

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

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1 **THE ROLE OF RESIDUAL CONTAMINANTS AND RECYCLING STEPS**
2 **ON RHEOLOGICAL PROPERTIES OF RECYCLED POLYPROPYLENE**

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10
11 **Abstract**

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

28 Keywords: polypropylene; recycling, migration; contaminants; degradation; food
29 simulants.

31 **1) INTRODUCTION**

32 Using post-consumer-recycled polymers for food packaging has been increasing in the
33 last few years and then, this has mitigated their environmental impact [1,2]. Despite
34 this, the usage of direct food contact packaging has some restrictions regulated by the
35 Food and Drugs Administration (FDA) [3], the European Regulations No. 1935/2004;
36 10/2011 and 282/2008 [4]; and the National Health Surveillance Agency (ANVISA) [5] in
37 Brazil and Mercosul [6]. This concern is associated with the misuse of packaging by the
38 consumer through contamination with, for example, pesticides, solvents and cleaning
39 products [7–11]. The decontamination process or the use of a functional barrier must
40 be employed after the recycling process to ensure that the final material is safe and thus
41 the migration is negligible [12]. The efficiency of the technology employed to recycle
42 polymers involves the use of a procedure entitled “challenge test” [13]. During the test,
43 the pristine polymer is exposed to a cocktail of contaminants with varying
44 physicochemical properties, volatility and polarity (volatile-nonpolar, volatile-polar,
45 nonvolatile-polar and nonvolatile-nonpolar) and then, it goes through the recycling
46 process. Early studies [9,14–17] focus on the efficiency of the decontamination step and
47 evaluate the migration of the surrogates to food simulants. However, most recycling
48 technologies and studies deal with PET and few studies are dedicated to evaluating the
49 stage of each recycling process in the decontamination of polyolefins.

50 However, polyolefins have lower thermal stability and products of the degradation
51 may be formed during the processes, as described by Coulier, Orbons and Rijk [18].
52 Although this is an important issue, literature regarding the impact of the presence of
53 residual contaminants on the physicochemical properties of the recycled polymer is

54 scarce. Nevertheless, our research group has investigated this topic [9,19]. For example,
55 Garcia, Scuracchio and Cruz [15] evaluated the different mechanical recycling (single-
56 screw, co-rotating twin-screw and cascade extruder) process on the post-consumer
57 polypropylene (PP). The molecular structure of the PP was analyzed by rheological
58 measurements, which demonstrated that different types of processing together with
59 contaminants showed distinct levels of degradation. In other words, the residual
60 contaminants play an important role in the recycling process, especially for polyolefins.
61 As described by Palkopoulus [16], most studies extrapolate the results obtained for PET
62 to the polyolefins. Notwithstanding, two aspects need to be addressed: (i) the PP is a
63 rubbery polymer, which means that procedure temperatures are above its glass
64 transition temperature. Consequently, it results in a high diffusion coefficient, when
65 compared to other glassy polymers; and (ii) the PP has reduced thermal stability, which
66 means the presence of residual contaminants may considerably influence its structural
67 characteristics. In this way, rheometry has long been used to provide information on
68 physicochemical properties, principally molar mass. Cruz and coworkers [29] used of
69 melt rheology and solution viscometry to evaluate the degradation of post-consumer
70 poly(ethylene terephthalate). The effects of the contaminants, reprocessing and solid
71 state polymerization were analyzed.

72 Therefore, this work addresses the evaluation of the migration of residual
73 contaminants and changes in the molecular structure of recycled polypropylene. It also
74 assesses these effects on the recycling steps, such as washing and reprocessing. Initially,
75 to simulate the worst-case scenario of misuse, polypropylene was contaminated with a
76 cocktail, according to an FDA protocol [20]. Then the samples were submitted to a
77 recycling process: washing and reprocessing via extrusion. Extractability tests were

78 performed with liquid food simulants and analysis by SPME-GC-MS to evaluate the
79 presence of contaminants released from the polymer, as well as its ability to migrate
80 into food simulants. Molar mass (MM) and molar mass distribution are the most
81 important parameters to evaluate the characteristics of the recycled polymer.
82 Therefore, molecular changes were evaluated by rheometry in an oscillatory regimen.
83 The main contribution of the present work was to study the extractability of residual
84 contaminants after going through the recycling process, as well as its impact on the
85 molar mass. In this way, MM distribution in recycled polypropylene for food contact will
86 be further investigated.

87

88 **2) METHODOLOGY**

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

94

95 **2.1) Materials**

96 Polypropylene in pellets form (Prism 2400) supplied by Braskem S.A, Brazil was
97 used in this project. It presents a melt flow index (MFI) of 20 g/10 min (ASTM 1238,
98 230°C, 2.16 kg) and density of 0.902 g/cm³ (ASTM D 792). It is used for food packaging,
99 such as transparent bottles for mineral water, teas and juices. The chemicals used for

100 the contamination were chloroform (Vetec, 99.8%, CAS No 67663), toluene (Vetec,
 101 99.5%, CAS No. 108883), benzophenone (Acros Organics, 99%, CAS No. 119619),
 102 tetracosane (Merck, 99%, CAS No 646311) and heptane (Synth, 99%, CAS No. 1422825).
 103 Ethanol (Merck, 99%) and acetic acid (Merck, 99%) were employed to prepare the food
 104 simulants, with 10% (v/v) ethanol and 3% (w/v) acetic acid respectively in MiliQ water.

105

106 2.2) Methods

107 2.2.1 Contamination and recycling (Step 1)

108 Polypropylene pellets were subjected to contamination based on USFDA (2006)
 109 protocol [20]. The contamination cocktail represents the worst post-consumer condition
 110 that the polymer might be exposed to. The contaminants, concentration
 111 (volume/volume or mass/volume) and physicochemical properties used were in Table
 112 1.

113 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	-

114 ^a is m/v and ^b is v/v.

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

120 The contaminated and washed PP pellets were then reprocessed in an AX Plastic
121 extruder at three extrusion temperatures of 180, 190 and 210°C. The screw speed was
122 maintained at 30 rpm and the pelletizing process was carried out. Table 1 shows the
123 correlation between the samples and their respective nomenclatures after the PP pellets
124 were submitted to the previously mentioned processes.

125 Table 1: 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

126

127 **2.2.2 Extractability tests (Step 2)**

128 Two different food simulants were used for the extractability tests: (a) acetic acid
129 3% and, (b) ethanol 10%. Acetic acid 3% and ethanol 10% simulate acidic foods with pH
130 ≤ 4.5 and low-fat foods or beverages with low ethanol content, respectively.

