Thermo-mechanical Degradation and VOC Emission of Unstabilized and Stabilized Polypropylene Copolymer During Multiple Extrusions

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The thermo-mechanical degradation during the multi-extrusion of unstabilized and stabilized polypropylene copolymer (cPP) was analyzed using the Chain Scission Distribution Function (CSDF) method. During the first extrusion of unstabilized cPP almost 60% of the initial polymeric chains were submitted to chain scission. The calculations using CSDF show a random chain scission process of chains with molecular weight below 100 kg.mol⁻¹, and above that a preferential chain scission process. When stabilized the cPP molecular weight is kept constant, even after four extrusions, independently of the stabilizers concentration used. Its chain scission is greatly reduced, only being noteworthy at high values of molecular weight, presenting in this case a preferential chain scission process. During extrusion the unstabilized cPP evolves Volatile Organic Compounds (VOC) due to the volatilization of low molecular weight oxidized chain segments. VOC's emissions are greatly reduced during the melt processing of stabilized cPP, even after multiple extrusions.

1. Introduction

Polypropylene versatility became it one of the most important thermoplastic materials nowadays, with several applications as commodity plastic or as engineering material[1]. Extrusion is a conventional process in polymer transformation used in mixing, homogenization and the conformation of final products. The molten polymer during extrusion is submitted to high shear rate, high temperature and consequently may undergo structural modifications, mainly chain scission, generally accompanied with deterioration of the physical and mechanical properties[2].

Suitable stabilization systems can be used to prevent or inhibit these deleterious effects by interfering with the degradation mechanisms. Usually the different types of stabilizers are molten mixed into the polymeric mass, via polymer extrusion. Several commercial antioxidant packages are based on combinations of two or more antioxidants which act as radical and/or hydroperoxide decomposers, and frequently their function can be improved by complementary anti-oxidant mechanisms, with synergistic effects[3]. Hindered amines, which act as radical scavenger during photochemical degradation, are consumed during the thermo-oxidative degradation due to side reactions with the radicals present in the molten polymer. A good side effect is their action as processing stabilizer[4]. The undesirable HALS consumption during PP processing reduces the performance of the final product. Knowledge on the interactions among additives contributes significantly to improved polymer stabilization[5]. The interactions involving mixtures containing stabilizers as hindered amines and phosphates during polypropylene processing[6], and among different classes of hindered amines[7] has been already analyzed, however there are few documents referring the mixture of the three classes of stabilizers during the extrusion or reprocessing, particularly their lost in terms of emissions of volatile organic compounds (VOC).

Volatile organic compounds are products formed during the thermo-mechanical degradation of a polymer, which particularly in the case of polypropylene can be chain fragments, impurities and fragments of different classes of additives[8,9]. Adams et al.[10] collected particulates and volatile organic compounds emissions during the PP extrusion. The VOC's included aliphatic (ethane, ethylene, propylene) and oxygenated compounds (aldehydes, ketones and carboxylic acids). The most common components found were particulates and VOC's, meanwhile oxygenated compounds appeared in lower concentrations, with emission rates directly proportional to the extrusion temperature. El Mansouri[11] found that Irganox 1010 degrade into di-tert-butyl-p-hydroxytoluene (BHT) in the ratio of one molecule of Irganox for four molecules of BHT.

Pyrolysis products characteristic of stabilizers also have been analyzed. Wang[12] presented Irganox 1010 and Irgafos 168 pyrolysis characteristic groups. In the first case, they found methylphenols, ethylphenols and vinylphenols, meanwhile in Irgafos 168 pyrolysis, there are substituted benzenes, toluenes and butylphenols. Hsiao et al.[13] studied polymer additives analysis using mass spectroscopy and found that in the midst of possible Tinuvin 770 fragments products were trimethyl piperidinyl ring, piperidinyl ring fragments, cleaved ester molecules and fragmented molecules at CH_2 groups. Coulier et al.[14] analyzed the pyrolysis of polymeric HALS, and in the case of oligomeric Chimassorb 944, the main products were trimethyl piperidinyl ring and the monomer unit.

The size exclusion chromatography (SEC) is a helpful tool to study the thermo-mechanical degradation of polymer during extrusion[15-20]. To quantify the intensity of degradation the average

number of chain scission (n_s) can be calculate from Equation 1[16,21,22]. The n_s is calculated from the ratio of number average molecular weight the non-degraded and degraded polymer expressed by $\overline{M}_{n(0)}$ and $\overline{M}_{n(f)}$, respectively.

$$n_s = \frac{\overline{M}_{n(0)}}{\overline{M}_{n(f)}} - 1 \tag{1}$$

The number of chains scission can be extended for the whole range of the molecular weight distribution (MWD), calculating for each molecular weight of the MWD curve (Equation 2).

$$N_s = \frac{M_{i(0)}}{M_{i(f)}} - 1 \tag{2}$$

Where N_s is the chains scission curve[15,16], $M_{i(0)}$ is a particular value of molecular weight of the MWD curve of the non-degraded polymer and $M_{i(f)}$ its corresponding value in the MWD curve after the polymer undergo a degradation process.

