

# Degradation and stabilization of polyolefins from municipal plastic waste during multiple extrusions under different reprocessing conditions

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## Abstract

The recyclability of the two main polyolefins from municipal plastic waste, HDPE and PP, was evaluated. The HDPE/PP blend (90:10)—the most commonly found weight proportion—was extruded three times at conventional (150–180 °C) and high (210–250 °C) reprocessing temperatures. The behavior of degradation was evaluated by infrared spectroscopy measurements (carbonyl index), melt flow index (MFI), capillary rheometry and differential scanning calorimetry (oxidation induction time—OIT). Different antioxidant additive concentrations were prepared according to the steps at which a considerable level of degradation was observed, including an evaluation of the best benefit/cost ratio of the studied additive formulations. © 2002 Published by Elsevier Science Ltd.

*Keywords:* Recycle; Degradation; LDPE; PP; HDPE; Restabilization; Oxidation induction time

## 1. Introduction

The growing volume of plastics contained in municipal waste and the demand for solutions for the social and environmental problems deriving therefrom is a current concern. In Brazil there is an annual loss of 2.5 million tonnes of residues (US\$ 4.6 billion/year), since only 20% of this potential is explored [1]. In this context, efforts to reduce, reuse and recycle plastics, including the contribution of research centers, have been made.

Recycling consists of several stages, the first of which is separation. This stage is often the major factor for the high cost of the process. This cost could often be avoided if recycling of plastics in mixtures were technically and economically viable. Various studies, therefore, focus on the recycling of blends of several types of plastics residues [2–4]. In the specific case of the present

study, the two polyolefins responsible for 86% of rigid plastic waste [5], excluding the fraction of PET, were recycled without previous separation.

LDPE and PP residues from labels and caps are common in HDPE and PP bottles, corresponding to approximately 6% of their mass, and are part of the fluctuation in composition that is intrinsic to this type of sampling. Another source of variation in composition is the packages sometimes produced from blends of the principal composition studied. Provided HDPE is the main component of the blend, such blends would merely interfere in the properties of the system as a whole if they represented a significant fraction of HDPE bottles. Although all these residues are compatible when present in small amounts of one component in another, LDPE and PP have less oxidative stability than HDPE, which is the main component of the blend. However, the presence of these additional residues under these conditions does not alter the behavior during reprocessing of the HDPE:PP system [6].

Polyolefins could undergo thermomechanical and thermo-oxidative degradation during short processing times. Regardless of the degradation process, the

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starting reactions form free radicals that can react with oxygen or undergo reactions by disproportionation or by combination, forming cross-links and chain branching. Depending on the polymer's composition and the oxidation conditions (particularly temperature and atmosphere), one of these reactions is generally predominant. HDPE with Chromium catalyzer usually undergoes reticulation, while PP and LDPE commonly undergo chain scission. During HDPE reticulation, the presence of vinyl groups is very important because they form radicals that can recombine without scission of the main chain. For this reason, the ratio between molar mass and vinyl groups is considered a good approximation of the resin's susceptibility to reticulation [7]. Vinylidene groups [ $\text{CH}_2=\text{C}(\text{CH}_3)-$ ] are commonly formed during the scission of the PP chain, but these double bonds are not attacked by radicals owing to the steric factor of the methyl ( $\text{CH}_3-$ ) substituted group [8].

Provided the degradation mechanisms are known, primary and secondary antioxidants are used to deactivate the peroxy radicals and decompose the hydroperoxides formed, respectively. This is the main role of stabilization processes, i.e., prevention or control of the degradation processes, i.e., prevention or control of the degradation process. Primary and secondary antioxidants are commonly used jointly so as to produce synergistic effects [9–13]. A 2:1 phosphite:phenol ratio is considered the optimized one for stabilization in PP and HDPE processing [10,14].

In a study carried out by Loutcheva et al. [15], reprocessing of HDPE bottles at short residence times and up to five cycles did not significantly alter their mechanical and rheological properties. However, degradation is significant when the number of cycles and residence times are increased, so that the addition of antioxidants may be required. According to Herbst et al. [16], post-consumer HDPE bottles have a previous stabilization since they present low levels of degradation in comparison to virgin HDPE.