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

137 DVB/CAR/PDMS (50/30 µm) fiber was used for extraction. The fiber was
138 immersed in the samples for 15 min at 60°C for acetic acid 3% and 30 min at 70°C for
139 ethanol 10%. Analytes were desorbed in GC 6890N gas chromatograph from an Agilent
140 (Palo Alto, CA, USA) injection port for 2 min. A CTC Analytics CombiPal from CTC Analytics
141 AG (Zwingen, Switzerland) was coupled to the gas chromatograph. An HP-5 MS (30 cm
142 x 0.25 cm x 0.25 µm) capillary column was used with the following temperature
143 program: start at 40°C for 5 min and increase 10°C min⁻¹ up to 300°C for 1 min. The
144 injector had a temperature of 250°C and helium was the carrier gas used with a flow of
145 1 mL min⁻¹. An Agilent 5975 Mass Spectrometer was used as the detector. The
146 temperatures of the MS source and the quadrupoles were 230°C and 250°C respectively.
147 The SCAN mode was applied with a mass range of 50 to 400 m/z. The compounds were
148 detected from the chromatograms obtained and identified using the mass spectra
149 library (US National Institute of Standards and Technology, NIST) [21].

150 A quantitative analysis was performed by external standard calibration. Standard
151 solutions were prepared in 3% acetic acid and 10% ethanol. The following analytical
152 parameters of the applied method were determined: linearity, linear range and limits of
153 detection (LOD) and quantification (LOQ). The signal-to-noise method was applied to

154 determine LOD and LIQ. Chromatograms of the analytes at a low concentration were
155 applied to determine the signal-to-noise value.

156

157 **2.2.3 Molecular changes (Step 3)**

158 The complex viscosity (η^*), the storage modulus (G') and the loss modulus (G'')
159 as a function of frequency (ω) were determined by a parallel plate rheometer (Anton
160 Paar MCR 305). The tests were performed at 190°C in oscillatory mode. The parameters
161 used were: 25 mm diameter plates, 1 mm gap, and the range of frequency used was 0.1
162 to 500 rad/s at 1% strain, which proved to be in the linear viscoelastic range according
163 to a prior amplitude sweep test.

164

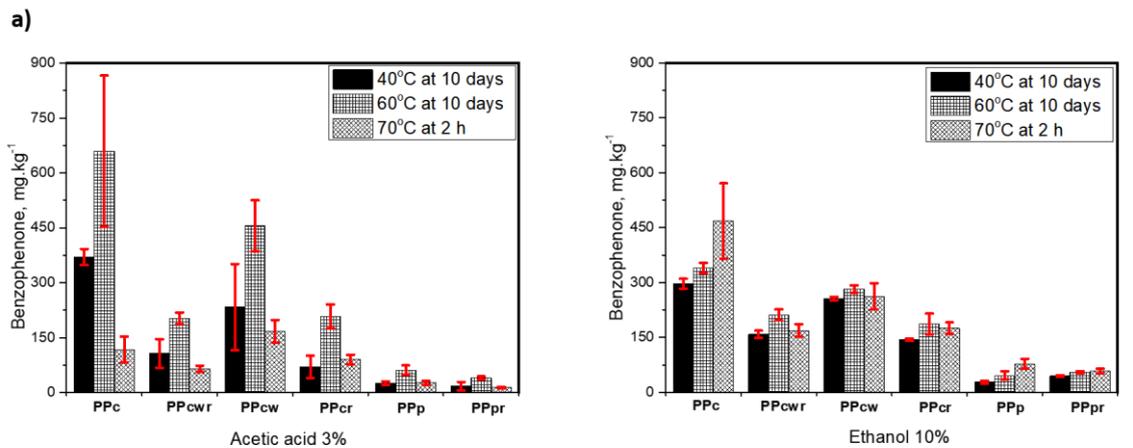
165 **3) RESULTS AND DISCUSSION**

166 **3.1) Migration of contaminants**

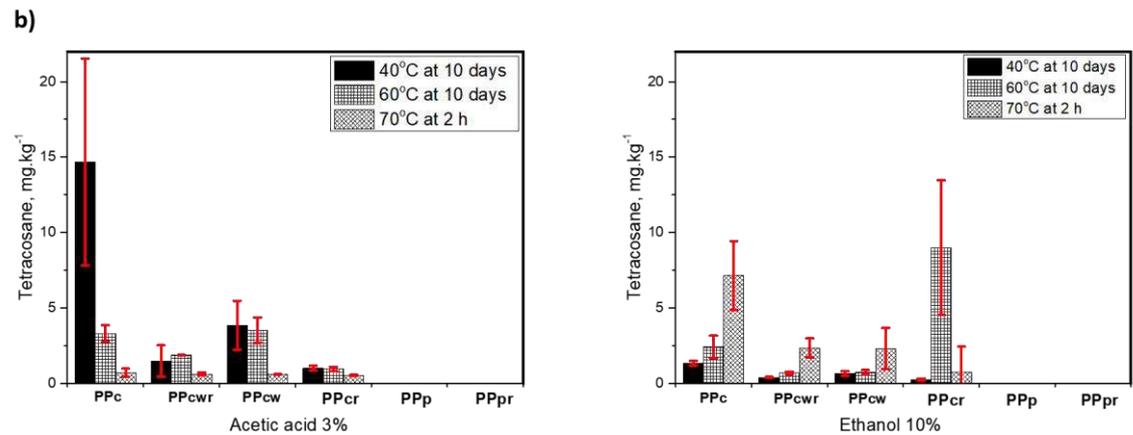
167 The analytical parameters are shown in supplementary material. Linear ranges
168 from 0.0002 mg kg⁻¹ to 4735 mg kg⁻¹ with regression coefficients (r) in the range of
169 0.9903 to 0.9997 were observed. The lowest values of LOD, indicating sensitivity of the
170 method, were obtained for toluene in both solvents 3% acetic acid (LOD = 0.00006 mg
171 kg⁻¹) and 10% ethanol (LOD = 0.00005 mg kg⁻¹). In contrast, the highest LOD was obtained
172 for tetracosane in 3% acetic acid (LOD = 0.0088mg kg⁻¹) and heptane in 10% ethanol
173 (LOD = 0.0031 mg kg⁻¹). The same tendency was noticed for LOQ values.

174

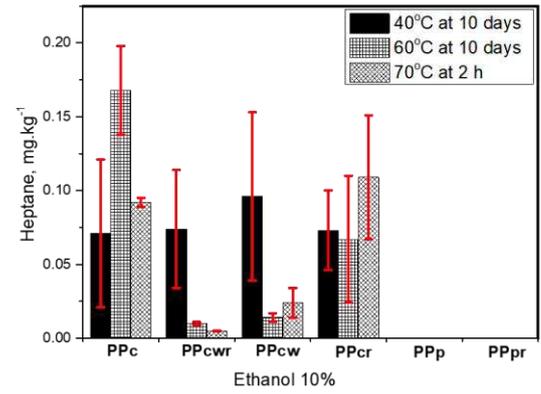
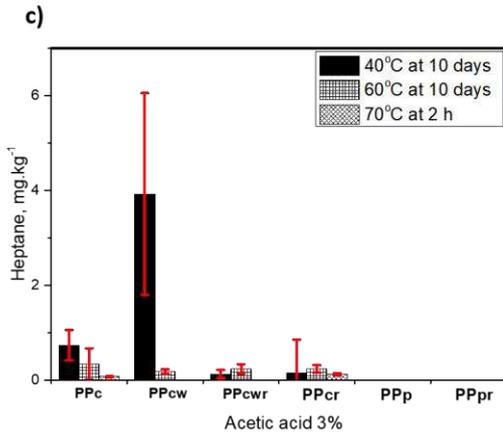
175 The residual contaminants that migrated into food in different conditions were
 176 analyzed by extractability tests since pellets instead of bottles or containers were
 177 available for the study. Therefore, it was possible to identify the influence of recycling
 178 on the decontamination process.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



