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A Recycling-Focused Assessment of the Oxidative Thermomechanical Degradation of HDPE Melt Containing Pro-oxidant

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Abstract
This study shows the effect of a pro-oxidant (oxo-biodegradable) additive on the oxidative thermomechanical degradation of high-density polyethylene (HDPE). It also allows us to predict the behavior of the material when subjected to mechanical recycling or to biodegradation. When HDPE, one of the most consumed thermoplastics worldwide, is transformed into a product or when subjected to primary and/or secondary recycling it will undergo thermomechanical degradation. According to current standards HDPE is not biodegradable, therefore pro-oxidants are added to many HDPE products, which can compromise the product's life. Knowledge on the influence of pro-oxidants on HDPE in the melt is limited and the objective of this study is to assess the behavior of HDPE containing pro-oxidant manganese stearate (MnSt) in the oxidative thermomechanical degradation process. Thermomechanical degradation tests were conducted in a closed-chamber torque rheometer. FTIR and SEC results agreed with those of torque rheometry and showed that oxidative thermomechanical degradation of HDPE increases with increasing manganese stearate concentration. Degradation resulted in an increase in the number of oxygenated functional groups, mainly ketones, aldehydes and carboxylic acids, and reduction in the weight-average molar mass of HDPE. MnSt may have acted both as a lubricant and pro-oxidant during processing with predominance of one or the other effect at different stages along the oxidative thermomechanical degradation of HDPE.

Keywords Polyethylene · Degradation · Pro-oxidant · Manganese stearate · Processing

Introduction

Polyethylenes, such as high-density polyethylene (HDPE), are primarily used in the manufacture of food packaging, personal care products, household and industrial cleaning products as well as plastic bags [1–3]. Due to the relatively short lifetime until disposal (average 12 min [2]) and to the relatively high resistance to biotic degradation processes, HDPE products may require tens or even hundreds of years to deteriorate, which may cause serious environmental impact [1–5]. PE buried for 10 years in soil (25 °C and absence of light) has shown to biodegrade < 0.2% [6]. Therefore, researchers have sought to reduce the environmental impact of thermoplastic polymer products, such as plastic bags, with short useful life, unfeasible mechanical recycling and relatively long decomposition time. One proposal is the addition of pro-oxidants which accelerate oxidative (thermo and photo-oxidative) abiotic degradation processes, and hence reduce molar mass and introduce oxygenated organic functional groups into the PE molecules. Large PE molecules are thus transformed into oxygenated oligomeric fragments that can become microbial substrates [6–16]. The most widely used pro-oxidants are based on transition metals, especially iron (Fe), manganese (Mn) and cobalt (Co), which are usually added to the polymer in the form of organic salts, particularly stearates [10–25]. In this study we used manganese stearate in virtue of the performance of both metal and stearate in the abiotic oxidative and biotic degradations reported in the literature [10, 16, 19–21, 23, 25]. The alterations caused by the pro-oxidant

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may reduce the biodegradation time of HDPE products when discarded in the environment. However, the pro-oxidant may also compromise the primary (reprocessing) and secondary (mechanical recycling) recyclability of the polymer [26–28]. Primary and secondary recycling are efficient ways to reduce the volume of polymer waste in industries and landfills, as well as the emission of carbon dioxide into the atmosphere. Therefore, knowledge of the action of pro-oxidants in the thermomechanical degradation of PE is very important for assessing the relation between the performance of the product during its service life and correct (recycling) or incorrect (biodegradation) disposal possibilities, after product use. Also, whether the product will perform satisfactorily when in use and if recycling and biodegradation will not be impaired by the pro-oxidant [29–35]. The effects of pro-oxidants on the oxidative degradation processes of polyethylenes in the solid state are well known [6–25]. However, the consequences of the presence of these additives in the liquid melt state have been little explored. Investigations are limited to a few studies such as the addition into virgin PE of fractions of already processed PE containing pro-oxidant, which showed that the presence of the pro-oxidant reduces service life and promotes biodegradation of the mixtures [26, 27]. On the other hand, oxidative thermomechanical degradation of PEs without pro-oxidant has been studied in depth [36–68]. In our study we compare these studies with results of the oxidative thermomechanical degradation of HDPE containing pro-oxidant.