On the other hand, in recent studies of Kartalis et al. [17,18], restabilization of HDPE deriving from long life applications (crates) on the first cycle of extrusion was necessary, mainly if they were intended to return to the original application. In this case, the residual antioxidant concentration was insignificant, and multiple reprocessing without restabilization would lead to severe degradation levels.

Changes in the rheological, structural and physico-chemical properties of a HDPE/PP blend during three reprocessing cycles were evaluated in this study. Because PET is one of the major components of MPW and because, in future, we intend to develop products extruded from HDPE/PP/PET, in this work, the HDPE/PP blend was subjected to three reprocessing cycles at a temperature profile appropriate for recycled PET. In addition, the viability of obtaining high quality

reprocessed plastics was evaluated based on a restabilization study.

## 2. Experimental

### 2.1. Materials

The raw materials used in this work were HDPE and PP taken from municipal plastic waste (MPW), such as containers for household cleaning products, food and lubricants. Caustic soda was used in the washing process as a cleaning additive (A.R.I Chemical Brazil Ltd.). The blend composition was a mixture of 90:10 of HDPE/PP i.e., the proportion found at the location where the study was carried out [5].

One lot of 40 kg of HDPE/PP residues was washed with caustic soda [19] and homogenized to minimize residue diversity. The lot was then dried for 28 h at 50 °C in a FABBE model 170 air circulation heater.

The following stabilization agent were used: antioxidant Irganox B215 (2:1 Irgafos 168: Irganox 1010)—Ciba Chemical Specialties Ltda., Brazil.

### 2.2. Characterization

Extrusions were carried out using a GERST extruder ( $\phi = 24$  mm,  $L/D = 24$  and 80 rpm), with the following temperature profiles: 150, 170 and 180 °C; and 210, 230 and 250 °C.

All the analyses were performed in triplicate to determine the experimental errors associated with each analysis. Due to the degradation level between flakes and reprocessed samples were almost similar [6], the analyses were performed only on extruded samples to improve their homogenization. When significant degradation level was observed, a stabilization step was added.

Infrared spectra were obtained by FTIR Perkin-Elmer-Spectrum 1000, and films of 250  $\mu\text{m}$  were compression moulded. The analyses consisted of measuring the carbonyl index at 1740  $\text{cm}^{-1}$  with respect to a reference peak at 840  $\text{cm}^{-1}$ .

Oxidation induction time (OIT) analyses were carried out in a modulated DSC TA Instruments, model 2920, according to the ASTM D 3895–80, with an isothermal temperature of 200 °C.

The melt flow index (MFI) was evaluated at 190 °C and 2.16 kg weight, following the ASTM D 1238, in a Davenport model 3. The rheological properties were measured in an INSTRON model 321 capillary rheometer, using a capillary with 1.52 mm diameter and  $L/D = 40$ . The end correction or “Bagley correction” was not made because of the large aspect ratio of the capillary. Only the Rabinowitsch correction was used to calculate the actual shear rate. The tests were performed

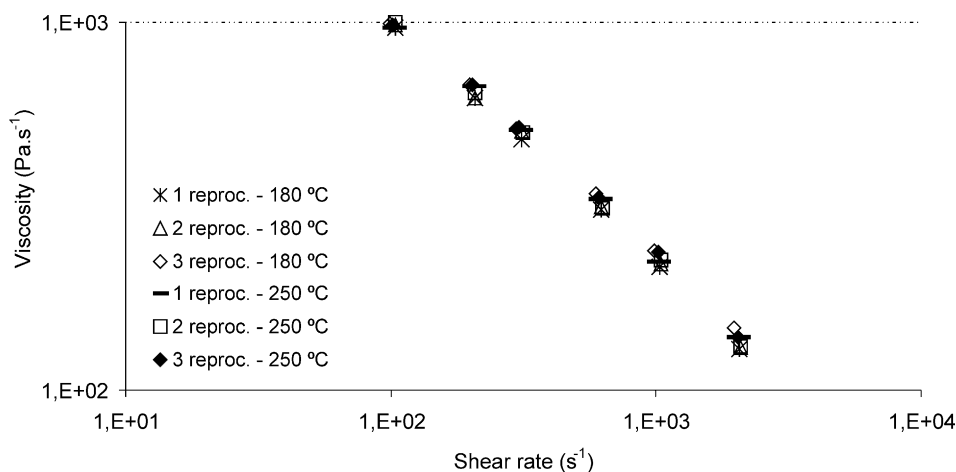


Fig. 1. Flow curves of recycled HDPE/PP blend under conventional and aggressive reprocessing conditions.

at 190 °C, with shear rates of 100, 200, 300, 600, 1.100 and 2.300 s<sup>-1</sup>.