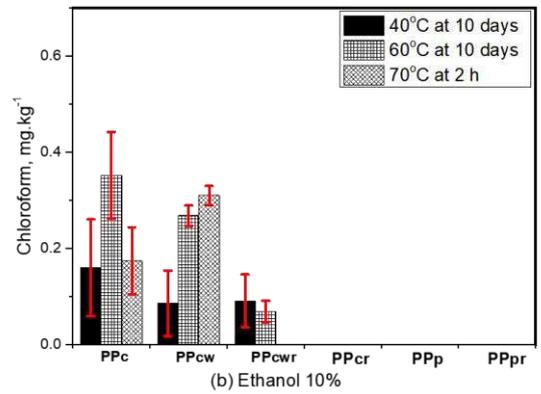
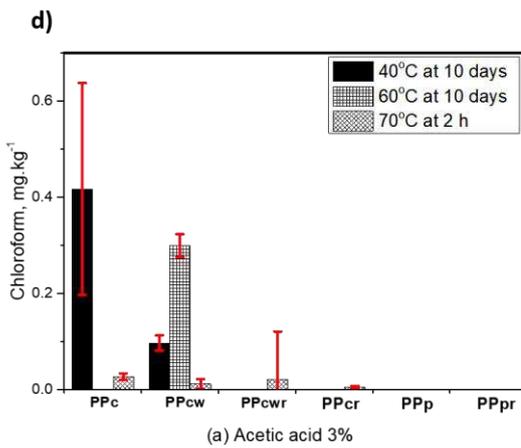
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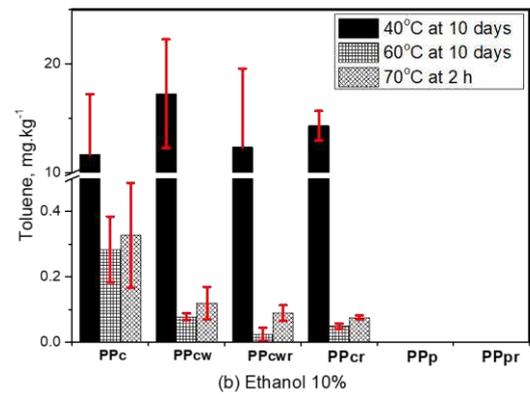
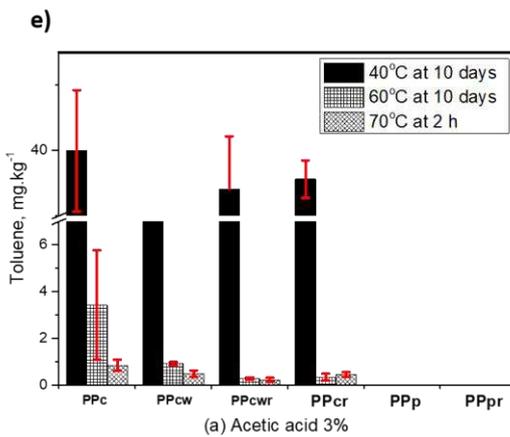
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183



184



185

186 Figure 1: Results of the extractability test on the PP samples for (a) benzophenone, (b)
 187 tetracosane, (c) heptane, (d) chloroform and (e) toluene for 40°C at 10 days, 60°C at 10
 188 days and 70°C at 2 h.

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

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

202 Although the diffusion process is mainly governed by the surrogate molar mass
203 and temperature, the results present in Figure 1 show that these parameters are not the
204 most important for this system. For example, the molar mass of the surrogates increases
205 in the following order: toluene (92.14 g/cm³) > chloroform (119.38 g/cm³) >
206 benzophenone (182.2 g/cm³) > tetracosane (338.65 g/cm³). Nevertheless, despite this
207 observation, there was no correlation between the molar mass of the surrogates and
208 the extractability (Figure 1). Therefore, the molar mass does not seem to be an
209 important parameter in this case.

210 As previously described, the time and temperature, as well as the intrinsic
211 characteristics of the surrogates and food simulants, are the key parameters for

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

228 Contrarily, chloroform (a polar and volatile compound) presents low
229 concentration, as expected. Consequently, it is impossible to detect it in the PPcr
230 sample, according to LOD and LOQ present in Table 2. The chloroform presents a high
231 vapor pressure, which is a parameter that controls the volatility of a chemical, and the
232 temperature of measurements (40, 60 and 70°C) may contribute to low values of
233 concentration of these surrogates.

234 Regarding the non-polar surrogates, the concentration of tetracosane and
235 toluene is lower since the chemical affinity with polymer (non-polar) is high. Considering
236 that the system consists of polymer, food simulant and surrogate, chemical similarity
237 plays an important role in this process. Both simulants present similar polarity [28] but
238 toluene presents a lower molar mass (92.10 g/mol) when compared to tetracosane
239 (338.65 g/mol). As described previously, the molar mass affects the diffusion process,
240 i.e., the higher the molar mass the lower the diffusion of contaminants. The chemical
241 similarity between polymer and surrogates explains the low concentration in food
242 simulants for non-polar surrogates. The opposite results were obtained by Oliveira et
243 al.[27] using PET as the matrix and toluene as the contaminant. PET is a polar polymer
244 and, according to the authors, the high concentration of these contaminants was due to
245 the low affinity with this polymer.

246

247 **3.2) Influence of recycling on the migration**

248 The effects of decontamination were verified and the obtained results were
249 analyzed considering each step (washing and reprocessing). There are several different
250 types of washing processes for post-consumer polymers. They are very dependent on
251 the available technology, as well as, the final destination of the product [29]. The
252 cleaning process for the food market is done in critical and extreme conditions to
253 guarantee high levels of decontamination[16]. In this work, we decided to use a common
254 process to clean recycled resin. In all cases, the cleaning process helps to decontaminate
255 the samples. This behavior is clear when the PPc is compared with the PPcw.

256 Additionally, the reprocessing in a single screw extruder assisted the
257 decontamination (comparing PPcw to PPcwr and PPc to PPcr). All samples that are
258 submitted to an extrusion process present a lower level of contaminants. First of all,
259 during the extrusion process, the polymer is melting and in the melting state, the
260 diffusion process increases significantly [16] and enhances the decontamination,
261 especially that of volatile compounds because of the high temperature. Additionally,
262 during the reprocessing, the polymer is continuously submitted to a high shear rate and
263 temperature. In both cases, the mobility of polymer chains and that of the molecules of
264 contaminants is favorable. Although technologies of PET decontamination are widely
265 investigated [2,30,31], literature is scarce when it comes to PP. One exception is the
266 work developed by Garcia, Cruz and Nerin [15] that analyzed different extrusion
267 processes during the decontamination of the PP samples. The obtained results showed
268 that the most efficient process was the co-rotating twin-screw extruder with forced
269 degassing, which was attributed to the higher shear rates and the degassing system.