Thermomechanical degradation of PE occurs during processing when the polymer is in the liquid melt state and at relatively high temperature and shear rate. At these conditions, alkyl macroradicals can be generated which may initiate and propagate the degradation process [36–68]. Oxygen, which is present in most transformation processes of PE, even at relatively small amounts, is an important component in the thermomechanical degradation of PE, and its presence or absence may define the products generated in abiotic degradation processes during processing [36, 37, 48, 68]. Relatively small amounts (ppm) of oxygen in extrusion processes are sufficient to cause significant oxidative thermomechanical degradation [37]. Whether in the solid state or in the liquid melt, the main reaction of the auto-oxidation processes of PEs is the decomposition of hydroperoxide (ROOH) into unstable chemical species (peroxy and alkoxy radicals). Thus, the formation of ROOH is the most important step, from which different oxygenated or non-oxygenated species, resulting from the oxidative degradation processes, will be produced [13, 19, 21, 25, 36, 40, 43, 45, 46, 68].

The study of the presence in HDPE of pro-oxidant based on transition metal has therefore become imperative, since, in oxidative abiotic degradation processes, the additive affects the decomposition of ROOH and may hence accelerate the auto-oxidation reactions of the polymer [10–25]. The

Haber–Weiss mechanism, main reaction of Scheme 1, has been proposed to explain how the transition metals accelerate the oxidative degradation processes in organic molecules. The metal, through its transition between the respective oxidation states, decomposes ROOH into unstable free radicals and, thereby, promotes the propagation of oxidative degradation reactions [10, 14, 18, 19, 22–25].

The resulting chemical structure of PE after one or more transformation processes, in which the polymer undergoes oxidative thermomechanical degradation, determines if the material will be recycled or discarded in the environment. To predict this behavior, we have assessed the influence of the pro-oxidant manganese stearate on the oxidative thermomechanical degradation of HDPE, to supply more information on a topic with scarce amount of scientific production.
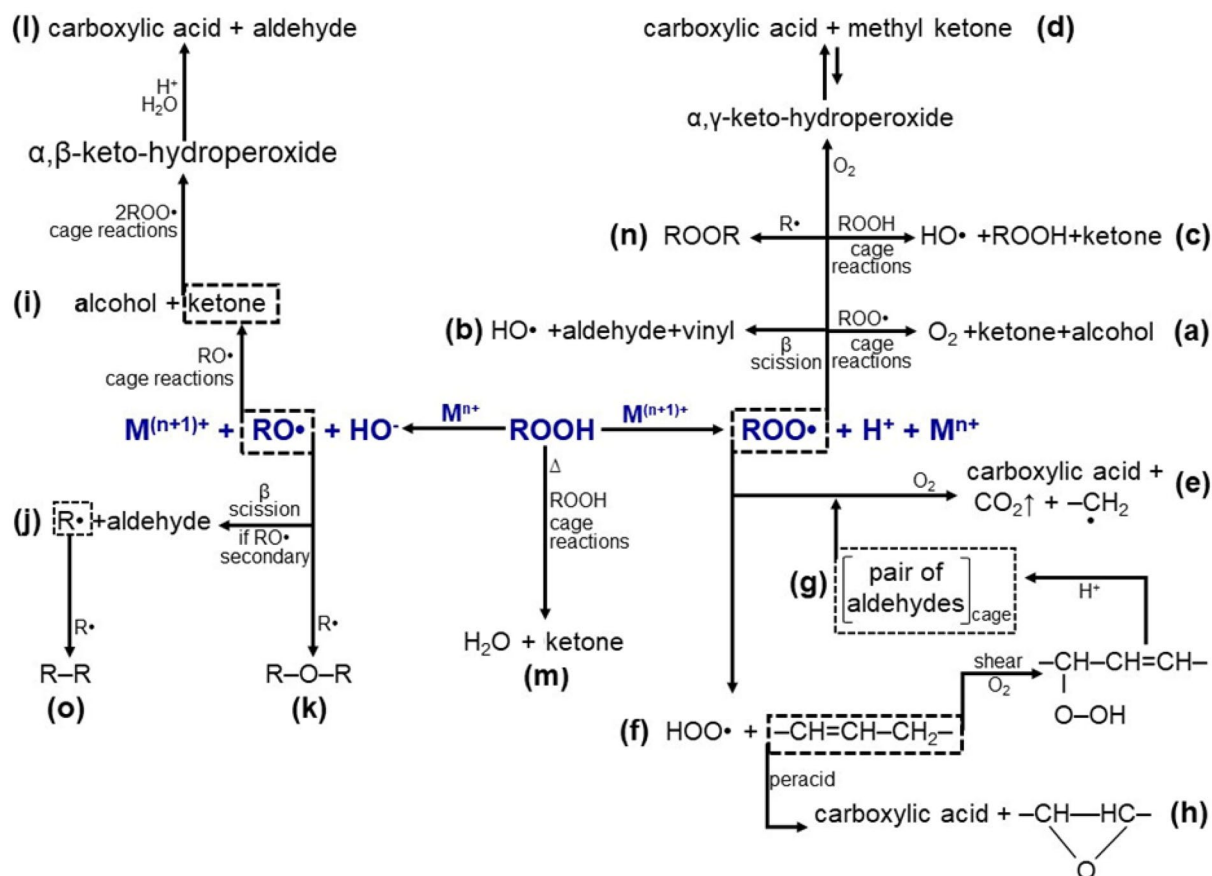
Experimental