### 3. Results and discussion

Fig. 1 depicts the flow curves of the three extrusion cycles under conventional (180 °C) and aggressive (250 °C) reprocessing conditions. Based on these measurements, no significant change was identified in the material's rheological properties, even after the third run at 250 °C, indicating the possibility of returning these residues (HDPE/PP) to the same original processes. However, a more in-depth analysis is needed due to the low sensitiveness of this methodology in detecting minor structural alterations under high shear rates. La Mantia et al., for instance, observed these slight differences by using rheometric tests at low shear rates [20].

The OIT analysis also proved insensitive in the detection of differences in the samples' levels of degradation. The results shown in Fig. 2 displayed variations in the order of 30s. These differences can be considered slight, implying that the samples' oxidative stability was very similar. This behavior indicates the technique's low sensitiveness for samples with the same composition, as evidenced previously [6].

On the other hand, a tendency was found for increased oxidative stability of the samples by increasing the number of extrusion steps. Epacher et al. also observed this behavior through a maximum in the OIT values as a function of the number of extrusion steps in samples with the same composition [21]. Initially, this tendency can be attributed to a probable decrease in the unsaturations of HDPE with reticulation (reduction of unstable bonds) and, in the case of samples reprocessed at 250 °C, to a reduction of the concentration of hydroperoxides due to their low thermal stability at temperatures above 210 °C [22]. Epacher et al. [21] also observed that this maximum shifted to the first extrusion

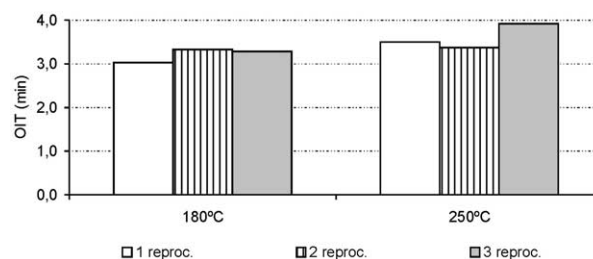


Fig. 2. OIT measurements of recycled HDPE/PP blend under conventional and aggressive reprocessing conditions.

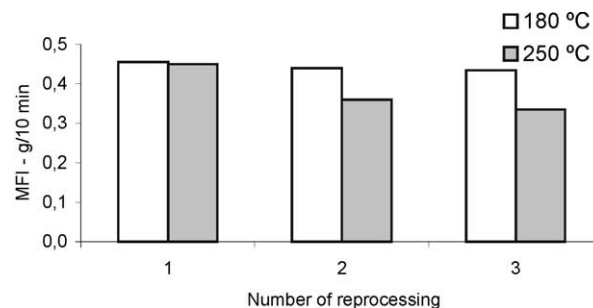


Fig. 3. MFI measurements of recycled HDPE/PP blend under conventional and aggressive reprocessing conditions.

steps as the concentration of antioxidant increased, a fact that further strengthens this hypothesis, since the oxidation induction time is dependent on the content of nonreacted residual antioxidant, whose concentration decreases as the number of extrusion cycles increases. Thus, the greater the concentration, the less the influence of other factors that also lead to increased oxidation induction times.

The MFI measurements (Fig. 3) show the tendency of the blend to form cross-links, suggesting the PP exerts a minor influence in the blend's composition. This finding is in agreement with reports in the literature, since a tendency to reticulate is always observed in ethylene polymers catalyzed with Chromium at reprocessing

temperatures of up to 290 °C [7,23]. A significant change on flow properties (over 20%) was observed only after the second extrusion step at 250 °C. This tendency for reticulation is represented by a decrease in MFI values owing to an increase in molecular mass or to chain branching [20,24].