270

271 **3.3) Influence of residual contaminants into the molecular structure**

272 The quality, aggregate value and employability of the recycled polymers are
273 associated with the degradation degree that polymers may suffer after the recycling
274 process. Two aspects must be considered when a polymer is submitted to high shear
275 rates, temperature and presence of contaminants: (i) the chain scission and thus, its
276 molar mass, which is reflected in mechanical and thermal properties, and (ii) the flow
277 characteristics, which affects the processability. Although this is an important aspect,
278 this literature does not discuss it. The presence of contaminants in each step of the

279 recycling process influences the molecular structure. Thus, the molar mass is one of the
 280 most important parameters and may be analyzed by the displacement of crossover
 281 point, that is $G'(\omega) = G''(\omega)$ [32,33], which is correlated with the increase or decrease of
 282 the molar mass, as well as the narrowing or widening of its distribution (Figure S1. –
 283 Supplementary Information).

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

288

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

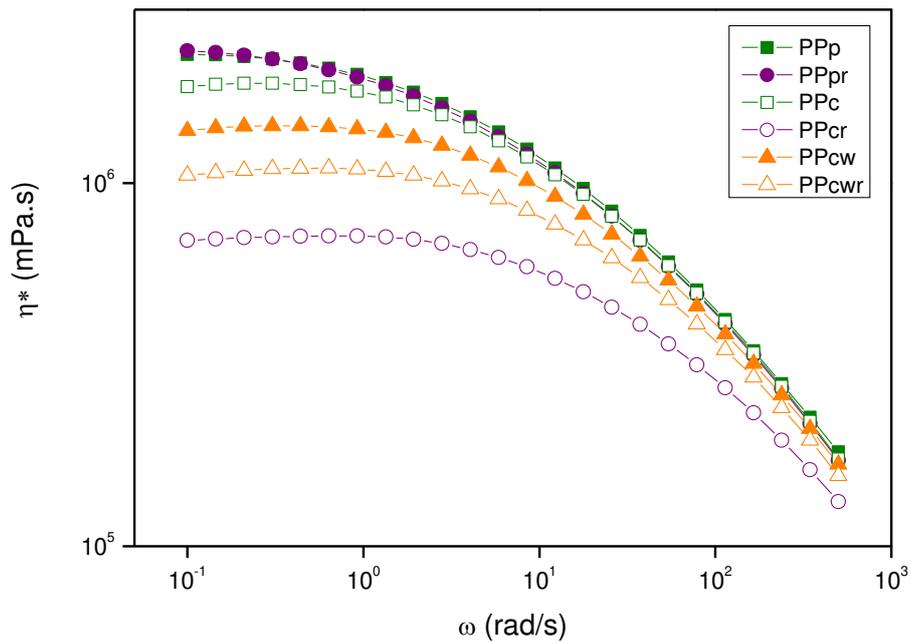
	$G'(\omega) = G''(\omega)$	ω (rad/s)
PPp	29072	84
PPpr	29409	92
PPc	30189	95
PPcr	36940	302
PPcw	31728	121
PPcwr	33892	164

290

291 The results in Table 3 show that the presence of contaminants affects the PP
 292 molar mass. This effect was clearly observed when the samples without contaminants
 293 (PPp, PPpr) were compared with their contaminated counterparts (PPc, PPcr). The
 294 samples submitted to reprocessing in the presence of contaminants (PPcr and PPcwr)
 295 showed higher levels of degradation, and, consequently, lower values of molar mass.

296 The presence of contaminants together with high shear rates and temperature,
297 characteristics of the extrusion process, lead to a scission of the PP chain. The
298 degradation of PP occurs by a radical scission chain, especially in the tertiary carbon [34].
299 The formation of free macroradicals occurs in the initiation phase, after which these
300 radicals react with oxygen forming peroxy radicals. In the propagation phase of the
301 reactions, the peroxy radicals abstract the hydrogens from the tertiary polypropylene
302 carbons to form the hydroperoxides and more free radicals. In the termination phase,
303 free radicals bind and there is also the formation of carbonyl groups, a typical
304 characteristic of the β scission of the polypropylene chain [34]. Another important
305 parameter, that was analyzed, is the molar mass distribution (MMD). The PP
306 degradation leads to narrowing the MMD, which means that the lower values of molar
307 mass presented a significant narrowing in the MMD [35–39]. Incarnato et al. conducted
308 a study about the effect of reprocessing steps on the physical and molecular properties
309 of recycled polypropylene. The results of the intrinsic viscosity analysis showed that
310 there was a decrease in molar mass and a narrowing distribution of molar mass
311 compared to pristine polypropylene [37].

312 The narrowing of the MMD can be observed also by the flow curve shown in
313 Figure 3. In the samples that present a high level of degradation (PPcr), a higher
314 Newtonian plateau can be observed. On the other hand, in the samples with higher
315 molar mass and widened MMD the plateau is significantly lower due to the inferior chain
316 length that can act as a lubricant, increasing the pseudoplastic behavior of the sample.



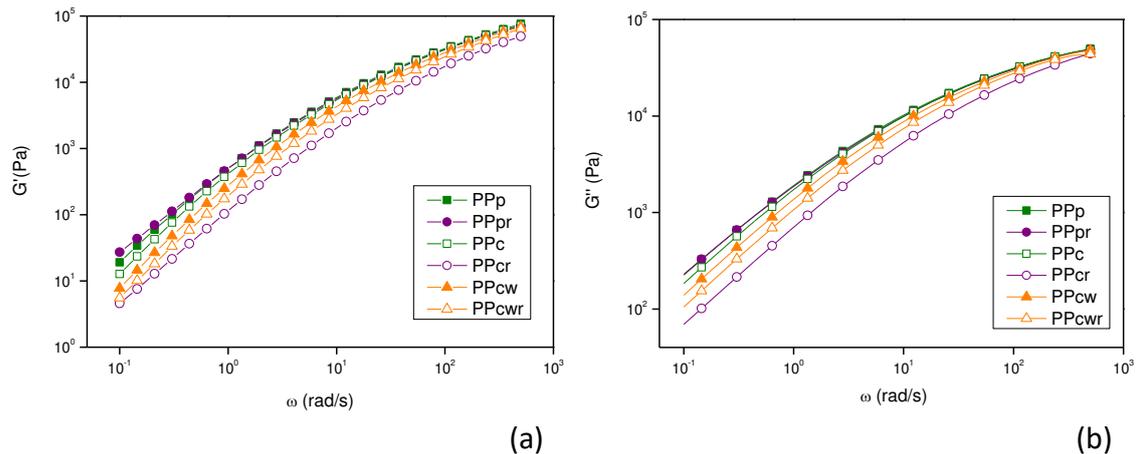
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318 Figure 3: Complex frequency as a function of frequency for all samples.

