, Exposure and Risk Assessment, 31*(11), 1914–1927. https://doi.org/10.1080/19440049.2014.968637

Os, M. T. Van (2000). Surface modification by plasma polymerization: film deposition, tailoring of surface properties and biocompatibility. *Film, 1–146*. https://doi.org/9036515130.

Osorio, J., Aznar, M., & Nerín, C. (2019). Identification of key odorant compounds in starch-based polymers intended for food contact materials. *Food Chemistry, 285* (September 2018), 39–45. https://doi.org/10.1016/j.foodchem.2019.01.157

Paiva, R., Veroneze, I. B., Wrona, M., Nerín, C., & Cruz, S. A. (2022). The role of residual contaminants and recycling steps on rheological properties of recycled polypropylene. *Journal of Polymers and the Environment, 30*(2), 494–503. https://doi.org/10.1007/s10924-021-02214-2

Paiva, R., Wrona, M., Nerín, C., Bertochi, I., Gavril, L., & Andrea, S. (2021). Importance of profile of volatile compounds from different recycled polypropylene used for food applications. *Food Chemistry, 350*(January), Article 129250. https://doi.org/10.1016/j.foodchem.2021.129250

Palkopoulou, S., Joly, C., Feigenbaum, A., Papaspyrides, C. D., & Dole, P. (2016). Critical review on challenge tests to demonstrate decontamination of polyolefins intended

for food contact applications. *Trends in Food Science and Technology, 49*, 110–120. https://doi.org/10.1016/j.tifs.2015.12.003

Pandiyaraj, K. N., Deshmukh, R. R., Arunkumar, A., Ramkumar, M. C., Ruzybayev, I., Ismat Shah, S., … Halim, A. S. (2015). Evaluation of mechanism of non-thermal plasma effect on the surface of polypropylene films for enhancement of adhesive and hemo compatible properties. *Applied Surface Science, 347*, 336–346. https://doi.org/10.1016/j.apsusc.2015.04.097

PlasticsEurope. (2011a). *Risk assessment of non-listed substances (NLS) and non-intetionally added substances (NIAS) under article 19. 32*(10).

PlasticsEurope, E. and C.-F (2011b). *Guidelines for Good Manufacturing Practice for Plastic Materials and articles intended for food contact applications. December 2005*.

Rodil, S. E., Olivares, R., Arzate, H., & Muhl, S. (2006). Biocompatibility, cytotoxicity and bioactivity of amorphous carbon films. In *Carbon* (Vol. 75, pp. 55–75). Springer Berlin Heidelberg. https://doi.org/10.1007/11378235_3

Sanbhal, N., Mao, Y., Sun, G., Xu, R. F., Zhang, Q., & Wang, L. (2018). Surface modification of polypropylene mesh devices with cyclodextrin via cold plasma for hernia repair: Characterization and antibacterial properties. *Applied Surface Science, 439*, 749–759. https://doi.org/10.1016/j.apsusc.2017.12.192

Silano, V., Bolognesi, C., Castle, L., Chipman, K., Cravedi, J., Engel, K., … Mennes, W. (2017). Safety of benzophenone to be used as flavouring. *EFSA Journal, 15*(11). https://doi.org/10.2903/j.efsa.2017.5013

Siracusa, V. (2012). Food packaging permeability behaviour: a report. *International Journal of Polymer Science, 2012*(i), 1–11. https://doi.org/10.1155/2012/302029

Stan, G. E., Marcov, D. A., Popa, A. C., & Husanu, M. A. (2010). Polymer-like and diamond-like carbon coatings prepared by RF-PECVD for biomedical applications. *Digest Journal of Nanomaterials and Biostructures, 5*(3), 705–718.

Suzuki, T., & Kodama, H. (2009). Diamond-like carbon films synthesized under atmospheric pressure synthesized on PET substrates. *Diamond and Related Materials, 18*(5–8), 990–994. https://doi.org/10.1016/j.diamond.2008.11.022

Tamor, M. A., & Vassell, W. C. (1994). Raman "fingerprinting" of amorphous carbon films. *Journal of Applied Physics, 76*(6), 3823–3830. https://doi.org/10.1063/1.357385

US Food and Drug Administration (FDA). (n.d.). Guidance for industry: Use of recycled plastics in food packaging. *Chemistry Considerations. HFS-275. Washington, DC: US FDA, Center for Food Safety and Applied Nutrition. 4*.

US Food and Drugs Administration (FDA). (2021). *Guidance for Industry: Use of Recycled Plastics in Food Packaging (Chemistry Considerations). December 1992*, 1–13. ⟨http://www.fda.gov/Food/GuidanceRegulation/GuidanceDocumentsRegulatoryInformation/IngredientsAdditivesGRASPackaging/ucm120762.htm⟩.

Vera, P., Uliaque, B., Canellas, E., Escudero, A., & Nerín, C. (2012). Identification and quantification of odorous compounds from adhesives used in food packaging materials by headspace solid phase extraction and headspace solid phase microextraction coupled to gas chromatography-olfactometry-mass spectrometry. *Analytica Chimica Acta, 745*, 53–63. https://doi.org/10.1016/j.aca.2012.07.045

Voultzatis, I. S., Papaspyrides, C. D., Tsenoglou, C. J., & Roussis, C. (2007). Diffusion of model contaminants in high-density polyethylene. *Macromolecular Materials and Engineering, 292*(3), 272–284. https://doi.org/10.1002/mame.200600420

Yang, S. B., Pan, F. M., Yang, Y. E., & Zhang, W. C. (2009). Effects of flow ratios on surface morphology and structure of hydrogenated amorphous carbon films prepared by microwave plasma chemical vapor deposition. *Applied Surface Science, 255*(22), 9058–9061. https://doi.org/10.1016/j.apsusc.2009.06.111

Yasuda, H., & Hsu, T. (1977). Some aspects of plasma polymerization investigated by pulsed R. F. discharge. *J Polym Sci Polym Chem Ed, 15*(1), 81–97. https://doi.org/10.1002/pol.1977.170150109

Yu, C., Wang, S. C., Sosnowski, M., & Iqbal, Z. (2008). Plasma-enhanced chemical vapor deposition of polyperinaphthalene thin films. *Synthetic Metals, 158*(10), 425–429. https://doi.org/10.1016/j.synthmet.2008.03.004

Zhang, Z., Song, R., Li, G., Hu, G., & Sun, Y. (2013). Improving barrier properties of PET by depositing a layer of DLC films on surface. *Advances in Materials Science and Engineering, 2013*. https://doi.org/10.1155/2013/861804

Zhao, Y., Huang, C., Huang, X., Huang, H., Zhao, H., Wang, S., & Liu, S. (2020). Effectiveness of PECVD deposited nano-silicon oxide protective layer for polylactic acid film: Barrier and surface properties. *Food Packaging and Shelf Life, 25*(October 2019), Article 100513. https://doi.org/10.1016/j.fpsl.2020.100513