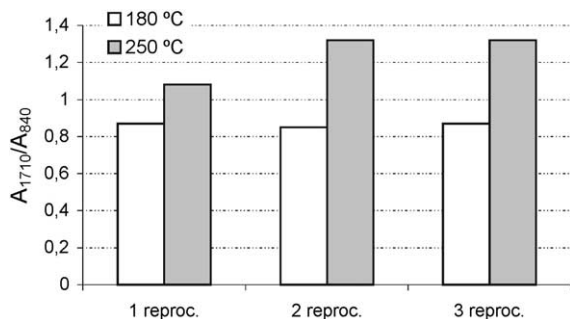


Fig. 4. Carbonyl index of recycled HDPE/PP blend under conventional and aggressive reprocessing conditions.

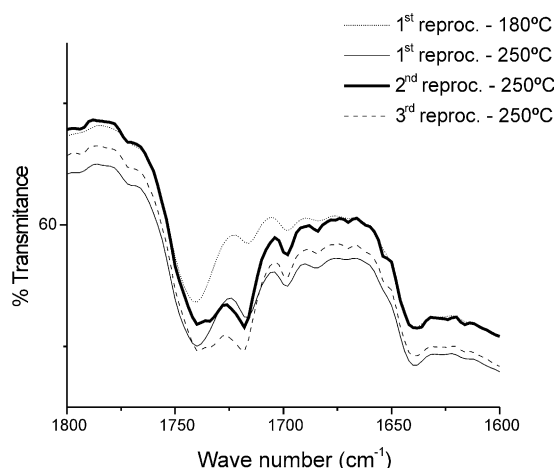


Fig. 5. Carbonyl band of recycled HDPE/PP blend under conventional and aggressive reprocessing conditions.

These results were corroborated by the infrared analysis illustrated in Fig. 4. The determination of the carbonyl index revealed a significant increase in these values only after the second extrusion step at 250 °C. As reported in an earlier paper [6], this technique can be considered sensitive to detect these structural changes. It is interesting to note, in Fig. 5 (FTIR spectrum of 1800–1600 cm<sup>-1</sup>), the broadening of the carbonyl band with the increase in the number of reprocessing steps. This behavior is typical in high degrees of degradation, as stated by Gugumus [7].

In general those low levels of degradation observed for the analyzed samples, mainly at conventional reprocessing temperatures, could be associated with the short life applications of the packages present on these residues and short residence time during extrusion. If compared with residues deriving from long life applications, the possible undesirable chemical reactions caused by the oxidation and photooxidation during its service life surely would have a minor contribution to the autocatalytic nature of degradation process [17]. The short residence time, using high screw speed, should be another factor for the observed low levels of degradation, mainly considering previous works results [15–17]. However a compromise between short residence times and plasticization should be achieved during HDPE reprocessings.

Because the loss in the structural and physical properties of the HDPE/PP blend was only observed after the second extrusion cycle at 250 °C, the polyolefin blend was only restabilized for this extrusion cycle. In the future, studies evaluating the stability of the samples during the aging and the need of restabilization under these conditions should be done.

A preliminary analysis of the MFI was made (Fig. 6) in order to identify the best interval of antioxidant concentration. This analysis indicated that the concentrations of less than 0.1 wt.% were insufficient to

