



The Role of Residual Contaminants and Recycling Steps on Rheological Properties of Recycled Polypropylene

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Abstract

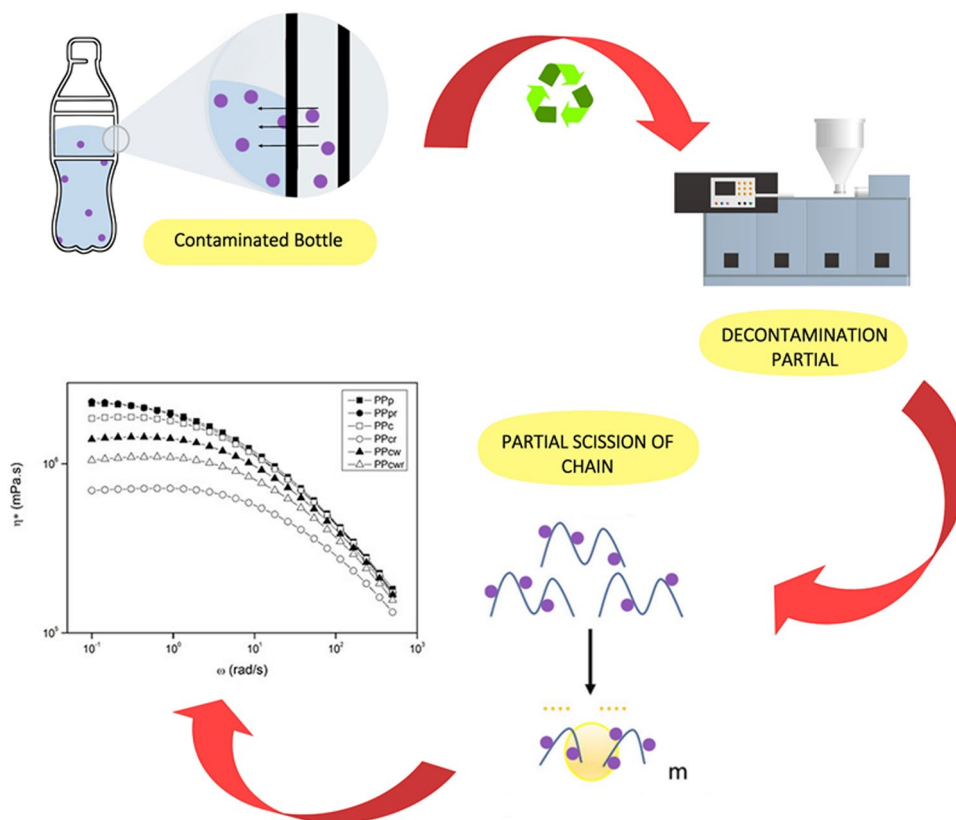
Recycling of polymers is one of the alternatives to reduce the impact of polymers presence on the environmental. However, the contaminants, defined as non-intentionally added substances, present in recycled material may migrate into food and also change its molecular structure. This work addresses the extractability/migration of contaminants from polypropylene (PP) samples into food simulants and the influence of these contaminants on the molecular structure of recycled PP. For this PP was contaminated with several substances to simulate a “worst-case” scenario and, then it was submitted to a recycling process. Extractability tests were performed by solid-phase microextraction and gas chromatography coupled to mass spectroscopy both to evaluate the presence of contaminants in the PP samples and their ability to migrate in food simulants. Additionally, molecular changes of the PP samples were evaluated by oscillatory rheometry. After washing and extrusion of the PP samples the extractability results showed considerable reductions of migrations in the food simulants and indicated, in some cases, compliance with regulations for using recycled polymer in contact with food. The residual contaminants were present in the polymer, the high temperatures and shear rates play an important role in molecular changes. Finally, the results highlight the importance of the use of rheological measurements to detect the influence of contaminants in recycled materials. Their presence result in material with different molar mass, that may be applied in different market applications.