319

320 Figure 4 depicts the results of the storage modulus (G') and the loss modulus
 321 (G'') as a function of the frequency. These parameters are dependent on the length and
 322 the level of the entanglements of the chains. The samples with a higher level of
 323 degradation show lower values of G' and G'' . These results confirm those previously
 324 obtained, indicating that the contaminants together with reprocessing significantly
 325 decrease the molar mass and the level of entanglements.

326



327 Figure 4: Storage modulus (G') as a function of the frequency for all samples (a) and loss
 328 modulus (G'') as a function of the frequency for all samples (b).

329

330 Additionally, an interesting behavior has been observed when the extractability
 331 measurements were compared to rheometry. First, the samples with a lower level of
 332 contaminants presented the higher molar mass (PPp and PPpr). Nevertheless, the
 333 contaminants alone have not been able to decrease the molar mass significantly (PPc),
 334 even when surrogates were present at high levels (Figure 2). The samples extruded with
 335 a high content of contaminants (PPcr) have lower molar mass. These results prove that
 336 the higher temperatures and shear rates, characteristics of the extrusion process,
 337 together with contaminants are the key points to understanding the molecular structure
 338 changes of the recycled polymer. Additionally, the reprocessing and cleaning process
 339 decreased the level of contaminants. Therefore, it is an important issue to make feasible
 340 the use of recycled material for direct contact with food.

341

342

343

344 **4) Conclusion**

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

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

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

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

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

377

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381

382 **Conflict of Interest**

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

385

386 **Availability of data and material**

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

388 **References**

- 389 [1] J.N. Hahladakis, C.A. Velis, R. Weber, E. Iacovidou, P. Purnell, An overview of
390 chemical additives present in plastics: Migration, release, fate and environmental
391 impact during their use, disposal and recycling, *J. Hazard. Mater.* 344 (2018) 179–
392 199. <https://doi.org/10.1016/j.jhazmat.2017.10.014>.
- 393 [2] C. Dutra, M.T.D.A. Freire, C. Nerín, K. Bentayeb, A. Rodriguez-Lafuente, M. Aznar,
394 F.G.R. Reyes, Migration of residual nonvolatile and inorganic compounds from
395 recycled post-consumer PET and HDPE, *J. Braz. Chem. Soc.* 25 (2014) 686–696.
396 <https://doi.org/10.5935/0103-5053.20140016>.
- 397 [3] US Food and Drug Administration (FDA), Guidance for industry: Use of recycled
398 plastics in food packaging, Chem. Considerations. HFS-275. Washington, DC US
399 FDA, Cent. Food Saf. Appl. Nutr. 4. (n.d.).
- 400 [4] COMMISSION REGULATION (EU), COMMISSION REGULATION (EU) No 10/2011 of
401 14 January 2011 on plastic materials and articles intended to come into contact
402 with food., 2011.
- 403 [5] ANVISA, Resolução-DOU nº- 228, de 30 de novembro de 2010. Regulamento
404 técnico MERCOSUL sobre migração em materiais, embalagens e equipamentos
405 plásticos destinados a entrar em contato com alimentos., *Diário Of. Da União,*
406 Brasília, DF. 1 (2010) 105. <https://doi.org/10.1017/CBO9781107415324.004>.
- 407 [6] C. Direto, Legislação de embalagem para contato com alimentos: MERCOSUL e
408 outros países Latinoamericanos, *Polímeros.* 14 (2004) E8–E13.
409 <https://doi.org/10.1590/s0104-14282004000100004>.
- 410 [7] C. Munoz, A. Eicher, M. Biedermann, K. Grob, Recycled paperboard with a barrier
411 layer for food contact: set-off during stacking or reeling. Analytical method and
412 preliminary results, *Food Addit. Contam. - Part A Chem. Anal. Control. Expo. Risk*
413 *Assess.* 35 (2018) 577–582. <https://doi.org/10.1080/19440049.2017.1411618>.
- 414 [8] C. Nerín, R. Batlle, Assessing the suitability of recycled plastics used as agricultural
415 soil covers: Migration study and experimental harvest, *J. Agric. Food Chem.* 47
416 (1999) 285–293. <https://doi.org/10.1021/jf9804950>.

- 417 [9] P.S. Garcia, S.A. Cruz, C. Nerín, Comparison of different extrusion processes for
418 cleaning the recycled polypropylene removing volatile and non-volatile
419 contaminants, *Prog. Rubber, Plast. Recycl. Technol.* 30 (2014) 37–54.
420 <https://doi.org/10.1177/147776061403000103>.
- 421 [10] Z.F. Chen, Q.B. Lin, X.C. Song, S. Chen, H.N. Zhong, C. Nerin, Discrimination of
422 Virgin and Recycled Polyethylene Based on Volatile Organic Compounds Using a
423 Headspace GC-MS Coupled with Chemometrics Approach, *Food Packag. Shelf
424 Life.* 26 (2020) 100553. <https://doi.org/10.1016/j.fpsl.2020.100553>.
- 425 [11] Q.-Z. Su, P. Vera, C. Nerín, Direct Immersion–Solid-Phase Microextraction
426 Coupled to Gas Chromatography–Mass Spectrometry and Response Surface
427 Methodology for Nontarget Screening of (Semi-) Volatile Migrants from Food
428 Contact Materials, *Anal. Chem.* 92 (2020) 5577–5584.
429 <https://doi.org/10.1021/acs.analchem.0c00532>.
- 430 [12] P. Dole, A.E. Feigenbaum, C. De La Cruz, S. Pastorelli, P. Paseiro, T. Hankemeier,
431 Y. Voulzatis, S. Aucejo, P. Saillard, C. Papaspyrides, Typical diffusion behaviour in
432 packaging polymers - Application to functional barriers, *Food Addit. Contam.* 23
433 (2006) 202–211. <https://doi.org/10.1080/02652030500373661>.
- 434 [13] PlasticsEurope, Risk assessment of non-listed substances (NLS) and non-
435 intentionally added substances (NIAS) under article 19, 32 (2011).
- 436 [14] B. Geueke, K. Groh, J. Muncke, Food packaging in the circular economy: Overview
437 of chemical safety aspects for commonly used materials, *J. Clean. Prod.* 193
438 (2018) 491–505. <https://doi.org/10.1016/j.jclepro.2018.05.005>.
- 439 [15] P.S. Garcia, C.H. Scuracchio, S.A. Cruz, Effect of residual contaminants and of
440 different types of extrusion processes on the rheological properties of the post-
441 consumer polypropylene, *Polym. Test.* 32 (2013) 1237–1243.
442 <https://doi.org/10.1016/j.polymertesting.2013.08.002>.
- 443 [16] S. Palkopoulou, C. Joly, A. Feigenbaum, C.D. Papaspyrides, P. Dole, Critical review
444 on challenge tests to demonstrate decontamination of polyolefins intended for
445 food contact applications, *Trends Food Sci. Technol.* 49 (2016) 110–120.
446 <https://doi.org/10.1016/j.tifs.2015.12.003>.