The MWD curve of a polymer shifts away from its original position according to the degradation type and extent. To better understand the polymer degradation processes occurring during extrusion, we have introduced a methodology called Chain Scission Distribution Function (CSDF)[15,16]. The CSDF can be calculated from N_s according to Equation 3.

$$CSDF = Log(N_s + 1) = Log(M_{i(0)}) - Log(M_{i(f)}) \tag{3}$$

The CSDF methodology quantifies the shift of the MWD curve of the polymer after thermo-mechanical degradation during the extrusion process, compared to the MWD curve of the non-processed polymer. The shape of the CSDF curve also carries other information i.e. the type of the changes in the polymer chain being either chain scission or chain branching[16-18]. Pinheiro et al.[18] studied the thermo-mechanical degradation of HDPE during extrusion applying the CSDF methodology to evaluate the simultaneous mechanisms of chain scission and branching. The chain branching (value of CSDF < 0) predominates during the degradation of HDPE chains with low molecular weight and, on the contrary, chain scission (value of CSDF > 0) dominates in chains having high molecular weight. Thermo-mechanical degradation during extrusion of commercials grades of PP also was studied via CSDF method and the predominant mechanism in all MWD curve extent is only chain scission[16,19,20].

In this work the thermo-mechanical degradation during the extrusion of unstabilized and stabilized polypropylene copolymer was studied. The stabilization system consists of one primary and one secondary antioxidant, beside two hindered amine light stabilizers. Changes in the molecular weight of the copolymer polypropylene were analyzed via the Chain Scission Distribution Function (CSDF) procedure and the volatile organic compounds (VOCs) evolved during extrusion were analyzed by Infrared Spectroscopy.

2. Experimental

2.1. Materials

The polymer was a random polypropylene copolymer (cPP) RP347, collected directly from the reactor without having any additive added, produced and kindly donated by BRASKEM, Brazil. The stabilizers were a phenolic primary antioxidant (Irganox 1010®) with molar mass MM of 1178 g.mol⁻¹, a phosphate secondary antioxidant (Irgafos 168®) with MM of 646.9 g.mol⁻¹, a low molecular weight HALS (Tinuvin 770®) with MM of 481 g.mol⁻¹, and a polymeric HALS (Chimassorb 944®) with MM of 2300 g.mol⁻¹. These stabilizers were gently provided by BASF S.A., Brazil and used as received. The four stabilizers were individually incorporated in pure cPP using a high rotation speed homogenizer Drais (MH Industries) model MH-250H forming master batches of cPP and a single stabilizer. After melt mixing the molten master batch was immediately hot pressed at 180 °C, cooled in a water bath and grinded in a KIE knife-mill, model MAK 250. Enough quantity of the four master batches was weighted, manually tumbled with pure cPP pellets and fed into the extruder.

2.2. Extrusion

The mixtures of the master batches and cPP pellets were melt mixed in a modular co-rotating intermeshing Werner & Pfleiderer ZSK30 extruder, with gravimetric K-Tron feeder, producing the stabilized cPP formulations with two levels of concentration: 0.2 and 0.4% (w/w) of each stabilizer. Each stabilized formulation was reprocessed several times. The screw profile used during extrusion is show in the Figure 1. The processing conditions, kept constant throughout all the extrusions were: screw rotation speed of 100 rpm, polymer feeding rate of 5 kg/h, a constant barrel temperature profile and die fixed at 200 °C. The volatile organic compounds (VOC) were trapped by a "cold finger", fitted at the degassing zone of the W&P
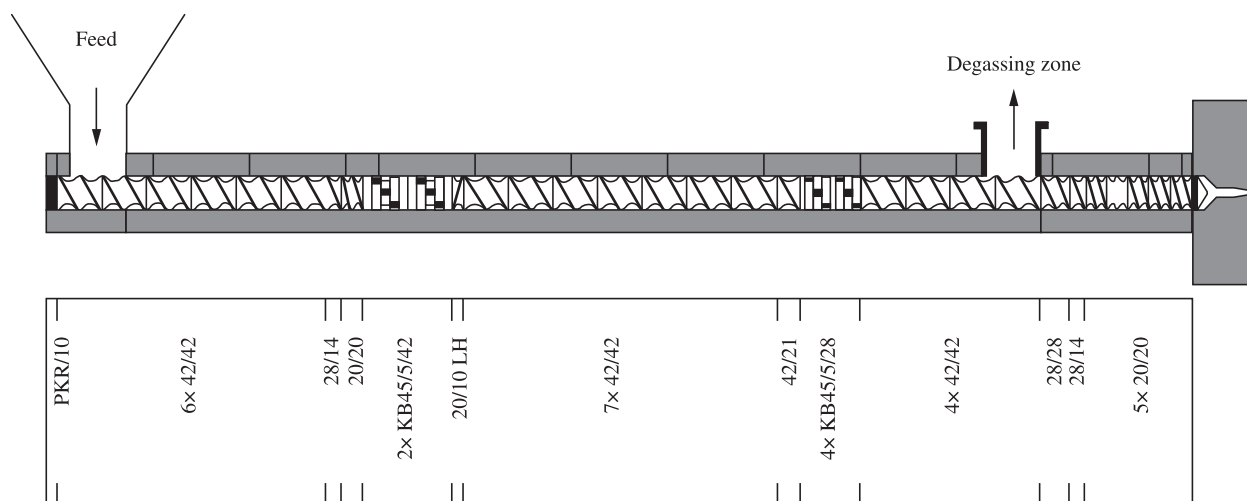