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Graphic Abstract



Keywords Polypropylene · Recycling, migration · Contaminants · Degradation · Food simulants

Introduction

Using post-consumer-recycled polymers for food packaging has been increasing in the last few years and then, this has mitigated their environmental impact [1, 2]. Despite this, the usage of direct food contact packaging has some restrictions regulated by the Food and Drugs Administration (FDA) [3], the European Regulations No. 1935/2004; 10/2011 and 282/2008 [4]; and the National Health Surveillance Agency (ANVISA) [5] in Brazil and Mercosul [6]. This concern is associated with the misuse of packaging by the consumer through contamination with, for example, pesticides, solvents and cleaning products [7–11]. The decontamination process or the use of a functional barrier must be employed after the recycling process to ensure that the final material is safe and thus the migration is negligible [12]. The efficiency of the technology employed to recycle polymers involves the use of a procedure entitled “challenge test” [13]. During the test, the pristine polymer is exposed to a cocktail of contaminants with varying physicochemical properties, volatility

and polarity (volatile-nonpolar, volatile-polar, nonvolatile-polar and nonvolatile-nonpolar) and then, it goes through the recycling process. Early studies [9, 14–17] focus on the efficiency of the decontamination step and evaluate the migration of the surrogates to food simulants. However, most recycling technologies and studies deal with PET and few studies are dedicated to evaluating the stage of each recycling process in the decontamination of polyolefins.

However, polyolefins have lower thermal stability and products of the degradation may be formed during the processes, as described by Coulier, Orbons and Rijk [18]. Although this is an important issue, literature regarding the impact of the presence of residual contaminants on the physicochemical properties of the recycled polymer is scarce. Nevertheless, our research group has investigated this topic [9, 19]. For example, Garcia, Scuracchio and Cruz [15] evaluated the different mechanical recycling (single-screw, co-rotating twin-screw and cascade extruder) process on the post-consumer polypropylene (PP). The molecular structure of the PP was analyzed by rheological measurements, which demonstrated that

different types of processing together with contaminants showed distinct levels of degradation. In other words, the residual contaminants play an important role in the recycling process, especially for polyolefins. As described by Palkopoulos et al. [16] most studies extrapolate the results obtained for PET to the polyolefins. Notwithstanding, two aspects need to be addressed: (i) the PP is a rubbery polymer, which means that procedure temperatures are above its glass transition temperature. Consequently, it results in a high diffusion coefficient, when compared to other glassy polymers; and (ii) the PP has reduced thermal stability, which means the presence of residual contaminants may considerably influence its structural characteristics. In this way, rheometry has long been used to provide information on physicochemical properties, principally molar mass. Cruz and coworkers [20] used of melt rheology and solution viscometry to evaluate the degradation of post-consumer poly(ethylene terephthalate). The effects of the contaminants, reprocessing and solid state polymerization were analyzed.

Therefore, this work addresses the evaluation of the migration of residual contaminants and changes in the molecular structure of recycled polypropylene. It also assesses these effects on the recycling steps, such as washing and reprocessing. Initially, to simulate the worst-case scenario of misuse, polypropylene was contaminated with a cocktail, according to an FDA protocol [21]. Then the samples were submitted to a recycling process: washing and reprocessing via extrusion. Extractability tests were performed with liquid food simulants and analysis by SPME–GC–MS to evaluate the presence of contaminants released from the polymer, as well as its ability to migrate into food simulants. Molar mass (MM) and molar mass distribution are the most important parameters to evaluate the characteristics of the recycled polymer. Therefore, molecular changes were evaluated by rheometry in an oscillatory regimen. The main contribution of the present work was to study the extractability of residual contaminants after going through the recycling process, as well as its impact on the molar mass. In this way, MM distribution in recycled polypropylene for food contact will be further investigated.

Methodology

The experiment was developed into three main steps as follows: **step 1** consists of contaminating the PP with a cocktail of surrogates and recycling it; in **step 2**, the efficiency of the recycling process was evaluated by an extractability test using different food simulants; in **step 3**, given the presence of contaminants, the molecular structure was assessed by rheometry after the recycling process.

Materials

Polypropylene in pellets form (Prism 2400) supplied by Braskem S.A, Brazil was used in this project. It 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 and juices. The chemicals used for the contamination 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. 1422825). Ethanol (Merck, 99%) and acetic acid (Merck, 99%) were employed to prepare the food simulants, with 10% (v/v) ethanol and 3% (w/v) acetic acid respectively in MiliQ water.