- 447 [17] X.C. Song, M. Wrona, C. Nerin, Q.B. Lin, H.N. Zhong, Volatile non-intentionally
448 added substances (NIAS) identified in recycled expanded polystyrene containers
449 and their migration into food simulants, *Food Packag. Shelf Life*. 20 (2019)
450 100318. <https://doi.org/10.1016/j.fpsl.2019.100318>.
- 451 [18] L. Coulier, H.G.M. Orbons, R. Rijk, Analytical protocol to study the food safety of
452 (multiple-)recycled high-density polyethylene (HDPE) and polypropylene (PP)
453 crates: Influence of recycling on the migration and formation of degradation
454 products, *Polym. Degrad. Stab.* 92 (2007) 2016–2025.
455 <https://doi.org/10.1016/j.polymdegradstab.2007.07.022>.
- 456 [19] S.A. Cruz, M. Zanin, P.A.P. Nascente, M.A. Bica de Moraes, Superficial
457 modification in recycled PET by plasma etching for food packaging, *J. Appl. Polym.*
458 *Sci.* 115 (2010) 2728–2733. <https://doi.org/10.1002/app.29958>.
- 459 [20] US Food and Drug Administration (FDA), Food and Drugs Administration (FDA),
460 *Guid. Ind. Food Contact Subst. Use Recycl. Plast. Food Packag. Chem.*
461 *Considerations*. (2006). [https://www.fda.gov/regulatory-information/search-](https://www.fda.gov/regulatory-information/search-fda-guidance-documents/guidance-industry-use-recycled-plastics-food-packaging-chemistry-considerations)
462 [fda-guidance-documents/guidance-industry-use-recycled-plastics-food-](https://www.fda.gov/regulatory-information/search-fda-guidance-documents/guidance-industry-use-recycled-plastics-food-packaging-chemistry-considerations)
463 [packaging-chemistry-considerations](https://www.fda.gov/regulatory-information/search-fda-guidance-documents/guidance-industry-use-recycled-plastics-food-packaging-chemistry-considerations) acceso em mar. 2020.
- 464 [21] NIST (National Institute of Standards and Technology), *Libro del Web de Química*
465 *del NIST, SRD 69*, Retrieved March 26, 2020, from [Https//Webbook.Nist.Gov/](https://Webbook.Nist.Gov/).
466 (n.d.).
- 467 [22] P. Vera, E. Canellas, C. Nerín, Compounds responsible for off-odors in several
468 samples composed by polypropylene, polyethylene, paper and cardboard used as
469 food packaging materials, *Food Chem.* 309 (2020) 125792.
470 <https://doi.org/10.1016/j.foodchem.2019.125792>.
- 471 [23] R. Paiva, M. Wrona, C. Nerín, I. Bertochi, L. Gavril, S. Andrea, Importance of profile
472 of volatile and off-odors compounds from different recycled polypropylene used
473 for food applications, *Food Chem.* 350 (2021) 129250.
474 <https://doi.org/10.1016/j.foodchem.2021.129250>.
- 475 [24] I.S. Voulzatis, C.D. Papaspyrides, C.J. Tsenoglou, C. Roussis, Diffusion of model
476 contaminants in high-density polyethylene, *Macromol. Mater. Eng.* 292 (2007)

- 477 272–284. <https://doi.org/10.1002/mame.200600420>.
- 478 [25] N. Ramesh, J.L. Duda, Diffusion in Polymers below the Glass Transition
479 Temperature: Comparison of Two Approaches Based on Free Volume Concepts,
480 Korean J. Chem. Eng. 17 (2000) 310–317. <https://doi.org/10.1007/BF02699046>.
- 481 [26] C. Kuswanti, G. Xu, J. Qiao, J.A. Stuart, K. Koelling, B. Lilly, An Engineering
482 Approach to Rheological Characterization, Ind. Eng. 6 (2003).
- 483 [27] É.C. Oliveira, S.A. Cruz, P.H.L. Aguiar, Effect of PECVD deposition parameters on
484 the DLC/PLC composition of a-C:H thin films, J. Braz. Chem. Soc. 23 (2012) 1657–
485 1662. <https://doi.org/10.1590/S0103-50532012005000027>.
- 486 [28] H. Nawaz, M.A. Shad, N. Rehman, H. Andaleeb, N. Ullah, Effect of solvent polarity
487 on extraction yield and antioxidant properties of phytochemicals from bean
488 (*Phaseolus vulgaris*) seeds, Brazilian J. Pharm. Sci. 56 (2020).
489 <https://doi.org/10.1590/s2175-97902019000417129>.
- 490 [29] R. Demets, M. Roosen, L. Vandermeersch, K. Ragaert, C. Walgraeve, S. De
491 Meester, Development and application of an analytical method to quantify odour
492 removal in plastic waste recycling processes, Resour. Conserv. Recycl. 161 (2020)
493 104907. <https://doi.org/10.1016/j.resconrec.2020.104907>.
- 494 [30] S.A. Cruz, C.H. Scuracchio, L.B. Fitaroni, C. Oliveira, The use of melt rheology and
495 solution viscometry for degradation study of post-consumer poly(ethylene
496 terephthalate): The effects of the contaminants, reprocessing and solid state
497 polymerization, Polym. Test. 60 (2017) 236–241.
498 <https://doi.org/10.1016/j.polymertesting.2017.03.026>.
- 499 [31] W. Romão, M.A.S. Spinacé, M.A. De Paoli, Poly(ethylene terephthalate), PET: A
500 review on the synthesis processes, degradation mechanisms and its recycling,
501 Polimeros. 19 (2009) 121–132. [https://doi.org/10.1590/s0104-
502 14282009000200009](https://doi.org/10.1590/s0104-14282009000200009).
- 503 [32] S.A. Cruz, M. Zanin, Evaluation and identification of degradative processes in post-
504 consumer recycled high-density polyethylene, Polym. Degrad. Stab. 80 (2003) 31–
505 37. [https://doi.org/10.1016/S0141-3910\(02\)00379-8](https://doi.org/10.1016/S0141-3910(02)00379-8).
- 506 [33] F.L.S. Freitas, A.C. Chinellato, S.A. Cruz, Molar Mass Alteration During Post-