Figure 1. Screw profile used during extrusion.

extruder, during twelve minutes of extrusion, corresponding to 1 kg of extruded polymer. The condensed material was collected by washing it out with 20 mL of chloroform and the solution volume reduced to 1.5 mL by evaporation at room temperature.

2.3. Polymer and VOC characterization

The molecular weight distribution (MWD) curves were obtained in a Waters GPC 150-CV chromatograph with refractive index detector using three Waters Styragel HT columns separating molecular weights from 10^2 to 10^6 g.mol^{-1}. The samples were solubilized in 1,2,4-triclorobenzene (TCB) with Irganox 1010 antioxidant at 140 °C, filtered and injected in a flow of 1 mL/min. The displacement of the MWD curves in relation of the initial MWD curve was calculated using the Chain Scission Distribution Function (CSDF) procedure presented elsewhere[16] using the CSDF 4.1 software, which is valuable to anyone, just ask the authors.

The characterization of the cPP extrudates was done by infrared spectroscopy using a Perkin-Elmer spectrometer model Spectrum 1000. The samples were hot-pressed at 190 °C during 60 seconds using spacers in order to produce films with a fixed thickness of 240 μm. This pressing condition was chosen in order to reduce as much as possible the thermal degradation during the preparation of the films. All spectra were measured in the range of 4000-400 cm^{-1} at a resolution of 4.0 cm^{-1} after 32 scans.

The concentrated solutions containing the volatile organic compounds (VOC's/CHCl$_3$) were analyzed using the ATR accessory of the FTIR spectrometer. The infrared spectra were obtained using a cell of ZnSe (incidence angle at 45°). All spectra were measured in the range of 4000-700 cm^{-1} at a resolution of 4.0 cm^{-1} and 10 scans.

3. Results and Discussion

3.1. Characterization of the thermo-mechanical degradation of the polypropylene copolymer

3.1.1. Molecular weight distribution curves

The averages molecular weights, polydispersity index, chains scission number (n_s), and melt flow rate (MFR) are presented on Table 1. The thermo-mechanical degradation imposed by the extrusion process in the virgin cPP (cPP – 1×), which has no stabilizer, was enough to reduce nearly 40% the value of the weight average molecular weight ($\overline{M}_w$) and approximately 60% of the initial chains were undergone to at least one chain scission ($n_s = 0.6$). On the other hand, when the cPP is stabilized with 0.2 and 0.4% w/w of each stabilizer it can be reprocessed up to four times, showing a minimum variation in $\overline{M}_w$ within the experimental error of the SEC. The melt flow rate (MFR) measurements corroborate the results indicating that the stabilized polypropylene copolymer presents only 1% difference in the second extrusion and about 4% in the fourth extrusion. The

n_s values closed to zero indicate a minimum level of chain scission during the extrusion.

Figure 2 shows the MWD curves of virgin polypropylene copolymer (cPP) and after one extrusion (cPP – 1×). The thermo-mechanical degradation produces an intense displacement of the MWD curve in the direction of the lower molecular weight range. On the other hand, upon stabilization the polypropylene copolymer after reprocessing (2x and 4x) showed a very low displacement in the MWD curves, seen in Figure 3, which is difficult to be seen and judged. In order to obtain a better view of MWD curves shift the CSDF methodology was applied and presented subsequently.

3.1.2. Chain scission distribution function, CSDF

The thermo-mechanical degradation process of cPP during extrusion was analyzed by CSDF curves and is shown in Figure 4. The CSDF curve obtained from the unstabilized cPP – 1× after only one extrusion shows a high level of chain scissions. The curve is kept approximately constant up to Log (MW) = 5 at the 0.15 level. This result indicates a random process of chain scission in molecules with molecular weight up to 100 kg.mol^{-1}, i.e., the number of scission is independent of the original molecular weight of the chain. For molecular weight above 100 kg.mol^{-1} the CSDF curve steps up to CSDF = 0.3 indicating that the chain scission mechanism has become preferential, i.e., the number of chain scission increases with the increase of the original molecular weight of the chain. The shape of the CSDF curve indicates that the thermo-mechanical degradation of unstabilized cPP is of a mixed type, random and preferential, depending of the original length of the chain. The CSDF values, ranging from 0.15 up to 0.3, indicate an elevated number of chain scissions, i.e. a great level of thermo-mechanical degradation after only one extrusion.