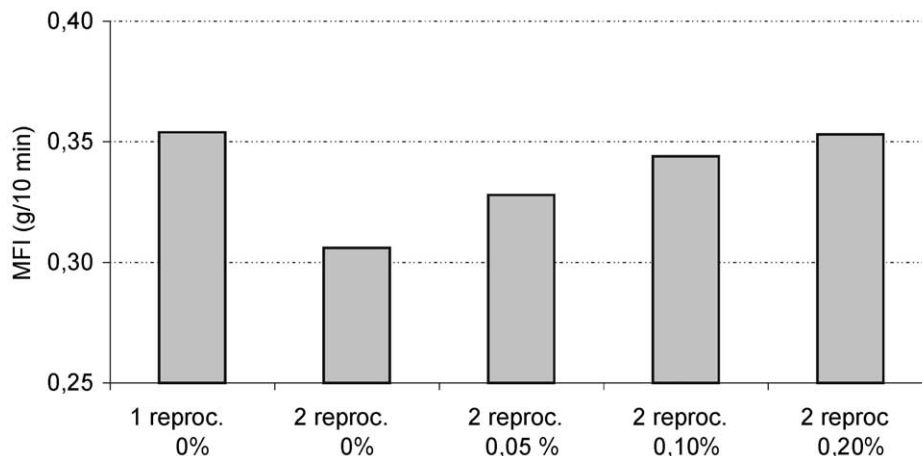


Fig. 6. Preliminary MFI measurements of stabilized samples at second reprocessing path.

stabilize the system, since the addition of 0.05 wt.% of antioxidant reduces the level of changes on melt flow rate by only 6%, i.e., a very small difference considering the low precision of this analysis.

New additive concentrations of containing 0.1, 0.2 and 0.4 wt.% of B-215 were therefore evaluated for the second and third extrusion steps at 250 °C, as portrayed by the results shown in Figs. 7–9. It should be noted that there was no re-addition of antioxidant in the third extrusion step. Again, the flow curves (Fig. 7) showed no differences in the samples' rheological properties.

No infrared analysis was carried out because the antioxidants have groups that absorb in the same region as the carbonyl groups and the samples contained different concentrations of antioxidants. Another option would be to use the absorption in the region of the vinyl and transvinyl groups to check other degradation mechanisms of HDPE, the principal component of the blend. According to El'Darov [25], mechanisms of chain scission may predominate in HDPE through the presence of antioxidants in oxygen-rich environments. For PP, another means of measuring the intensity of degradation is to determine the absorption in the region of vinyl groups. Again, since all these groups contain double bonds as well as antioxidants, the results of this were inconclusive as also observed by Epacher et al. [21].

In comparison to the first reprocessing cycle at 250 °C, the MFI values for the samples with 0.1, 0.2 and 0.4

wt.% of antioxidants amounts in the second cycle at 250 °C displayed, respectively, a slight decrease, a constant value and a small increment (Fig. 8). As can be observed, there was but a slight gain in stabilization efficiency in the samples containing 0.2 wt.% of antioxidants compared to the samples with 0.1 wt.%, particularly when one considers that the antioxidant concentration was doubled.

The tendency of the formulation with 0.4 wt.% antioxidant to increase the MFI value was also observed in the third cycle in all the formulations. This increase may be associated with the tendency of Cr-catalyzed HDPE to chain scission in the presence of antioxidants and in oxygen-rich atmosphere, as observed by El'Darov et al. [25]. The presence of PP in the blend can also be contributing, since PP, even when stabilized, undergoes chain scission, albeit at lower rates. Because the total concentration of PP was very low, only under these conditions it was possible to detect its influence on the mechanism of degradation of the blend as a whole. It is interesting to note that the sample containing 0.1 wt.% of antioxidant exhibited two distinct mechanisms during reprocessing. In these mechanisms, the rate of chain scission of PP only sufficed to overcome any tendency toward reticulation of HDPE from the third reprocessing run onward, when the oxidative stability of PP was lower.

Finally, the differences among the additive packages were evidenced through the OIT results (Fig. 9). The oxidation induction time of the samples with 0.2 wt.% of antioxidant was significantly longer than that presented by the sample containing 0.1 wt.% of stabilizer. Since this significant difference between these concentrations had not been detected through the other analyses, the 0.2 wt.% antioxidant sample probably contained an excess of stabilizer. Therefore, according to the results obtained, the 0.1 wt.% formulation was considered to show the best relation between cost and effectiveness.