- 507 Consumer PET Recycling Using Polycarbodiimide-Based Additive, *J. Polym.*
508 *Environ.* 29 (2021) 734–744. <https://doi.org/10.1007/s10924-020-01896-4>.
- 509 [34] J. a. M. Agnelli, M. a. Chinelatto, Degradação de Polipropileno : Aspectos Teóricos
510 e Recentes Avanços Em Sua Estabilização, *Polímeros Ciência e Tecnol.* 2 (1992)
511 27–31.
- 512 [35] L.B. Fitaroni, J.A. De Lima, S.A. Cruz, W.R. Waldman, Thermal stability of
513 polypropylene-montmorillonite clay nanocomposites: Limitation of the
514 thermogravimetric analysis, *Polym. Degrad. Stab.* 111 (2015) 102–108.
515 <https://doi.org/10.1016/j.polymdegradstab.2014.10.016>.
- 516 [36] L. Incarnato, P. Scarfato, D. Acierno, M.R. Milana, R. Feliciani, Influence of
517 recycling and contamination on structure and transport properties of
518 polypropylene, *J. Appl. Polym. Sci.* 89 (2003) 1768–1778.
519 <https://doi.org/10.1002/app.12168>.
- 520 [37] L. Incarnato, P. Scarfato, D. Acierno, Rheological and mechanical properties of
521 recycled polypropylene, *Polym. Eng. Sci.* 39 (1999) 749–755.
522 <https://doi.org/10.1002/pen.11463>.
- 523 [38] L. Incarnato, L. Di Maio, D. Acierno, M. Denaro, L. Arrivabene, Relationships
524 between processing-structure-migration properties for recycled polypropylene in
525 food packaging, *Food Addit. Contam.* 15 (1998) 195–202.
526 <https://doi.org/10.1080/02652039809374630>.
- 527 [39] R.V. de Camargo, C. Saron, Mechanical–Chemical Recycling of Low-Density
528 Polyethylene Waste with Polypropylene, *J. Polym. Environ.* 28 (2020) 794–802.
529 <https://doi.org/10.1007/s10924-019-01642-5>.

530

Figures

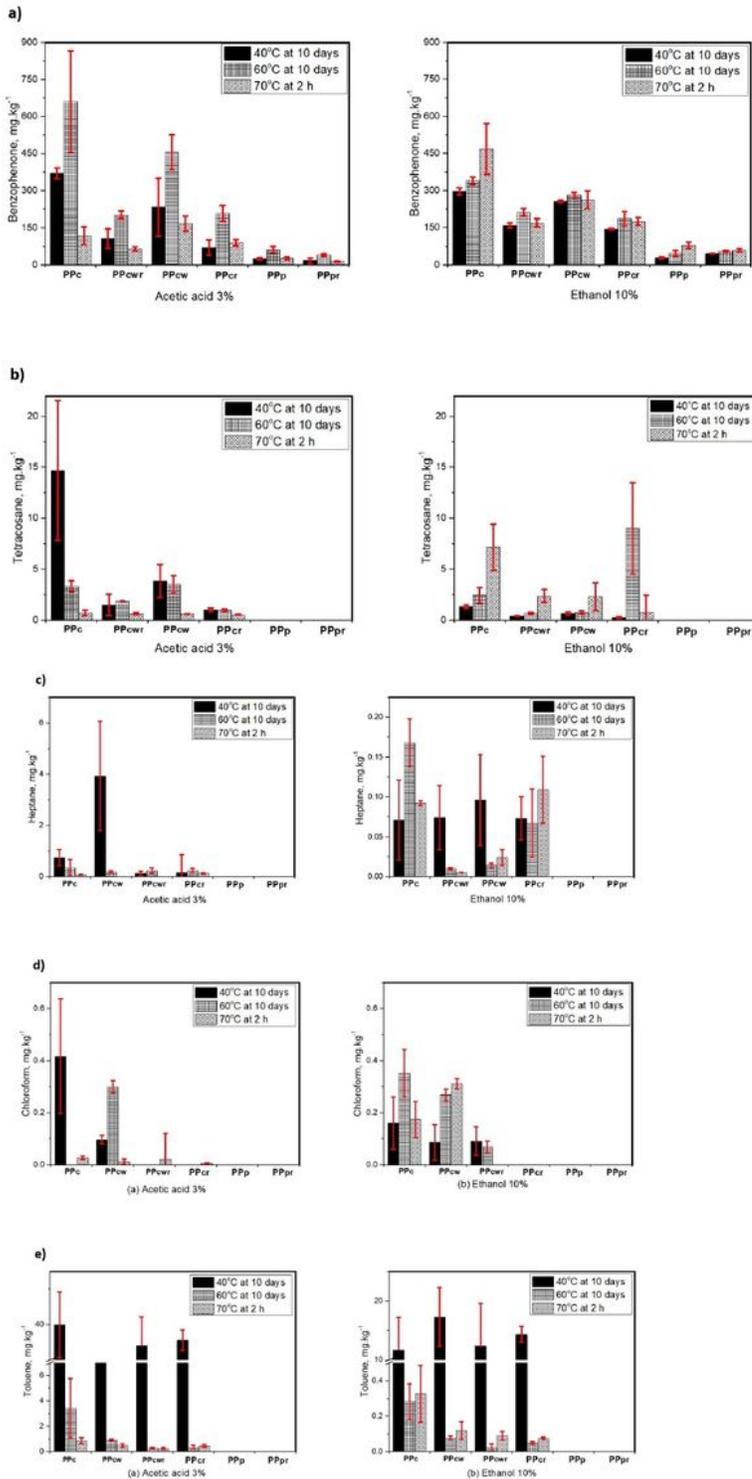


Figure 1

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.