Upon stabilization with the four stabilizers used (at 0.2 and 0.4% w/w of each stabilizer) the thermo-mechanical degradation is greatly reduced, even when the reprocessing is taken up to four times. The CSDF values are low, in the range up to 0.07, indicating a low level of chain scission, almost independent of the number of extrusions and stabilizers concentration. This effect can be due to the synergistic behaviour between HALS and phosphite, as shown by Al-Malaika's group[6]. The shape of the CSDF curves indicates that only chains with very high molecular weight do show a weak but preferential chain scission process. Again the longer chains (higher molecular weights) are the ones more prone to suffer scission due to the higher level of chain entanglements. Is difficult to judge but the 100 kg.mol^{-1} critical molecular weight level seems to still holds which is in agreement with previous publications[15-17].

3.1.3. Infrared spectroscopy

Figure 5 presents the IR spectra of hot-pressed films of unstabilized cPP virgin and after been processed once, in the 1800 to 700 cm^{-1} range. All characteristic bands of the polypropylene

Table 1. Average molecular weight, polydispersity ($\overline{M}_z / \overline{M}_w$), chain scission number (n_s), and melt flow rate (MFR) of multi-extruded polypropylene copolymer.

| Samples	$\overline{M}_n$ (kg.mol^{-1})	$\overline{M}_w$ (kg.mol^{-1})	$\overline{M}_z$ (kg.mol^{-1})	$\overline{M}_w / \overline{M}_n$	n_s	MFR (g/10 minutes)
cPP	51	190	630	3.7	-	16.7
cPP – 1×	32	120	270	3.8	0.59	-
cPP(0.2%) – 2×	58	200	610	3.4	−0.12	9.9
cPP(0.2%) – 4×	51	190	580	3.7	0.00	10.4
cPP(0.4%) – 2×	52	180	520	3.5	0.00	9.7
cPP(0.4%) – 4×	56	200	630	3.6	−0.09	9.9
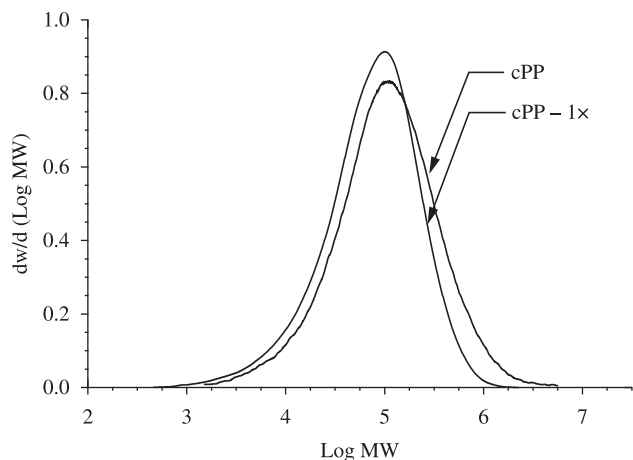
Figure 2. Molecular Weight Distribution curves of unstabilized polypropylene copolymer virgin (cPP) and after one processing (cPP – 1×) in an extruder.


(a)

(b)
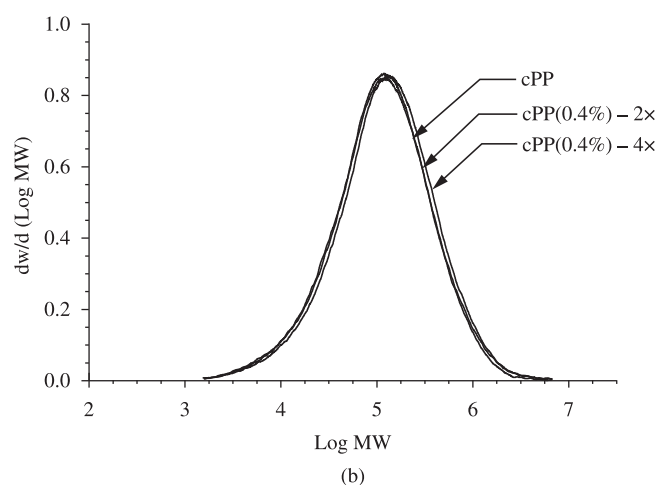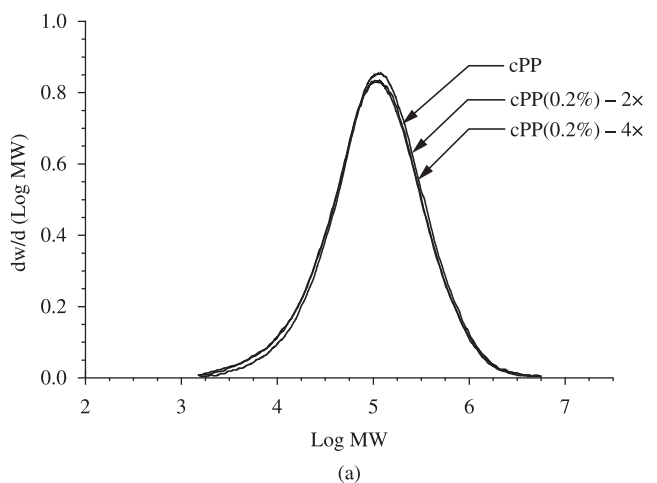
Figure 3. Molecular Weight Distribution curves of stabilized polypropylene copolymer, virgin (cPP), after two (2×) and four times (4×) reprocessed in an extruder: a) 0.2% w/w stabilizers concentration; and in b) 0.4%