Methods

Contamination and Recycling (Step 1)

Polypropylene pellets were subjected to contamination based on USFDA (2006) protocol [21]. The contamination cocktail represents the worst post-consumer condition that the polymer might be exposed to. The contaminants, concentration (volume/volume or mass/volume) and physicochemical properties used were in Table 1.

The samples were hermetically sealed for 14 days in constant stirring and at the temperature of 40 °C. After the contamination process, the PP pellets were subjected to three washing stages: (a) 10 min with 1 L of distilled water, (b) 1 L of 1% NaOH solution for 5 min and, (c) 1 L of distilled water finishing with air drying at a temperature of 25 °C. This methodology is well established by Garcia et al. [9].

The contaminated and washed PP pellets were then reprocessed in an AX Plastic extruder at three extrusion temperatures of 180, 190 and 210 °C. The screw speed was maintained at 30 rpm and the pelletizing process was carried out. Table 2 shows the correlation between the samples and their

Table 1 Concentration and physicochemical properties of the surrogates

| Contaminants | Concentration (%) | Physicochemical | Vapor pressure (hPa) |
|--------------|-------------------|----------------------------|----------------------|
| Benzophenone | 1 ^a | Non-volatile and polar | 1.33 |
| Chloroform | 10 ^b | Volatile and polar | 210 |
| Heptane | 78 ^b | Volatile and non-polar | 111 |
| Toluene | 10 ^b | Volatile and non-polar | 30.88 |
| Tetracosane | 1 ^a | Non-volatile and non-polar | – |

^ais m/v and ^b is v/v

respective nomenclatures after the PP pellets were submitted to the previously mentioned processes.

Extractability Tests (Step 2)

Two different food simulants were used for the extractability tests: (a) acetic acid 3% and, (b) ethanol 10%. Acetic acid 3% and ethanol 10% simulate acidic foods with $\text{pH} \leq 4.5$ and low-fat foods or beverages with low ethanol content, respectively.

Approximately 0.5 g of PP pellets were immersed in 18 g of the acetic acid 3% and ethanol 10%, employed as food simulants. The mixture was hermetically sealed in glass vials and maintained in different conditions: (1) 10 days at 40 °C, (2) 10 days at 60 °C and (3) 2 h at 70 °C. After the extractability tests, the solutions were filtered, and the surrogates in the simulants were extracted using solid-phase microextraction (SPME) and analyzed by gas chromatography coupled to the mass spectrometer (GC–MS).

DVB/CAR/PDMS (50/30 μm) fiber was used for extraction. The fiber was immersed in the samples for 15 min at 60 °C for acetic acid 3% and 30 min at 70 °C for ethanol 10%. Analytes were desorbed in GC 6890 N gas chromatograph from an Agilent (Palo Alto, CA, USA) injection port for 2 min. A CTC Analytics CombiPal from CTC Analytics AG (Zwingen, Switzerland) was coupled to the gas chromatograph. An HP-5 MS (30 cm \times 0.25 cm \times 0.25 μm) capillary column was used with the following temperature program: start at 40 °C for 5 min and increase 10 °C min^{-1} up to 300 °C 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} . An Agilent 5975 Mass Spectrometer was used as the detector. The temperatures of the MS source and the quadrupoles were 230 °C and 250 °C respectively. The SCAN mode was applied with a mass range of 50 to 400 m/z . The compounds were detected from the chromatograms obtained and identified using the mass spectra library (US National Institute of Standards and Technology, NIST) [22].

A quantitative analysis was performed by external standard calibration. Standard solutions were prepared in 3% acetic acid and 10% ethanol. The following analytical parameters of the applied method were determined: linearity, linear range and limits of detection (LOD) and quantification (LOQ). The signal-to-noise method was applied to determine LOD and LIQ. Chromatograms of the analytes at a low concentration were applied to determine the signal-to-noise value.

Molecular Changes (Step 3)

The complex viscosity (η^*), the storage modulus (G') and the loss modulus (G'') as a function of frequency (ω) were

determined by a parallel plate rheometer (Anton Paar MCR 305). The tests were performed at 190 °C in oscillatory mode. The parameters used were: 25 mm diameter plates, 1 mm gap, and the range of frequency used was 0.1 to 500 rad/s at 1% strain, which proved to be in the linear viscoelastic range according to a prior amplitude sweep test.