On the other hand the observed OIT results for samples with 0.2 and 0.4% wt.% of stabilizers did not increase in the same proportion as the antioxidant

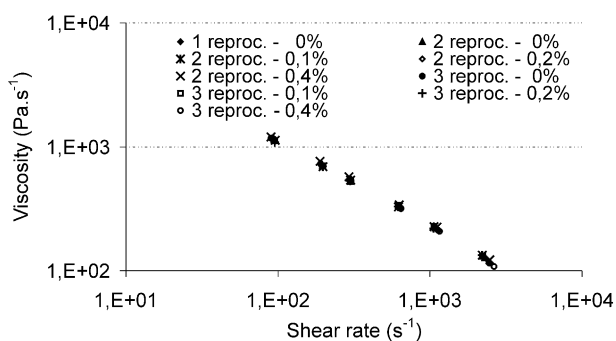


Fig. 7. Flow curves of samples with different antioxidants concentrations.

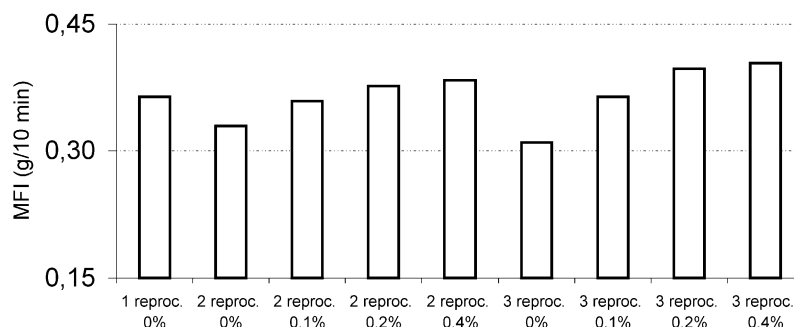


Fig. 8. MFI measurements of samples with different antioxidants concentrations.

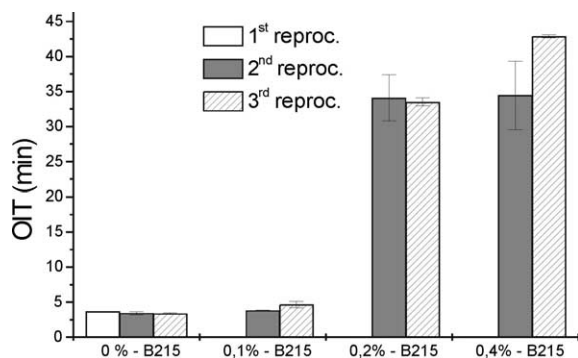


Fig. 9. OIT measurements of samples with different antioxidants concentrations.

concentration. Those results corroborate to associate the increase of MFI observed for samples containing 0.4% wt of antioxidant on the second cycle at high reprocessing temperatures to the tendency of HDPE to chain scission, as observed by El'Darov et al. under similar reprocessing conditions [25]. In this way the contribution of PP's chain scission mechanisms on MFI values was more probable on samples of same composition but from different cycles.

With regard to the stabilization for the different extrusion cycles, again, considering the same sample, the oxidation induction time remained practically constant. Hence, this analysis was insufficiently sensitive to differentiate between levels of degradation among samples with the same composition, as observed previously [6]. The only contradiction was in regard to the 0.4 wt.% of antioxidant concentration. However, taking into account experimental errors, the difference among the samples with the same composition was minimal.

#### 4. Conclusions

Despite the wide diversity of polyolefin residues in municipal plastic garbage, their characterization based on a single homogenized and extruded lot displayed acceptable levels of experimental error.

The degradation mechanisms of PP could not be evidenced due to the low concentration of PP in the blend. Therefore, the blend displayed a tendency to reticulate with increasing numbers of cycles and under aggressive conditions of extrusion. However, the degree of degradation was found to be greater than 20% only from the second extrusion cycle at 250 °C onward. The blend's rheological behavior and structural properties remained unaltered up to the third cycle at a conventional temperature profile, revealing the low cost of a recycling process and the possibility of returning these residues to the same application as their original one.

In the case of aggressive reprocessing conditions, i.e., those in which the polymer may be extruded with

materials having a higher melting point, stabilization is only necessary from the second extrusion cycle on, by means of the addition of 0.1 of B-215 antioxidant.

Finally, another interesting aspect is the blend's tendency for chain scission in the presence of antioxidants. This observed behavior was probably due to the presence of PP, which was only evidenced under these conditions owing to its small proportion in the blend, and to the tendency of HDPE to chain scission in the presence of oxygen and an excess of inhibitor.

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