chains are present including the band at 720 cm⁻¹, which is due to a sequence of at least two ethylene mers confirming it to be a propylene-ethylene copolymer. The lack of the doublet at this band indicates that the ethylene sequences are short and not able to crystallize. The spectra of the virgin cPP will be used as the reference over which
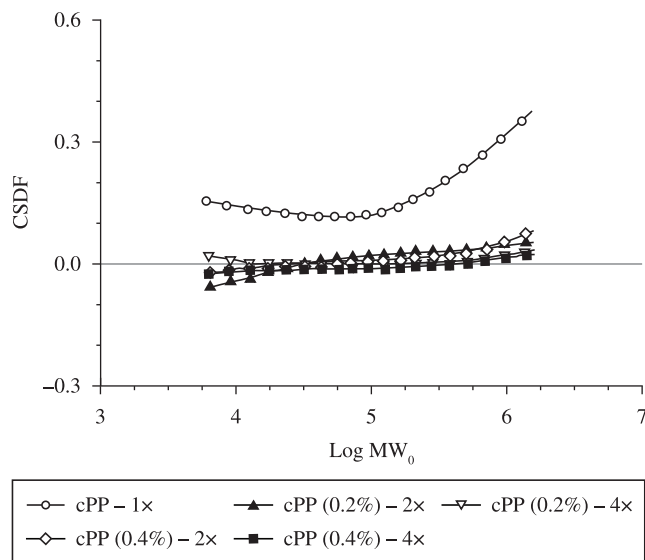
Figure 4. Chain Scission Distribution Function of unstabilized and stabilized polypropylene copolymer. The polymers were multi-processed up to 4 times in an extruder, as indicated.
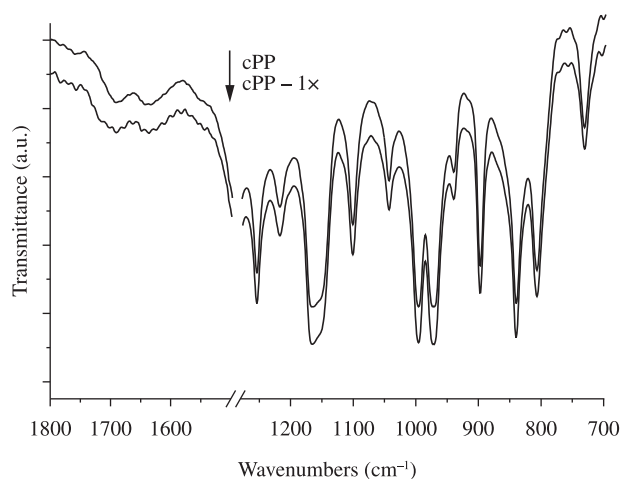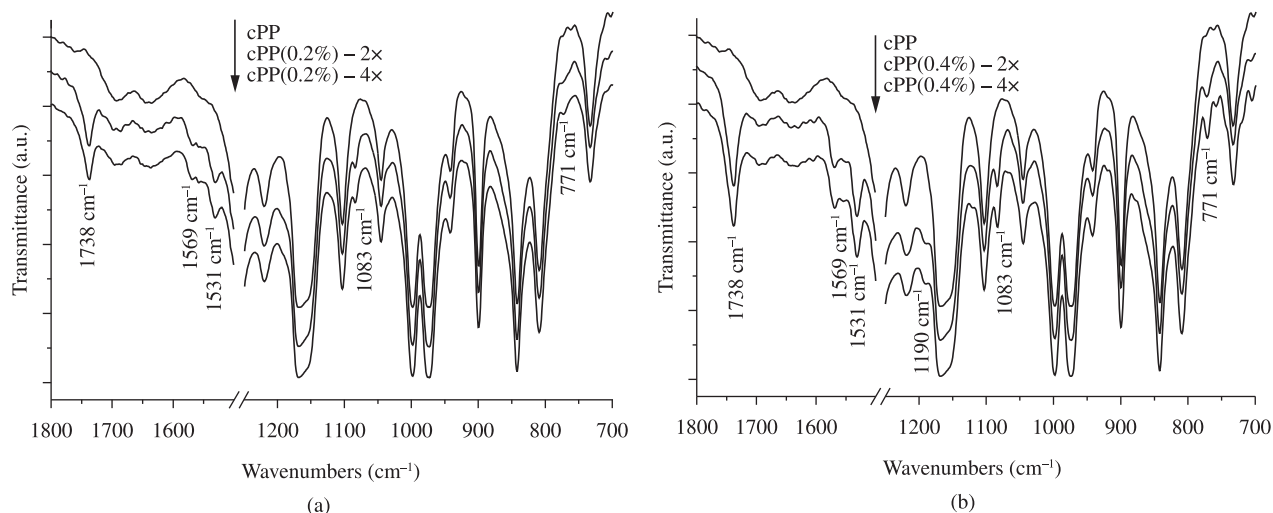