Results and Discussion

Migration of Contaminants

The analytical parameters are shown in supplementary material. Linear ranges from 0.0002 to 4735 mg kg^{-1} with regression coefficients (r) in the range of 0.9903 to 0.9997 were observed. The lowest values of LOD, indicating sensitivity of the method, were obtained for toluene in both solvents 3% acetic acid (LOD = 0.00006 mg kg^{-1}) and 10% ethanol (LOD = 0.00005 mg kg^{-1}). In contrast, the highest LOD was obtained for tetracosane in 3% acetic acid (LOD = 0.0088 mg kg^{-1}) and heptane in 10% ethanol (LOD = 0.0031 mg kg^{-1}). The same tendency was noticed for LOQ values.

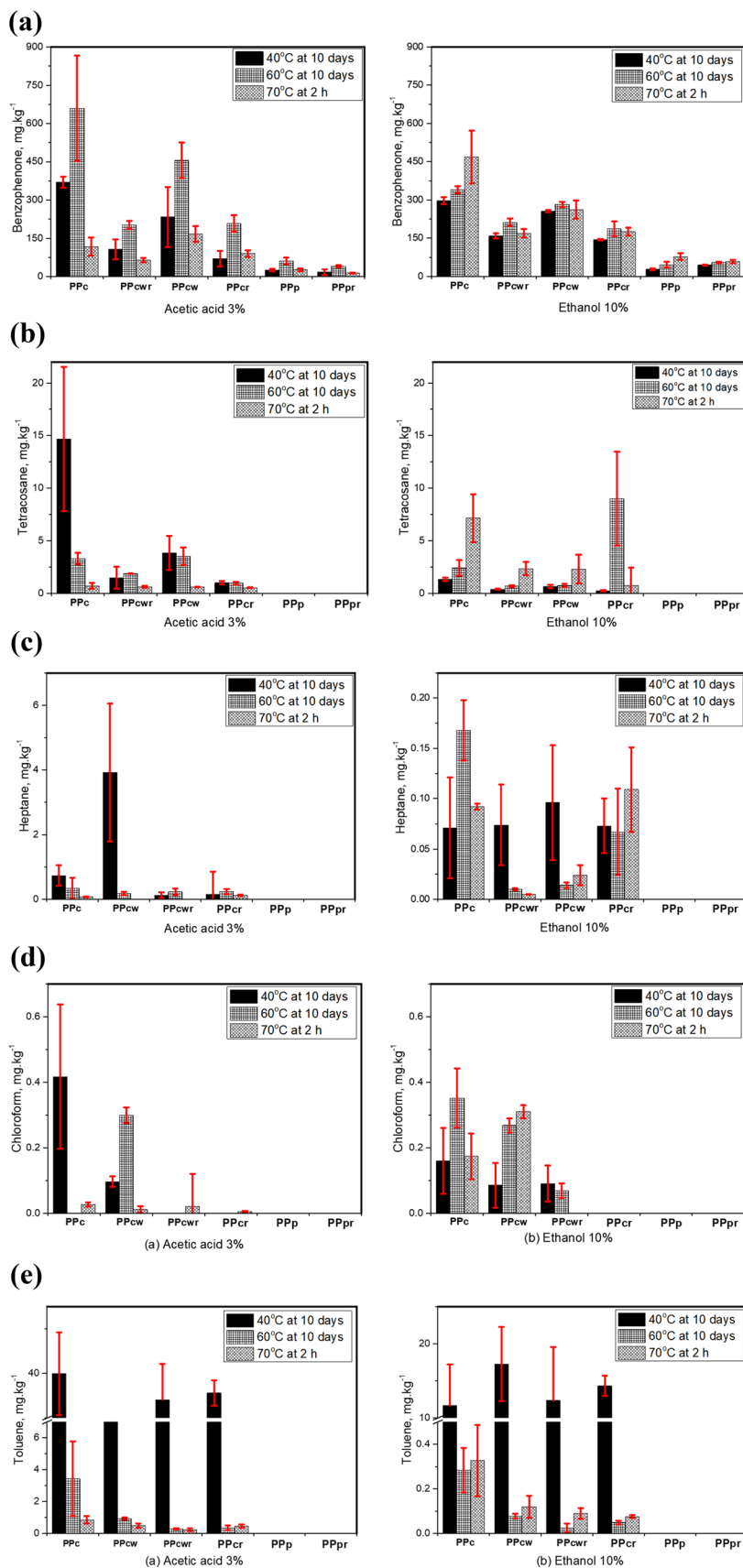
The residual contaminants that migrated into food in different conditions were analyzed by extractability tests since pellets instead of bottles or containers were available for the study. Therefore, it was possible to identify the influence of recycling on the decontamination process. Figure 1a–e) presents the results of the extractability for toluene, tetracosane, chloroform and benzophenone in acetic acid 3% and ethanol 10% as food simulants.