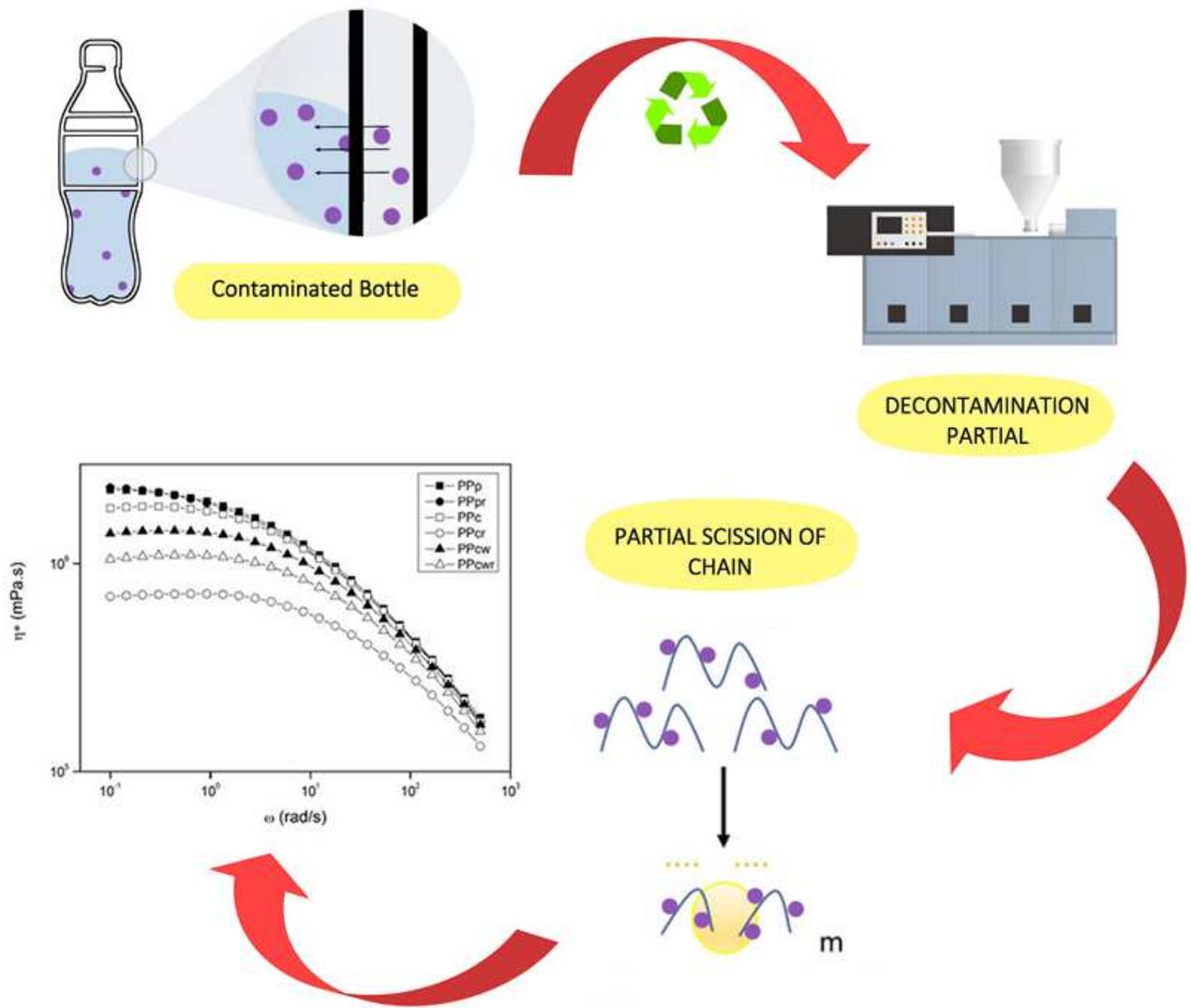


Figure 2

Nevertheless, the contaminants alone have not been able to decrease the molar mass significantly (PPc), even when surrogates were present at high levels (Figure 2).

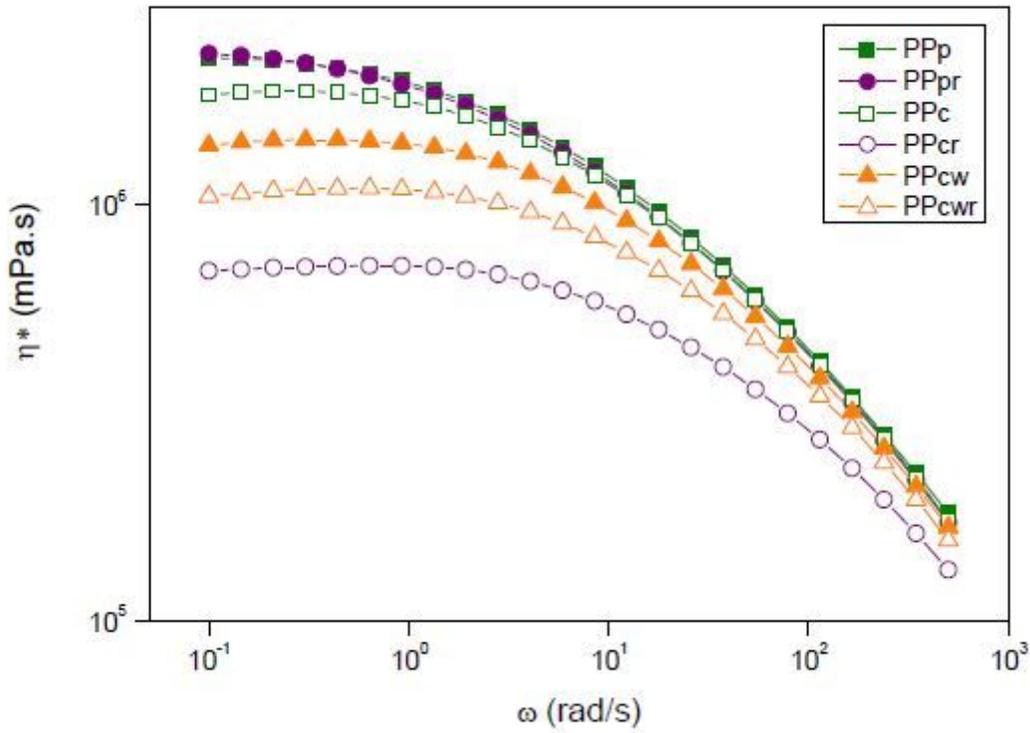


Figure 3

Complex frequency as a function of frequency for all samples.

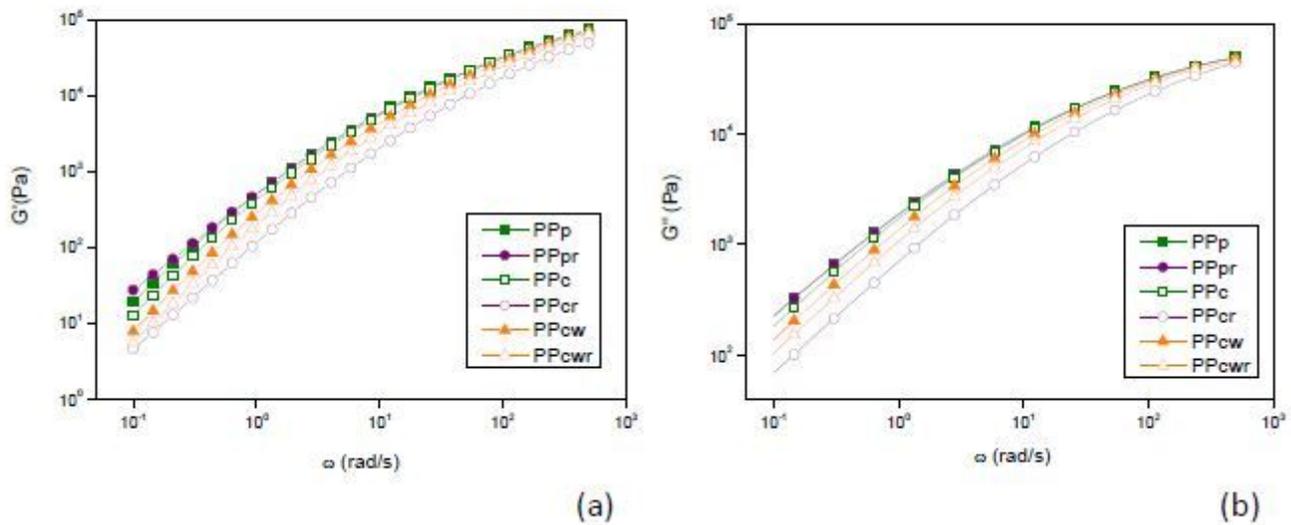


Figure 4

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).