Figure 5. IR spectra of virgin (cPP) and once processed (cPP – 1×) unstabilized polypropylene copolymer films showing the absorption band at 720 cm⁻¹ due to the short ethylene mer sequences.

the bands of the stabilizers will be identified. After one extrusion the cPP thermo-mechanical degradation, as shown in Figure 4, heavily reduces the molecular weight of the cPP – 1× sample, but does not produces significant changes in the IR spectra. The expected level of oxidation, seen in the carbonyl absorption range (1800 to 1700 cm⁻¹), is not measurable, indicating that the oxygen content inside the extruder and available to react with the radical chains is low enough to avoid the formation of measurable carbonyl quantities by the FTIR technique. This has been already seen previously in the works of Gonzáles[2] and Babeto[23] were low levels of carbonyl were detected after multi-reprocessing PP in an extruder.

Figure 6 presents the IR spectra of stabilized cPP samples in the two additive concentrations Figure 6a at 0.2% and Figure 6b at 0.4%. In it is seen an intense band at 1738 cm⁻¹ attributed to the ester groups of Irganox 1010. The stabilizer Chimassorb 944 is seen as two bands at 1569 and 1531 cm⁻¹, attributed to the stretching of the ring bond of the triazine group present in the oligomers repeating

unit. The characteristic bands of Irgafos 168 are at 1083 and 771 cm⁻¹ due to the symmetric axial stretching of the aromatic P-O-C groups. These bands indicate the presence of all stabilizers even after multiple extrusions. In another work[24] we have shown the high consumption' level of Chimassorb 944 (almost 70% after three extrusions) and Tinuvin 770 in polypropylene and their role during reprocessing.

Figure 7 shows the IR spectra of the samples at higher wavenumbers, in which is seen an absorption band at 3650 cm⁻¹, which is not present neither in the virgin nor in the unstabilized extruded samples. It is attributed to the O-H bond of phenolic antioxidant Irganox 1010, which intensity increases in samples with higher concentration of this antioxidant. These results indicate the presence of this stabilizer in the cPP even after multiple extrusions. In a previous work[24] we have shown that its consumption is of 42% after the third extrusion for stabilized cPP with 0.2 % w/w and 34% when the stabilizer concentration was doubled (0.4% w/w).

3.2. Volatile organic compounds, VOC

3.2.1. VOC evolved during the extrusion of unstabilized polypropylene copolymer

Volatile organic compounds evolved during the extrusion of the polypropylene copolymer were collected by the cold-finger fitted at degassing vent of the extruder, washed out with chloroform and analyzed via FTIR-ATR. Figure 8 shows the spectra of pure chloroform in which its characteristic bands can be seen. The second spectrum presented in this figure is from the chloroform solution containing the VOC evolved during the first extrusion of the unstabilized polypropylene copolymer (cPP – 1×). The chloroform bands are well defined and do not interfere with the characteristic bands of the VOC present in the solution. The new bands, produced by the VOC are: the axial deformation of C-H at 2958 cm⁻¹

(a)

(b)