The extractability of contaminants depends on sorption, diffusion and migration processes and all of them may occur in the step of contamination as well as during the extractability test. Additionally, the time, temperature, physicochemical properties of the surrogate and molecular characteristics of the polymer impact these processes. Consequently, this is a complex system and its workability depends on intrinsic and extrinsic factors and its relationship with the characteristics of each polymer.

The results present in Fig. 1 show that, as expected, almost all contaminants are not present in the Ppp and Pppr, with exception of benzophenone. This contaminant is considered a non-intentionally added substance (NIAS), once it is widely used as a photoinitiator in the polymerization process. A recent study regarding the identification of different volatile compounds and odoriferous compounds present in recycled polypropylene carried out by Paiva et al. [23], showed that benzophenone is present in all studied samples, including pristine polypropylene.

Although the diffusion process is mainly governed by the surrogate molar mass and temperature, the results present in Fig. 1 show that these parameters are not the most

Fig. 1 Results of the extractability test on the PP samples for **a** benzophenone, **b** tetracosane, **c** heptane, **d** chloroform and **e** toluene for 40 °C at 10 days, 60 °C at 10 days and 70 °C at 2 h



important for this system. For example, the molar mass of the surrogates increases in the following order: toluene (92.14 g mol^{-1}) < chloroform ($119.38 \text{ g mol}^{-1}$) < benzophenone (182.2 g mol^{-1}) < tetracosane ($338.65 \text{ g mol}^{-1}$). Nevertheless, despite this observation, there was no correlation between the molar mass of the surrogates and the extractability (Fig. 1). Therefore, the molar mass does not seem to be an important parameter in this case.

As previously described, the time and temperature, as well as the intrinsic characteristics of the surrogates and food simulants, are the key parameters for understanding the diffusion process. It would be expected that the rate of diffusion increases with the temperature, as described by Voulzatis et al. [24]. Based on this consideration, the diffusion of surrogates was expected to be faster at $70 \text{ }^\circ\text{C}$ and slower at $60 \text{ }^\circ\text{C}$, considering the same time (10 days). The glass transition temperature was significantly lower for the PP [25] ($T_g \cong -20 \text{ }^\circ\text{C}$), which means that at the experimental temperature, the PP is in a rubbery state ($T > T_g$). It consists of a liquid-like structure with high segmental motions resulting in an increase of free volume as a function of temperature. This behavior explains the greater diffusivity in polyolefins, such as PP and PE compared to PET ($T_g \cong 69 \text{ }^\circ\text{C}$), as described by Palkopoulou et al. [26]. However, the influence of temperature is not linear for all contaminants since it was observed, for example, that tetracosane and chloroform migrated more at $40 \text{ }^\circ\text{C}$ in 3% acetic acid than in 10% ethanol. In most cases, time is a crucial parameter for migration, since the diffusion process depends on it as previously mentioned. The highest migration was observed for benzophenone. Benzophenone is a polar, non-volatile compound with a chemical group with free electrons in the oxygen that can strongly interact with the oxygen in 3% acetic acid and 10% ethanol [27].

Contrarily, chloroform (a polar and volatile compound) presents low concentration, as expected. Consequently, it is impossible to detect it in the PPcr sample, according to LOD and LOQ present in Table 2. The chloroform presents a high vapor pressure, which is a parameter that controls the volatility of a chemical, and the temperature of measurements (40 , 60 and $70 \text{ }^\circ\text{C}$) may contribute to low values of concentration of these surrogates.

Table 2 Nomenclature of the PP samples employed in this work

| Samples | Nomenclature |
|------------------------------------|--------------|
| Pristine (unused) PP | PPp |
| Pristine-reprocessed PP | PPpr |
| Contaminated PP | PPc |
| Contaminated-reprocessed PP | PPcr |
| Contaminated-washed PP | PPcw |
| Contaminated-washed-reprocessed PP | PPcwr |

Regarding the non-polar surrogates, the concentration of tetracosane and toluene is lower since the chemical affinity with polymer (non-polar) is high. Considering that the system consists of polymer, food simulant and surrogate, chemical similarity plays an important role in this process. Both simulants present similar polarity [28] but toluene presents a lower molar mass (92.10 g/mol) when compared to tetracosane (338.65 g/mol). As described previously, the molar mass affects the diffusion process, i.e., the higher the molar mass the lower the diffusion of contaminants. The chemical similarity between polymer and surrogates explains the low concentration in food simulants for non-polar surrogates. The opposite results were obtained by Oliveira et al. [20] using PET as the matrix and toluene as the contaminant. PET is a polar polymer and, according to the authors, the high concentration of these contaminants was due to the low affinity with this polymer.

Influence of Recycling on the Migration

The effects of decontamination were verified and the obtained results were analyzed considering each step (washing and reprocessing). There are several different types of washing processes for post-consumer polymers. They are very dependent on the available technology, as well as, the final destination of the product [29]. The cleaning process for the food market is done in critical and extreme conditions to guarantee high levels of decontamination [16]. In this work, we decided to use a common process to clean recycled resin. In most cases, the cleaning process helps to decontaminate the samples. This behavior is clear when the PPc is compared with the PPcw. However, heptane and chloroform compounds are volatile and have a high vapor pressure, 210 hPa and 111 hPa respectively, which can result in volatility and high standard deviation in the measurements. In addition to this fact, extractability tests were performed on samples in pellet format, which are relatively irregular. Thus, it is not possible to use a correction factor [27] to standardize the samples to minimize surface imperfection errors, which would delimit the area of analysis performed on the samples in the film form. This problem is accentuated since the simulant and contaminant interaction is high, as in the case of 3% acetic acid and volatile contaminants (chloroform), which is seen in Fig. 1c and d.

Additionally, the reprocessing in a single screw extruder assisted the decontamination (comparing PPcw to PPcwr and PPc to PPcr). All samples that are submitted to an extrusion process present a lower level of contaminants. First of all, during the extrusion process, the polymer is melting and in the melting state, the diffusion process increases significantly [16] and enhances the decontamination, especially that of volatile compounds because of the high temperature. Additionally, during the reprocessing, the polymer is

continuously submitted to a high shear rate and temperature. In both cases, the mobility of polymer chains and that of the molecules of contaminants is favorable. Although technologies of PET decontamination are widely investigated [2, 30, 31], literature is scarce when it comes to PP. One exception is the work developed by Garcia, Cruz and Nerin [15] that analyzed different extrusion processes during the decontamination of the PP samples. The obtained results showed that the most efficient process was the co-rotating twin-screw extruder with forced degassing, which was attributed to the higher shear rates and the degassing system.

Influence of Residual Contaminants into the Molecular Structure

The quality, aggregate value and employability of the recycled polymers are associated with the degradation degree that polymers may suffer after the recycling process. Two aspects must be considered when a polymer is submitted to high shear rates, temperature and presence of contaminants: (i) the chain scission and thus, its molar mass, which is reflected in mechanical and thermal properties, and (ii) the flow characteristics, which affects the processability. Although this is an important aspect, this literature does not discuss it. The presence of contaminants in each step of the recycling process influences the molecular structure. Thus, the molar mass is one of the most important parameters and may be analyzed by the displacement of crossover point, that is $G'(\omega) = G''(\omega)$ [32, 33], which is correlated with the increase or decrease of the molar mass, as well as the narrowing or widening of its distribution (Figure S1.—Supplementary Information).

Table 3 presents the results of the crossover point, $G(\omega) = G''(\omega)$, for all samples, analyzed by its displacement. The results indicated that the molar mass and its distribution were altered as a function of the presence of contaminants, reprocessing and washing.