Figure 6. IR spectra of multi-processed stabilized cPP films with two different additives concentration: a) 0.2% w/w and b) 0.4%. The absorption band of each added additive is seen in the spectra. See text for the attributions.
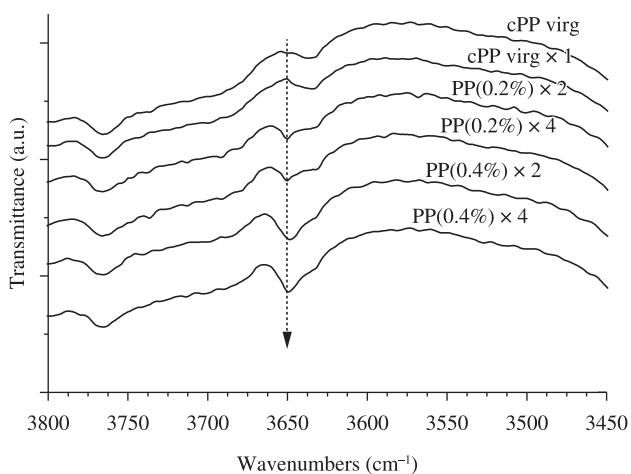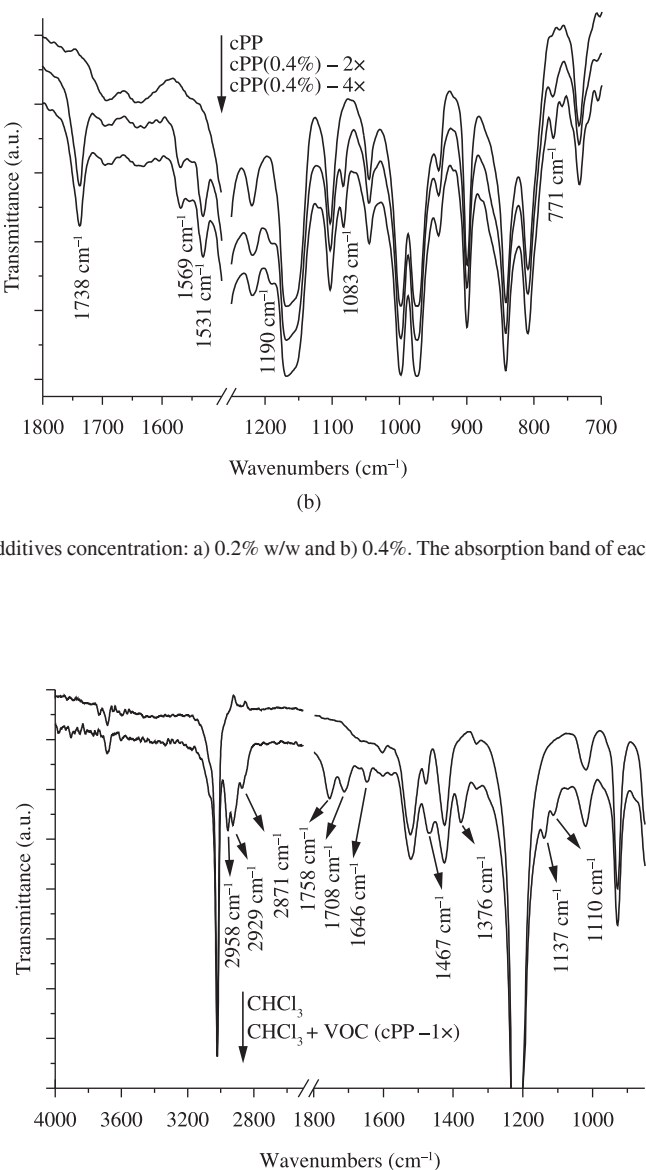

Figure 7. IR spectra of unstabilized and stabilized polypropylene copolymer films after multiple extrusions. The Ar-OH absorption band of Irganox 1010 at 3650 cm⁻¹ is seen only for stabilized samples and is proportional to its concentration.

Figure 8. IR spectra of volatile organic compounds VOC's in chloroform solution evolved during extrusion of unstabilized polypropylene copolymer. The pure chloroform is shown in the upper spectrum.
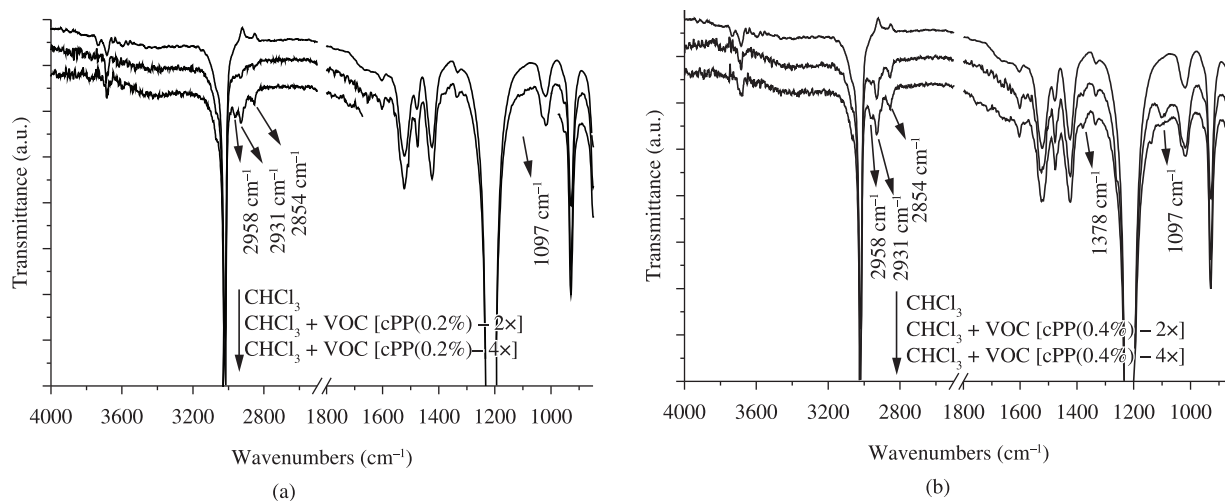
Figure 9. IR spectra of VOC in chloroform solution evolved during multi-extrusion of stabilized polypropylene copolymer with two different additives concentrations: a) 0.2% w/w and b) 0.4%.