It is important to notice that the surrogates may act as a plasticizer to PP. The plasticizing effect of organic compounds was described in the literature [34]. Analyzing the pristine PP (PPp) with contaminated PP (PPc) a slight decrease in complex viscosity is observed. However, it is

Table 3 Crossover point values, $G'(\omega) = G''(\omega)$, for the samples

| | $G'(\omega) = G''(\omega)$ | ω (rad/s) |
|-------|----------------------------|------------------|
| PPp | 29,072 | 84 |
| PPpr | 29,409 | 92 |
| PPc | 30,189 | 95 |
| PPcr | 36,940 | 302 |
| PPcwr | 31,728 | 121 |
| PPcwr | 33,892 | 164 |

expected that this effect is reduced for samples that have gone through the washing and reprocessing steps. As described by Garcia et al. in a study on polypropylene decontamination using different processes, the recycling step plays an important role in reducing the presence of contaminants.

The results in Table 3 show that the presence of contaminants affects the PP molar mass. This effect was clearly observed when the samples without contaminants (PPpr) were compared with their contaminated counterparts (PPcr). The samples submitted to reprocessing in the presence of contaminants (PPcr and PPcwr) showed higher levels of degradation, and, consequently, lower values of molar mass. The presence of contaminants together with high shear rates and temperature, characteristics of the extrusion process, lead to a scission of the PP chain. The degradation of PP occurs by a radical scission chain, especially in the tertiary carbon [35]. The formation of free macroradicals occurs in the initiation phase, after which these radicals react with oxygen forming peroxy radicals. In the propagation phase of the reactions, the peroxy radicals abstract the hydrogens from the tertiary polypropylene carbons to form the hydroperoxides and more free radicals. In the termination phase, free radicals bind and there is also the formation of carbonyl groups, a typical characteristic of the β scission of the polypropylene chain [35]. Another important parameter, that was analyzed, is the molar mass distribution (MMD). The PP degradation leads to narrowing the MMD, which means that the lower values of molar mass presented a significant narrowing in the MMD [36–40]. Incarnato et al. conducted a study about the effect of reprocessing steps on the physical and molecular properties of recycled polypropylene. The results of the intrinsic viscosity analysis showed that there was a decrease in molar mass and a narrowing distribution of molar mass compared to pristine polypropylene [38].

The narrowing of the MMD can be observed also by the flow curve shown in Fig. 2. In the samples that present a

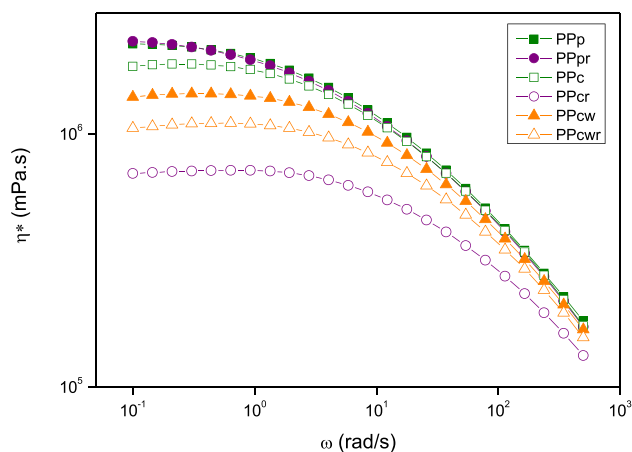


Fig. 2 Complex frequency as a function of frequency for all samples

high level of degradation (PPcr), a higher Newtonian plateau can be observed. On the other hand, in the samples with higher molar mass and widened MMD the plateau is significantly lower due to the inferior chain length that can act as a lubricant, increasing the pseudoplastic behavior of the sample.

Figure 3 depicts the results of the storage modulus (G') and the loss modulus (G'') as a function of the frequency. These parameters are dependent on the length and the level of the entanglements of the chains. The samples with a higher level of degradation show lower values of G' and G'' . These results confirm those previously obtained, indicating that the contaminants together with reprocessing significantly decrease the molar mass and the level of entanglements.

Additionally, an interesting behavior has been observed when the extractability measurements were compared to rheometry. First, the samples with a lower level of contaminants presented the higher molar mass (PPp and PPpr). Nevertheless, the contaminants alone have not been able to decrease the molar mass significantly (PPc) and as previously described, this fact could be associated with the plasticizing effect of the surrogates. The samples extruded with a high content of contaminants (PPcr) have lower molar mass when compared PPc. These results prove that the higher temperatures and shear rates, characteristics of the extrusion process, together with contaminants are the key points to understanding the molecular structure changes of the recycled polymer. Additionally, the reprocessing and cleaning process decreased the level of contaminants. Therefore, it is an important issue to make feasible the use of recycled material for direct contact with food.

Conclusion

This work addressed the extractability of residual contaminants after going through the recycling process, as well as its impact on the polypropylene molecular structure. This was associated with the packaging misuse that leads to the contamination of the polymer with chemical products, which will eventually migrate into food or decrease the molar mass making its applicability unfeasible.

The extractability results showed that there was no correlation between the molar mass of the surrogates and employed temperature. On the other hand, the chemical affinity between the surrogate and food plays an important role in this complex process. Almost all contaminants were not present in the PPp and PPpr, with exception of benzophenone. It should be highlighted that this contaminant is considered as an intentionally added substance, once it is widely used as a photoinitiator in the polymerization process. Chloroform presented high vapor pressure and it was determined to have a low concentration. Regarding the non-polar surrogates, the concentration of tetracosane and toluene was low, since its chemical affinity with the polymer (non-polar) was high.

Additionally, the reprocessing in a single screw extruder assisted the decontamination process (comparing PPcw to PPcwr and PPc to PPcr) due to the high temperatures and shear rates. For all surrogates, their quantified concentration was significantly lower after the washing and extrusion processes.

The quality of the recycled polymers was associated with the degradation degree that they may suffer after the recycling process. It may affect its molar mass, which not only impacts its properties but also its flow characteristics, which affects the processability. Rheometry results showed that the

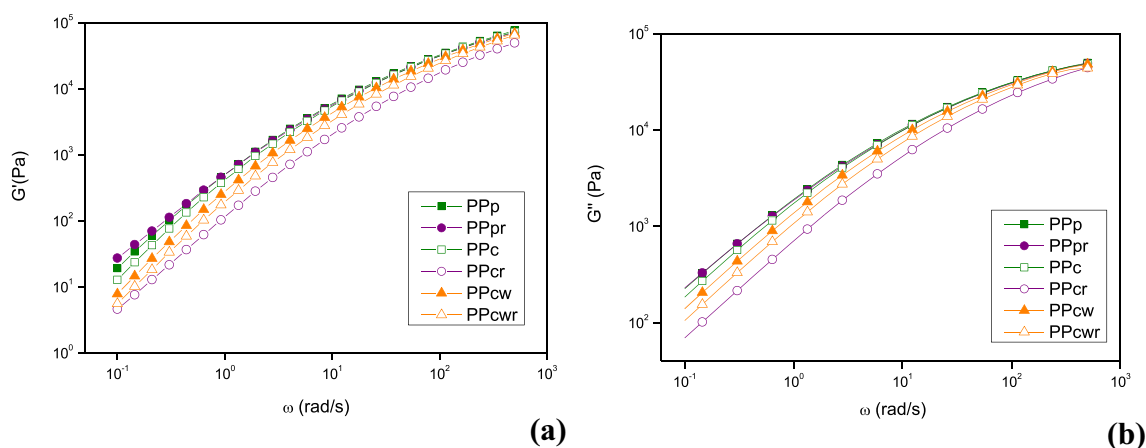


Fig. 3 Storage modulus (G') as a function of the frequency for all samples (a) and loss modulus (G'') as a function of the frequency for all samples (b)

presence of contaminants affected the PP molar mass. This effect was more significant when the samples were submitted to reprocessing in the presence of surrogates. Also, the samples with higher molar mass and widening MMD presented a significant lower Newtonian plateau, due to the inferior chain length that can act as a lubricant increasing the pseudoplastic behavior of the sample. These results prove that the high temperatures and shear rates, characteristics of the extrusion process, together with contaminants are the keys to understanding the molecular structure changes of the recycled polymer. Notwithstanding, in some cases, residual levels of some surrogates above those permitted by the legislation were still detected in the resin even after the recycling process.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10924-021-02214-2>.

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Data availability The data are in public repository at UFSCar: <https://repositorio.ufscar.br/>

Declarations

Conflict of interest The authors confirm that they have no conflicts of interest with respect to the work described in this manuscript.

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