(υ CH$_3$ asym), 2871 cm^{-1} (υ CH$_3$ sym) and 2929 cm^{-1} (υ CH$_2$ sym), angular deformations of C-H at 1467 cm^{-1} (δ CH$_2$ sym), 1458 cm^{-1} (δ CH$_3$ asym) and 1376 cm^{-1} (δ CH$_3$ sym), axial deformation of C=C bonds at 1646 cm^{-1}, alcohol vibrations (υ C-O) band at 1110 cm^{-1}, a weak absorption band at 1065 cm^{-1} attributed to aliphatic ethers (υ C-O). A band at 1708 cm^{-1} can be attributed to aliphatic carboxylic acid (υ C=O) and the band at 1758 cm^{-1} can be related to the axial deformation (υ C=O) of R-O-CO-C-R aliphatic ester groups.

During the extrusion the polymer chains are melted and forced to flow in an ambient with high shear fields, temperature and oxygen. This harsh environment causes the thermo-mechanical degradation of the chains that, in the case of polypropylene, include mainly chain scission and reaction of the radical chain ends with oxygen. The products are mainly shorter polymer chains with oxidized ends, which reduces the averages molecular weight, increases the melt flow rate and tints the degraded polymer in light yellow. During this process a smaller amount of very short chains, oligomers, are also generated and can be pyrolysed from the molten polymer, pumped out by the vacuum at the degassing vent of the extruder as VOC's. These constituents are predominantly alkanes with carbons numbers of 14 to 19[25]. If the polymer has no additives, which is the case of the polypropylene copolymer spectra presented in Figure 8, the VOC evolved is composed only by partially oxidized olefinic molecules. Thus the IR-spectra do show the presence of CH$_2$, CH$_3$, C=C, C-O and C=O bonds in the VOC, indication of short olefinic molecules some of them oxidized forming alcohol, ethers, esters, ketones, and aldehydes.

3.2.2. VOC evolved during the extrusion of stabilized polypropylene copolymer

The IR-spectra of VOC's collected during the extrusion of a stabilized polypropylene copolymer are shown in Figure 9. Figure 9a presents data for a concentration of the four stabilizers fixed at 0.2% and Figure 9b the case in which the concentration was doubled to 0.4%. The two sets of curves are quite similar varying only the peak intensities, which are greater in samples with higher stabilizers concentration. The IR-spectra show bands attributed to C-H axial deformations at 2931 cm^{-1} (υ CH$_2$ asym) and 2854 cm^{-1} (υ CH$_2$ sym), a weak band at 2958 cm^{-1} attributed to methyl group deformation (υ CH$_3$ asym), another weak band attributed to C-H angular deformation at 1378 cm^{-1} (δ CH$_3$ sym) and at 1097 cm^{-1}

(δ P-H) possibly due to Ar-P-H group suggesting the volatilization of Irgafos 168 fragments.

It is also seen in the spectra of the VOC solution got from stabilized cPP an absorption band at 2854 cm^{-1}, which could be attributed to possible presence of Tinuvin 770 fragments. It was not possible to detect an isolated characteristic absorption band of the Tinuvin 770, present in the stabilized cPP films spectra. Tinuvin 770, having the smallest molecular weight and melting point of all added stabilizers, decomposes easier and in greater amounts during the extrusion. Besides, at the extrusion conditions used it is also expected some fragmentation of the other stabilizers due to high shear stresses and temperature common to this environment.

A marked difference between the VOC produced during the extrusion of polypropylene copolymer when protected by the addition of stabilizers is the great reduction in the formation of oxidized volatile organic products. They can be detected by their absorption bands in the range 1800-1700 cm^{-1}, characterizing the efficient protection promoted by the stabilizers against the oxidation of the polymer.

4. Conclusions

Thermo-mechanical degradation of unstabilized cPP during extrusion caused scission in 60% of the initial chains at least once. It reduced the initial $\overline{M}_w$ in 40%. With stabilized cPP the average chain scission number was reduced but the molecular weight $\overline{M}_w$ is not affected even after four extrusions. The calculated CSDF values of unstabilized cPP showed a random chains scission process for molecular weight up to 100 kg.mol^{-1}, for higher values a preferential chain scission process is dominant. In the case of stabilized cPP the CSDF values showed that only the higher molecular weight chains do show a preferential chain scission process. At the stabilizers concentration above 0.2% w/w used the CSDF values do not detect any changes in the chain scission number, independent of the number of extrusions. During the extrusion of unstabilized cPP there is the evolution of VOCs emissions, which are degradation products produced during processing. In the case of stabilized cPP the VOCs evolution is kept very low, up to the fourth extrusion.

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