Materials

HDPE used in this study was a grade produced using Phillips catalyst and UNIPOL™ process (Braskem BF4810). Melt flow rate was 0.45 g/10 min (190 °C, 5 kg) and 10 g/10 min (190 °C, 21.6 kg) (ASTM D1238) and density 0.948 g/cm^3 (ASTM D792). The pro-oxidant used was manganese stearate, $C_{36}H_{70}O_4Mn$, CAS 3353-05-7, molar mass 621.89 g/mol, melt temperature between 100 and 110 °C, maximum moisture of 2% and average particle size of 200 mesh, i.e., 74 μm (99%).

Thermomechanical Degradation

Processing was performed in a Haake Polylab OS Rheomix 600 OS torque rheometer (rotor Roller 600 OS, counter-rotating, 3:2 angular speed ratio of the rotors [69]). The experimental conditions used were: nominal temperature of 190 °C, constant volume, rotor angular speed of 120:80 rpm and test/processing time of 50 min). The mass of the material (neat HDPE and HDPE containing different stearate concentrations) used in each test was 40 g and, depending on the density of HDPE in the liquid state (approximately 0.76 g/cm^3 at 190 °C [70]), approximately 76% of the volume of the rheometer chamber was occupied. The nominal concentrations of MnSt in the formulations were 0.06 wt% (sample MnSt 0.06) and 0.35 wt% (sample MnSt 0.35). HDPE with no pro-oxidant (neat), non processed (neat sample NP) and processed (neat sample P) were used as reference before and after processing. The influence of metal stearates on HDPE during processing was monitored by the variation in torque with test time. At the end of processing of each formulation, a sample was removed and compression molded into films with a thickness of 1.105 ± 0.080 mm, using a Bovenau

Scheme 1 Thermomechanical oxidation reactions of polyethylene. (Adapted from [8, 9, 13, 17, 32–35, 52–55, 60, 62–66, 68, 83–87])

P15-ST hydraulic press (platens temperature of 170 °C, pressure of 3 tons, 2 min pressing time and cooling of the film in water at 2 ± 2 °C). The non processed neat formulation NP was also subjected to compression molding. The thermomechanical abiotic degradation assays were performed in triplicate.

Determination of Gel Content

The gel content (insoluble fraction) produced in the HDPE samples by crosslinking was determined according to ASTM D2765-16 [71], by extracting with xylene (reagent ACS), stabilized with 1 wt% *Tetrakis-(methylene-(3,5-di-(tert)-butyl-4-hydrocinnamate))methane* (CAS 6683-19-8). In this test method gel was defined as the particles retained in a cage made of 120-mesh stainless steel cloth (openings of 125 μm [72]) after extraction at 132 °C for 12 h. Extraction was performed in triplicate on (300 ± 15) mg ground polymer with fineness between 30 and 60 mesh. Four formulations were tested: neat P, MnSt 0.06, MnSt 0.35 (subjected to thermomechanical degradation for 50 min), and the unprocessed reference sample (neat NP). The residue (gel)

contained within the stainless steel cages, after extraction, was analyzed by infrared spectroscopy (FTIR).

Infrared Spectroscopy (FTIR)

The compression molded films were subjected to infrared transmission spectroscopy in the region between 4000 and 400 cm^{-1}, resolution of 2 cm^{-1} and 64 scans, in a Nicolet 6700 FTIR spectrometer to assess the oxidative degradation after processing. The relatively high film thickness was necessary to enable detection of the presence or absence of carbonyl groups (1719 cm^{-1}; stretching vibration of the ketone C=O bond [44, 73]) and unsaturated groups (965, 909 and 888 cm^{-1}; C–H olefinic out-of-plane bending vibration [44, 73]) in the samples. In thick films, a relatively large amount of radiation will be absorbed and HDPE reference absorption bands become too intense to be used, such as at 730 cm^{-1} (concerted rocking vibrational mode of CH$_2$ groups, when four or more CH$_2$ groups are in a chain [74]). However, the PE infrared spectrum reveals a relatively weak peak in the 2000–2050 cm^{-1} region, which has been used by some authors as reference absorption band, and attributed to a CH$_2$ stretching vibration [38, 39, 75–81]. This weak band

enables relative quantification of carbonyl and unsaturated groups in thick specimens, using transmission mode. Thick specimens are those above the recommended upper thickness limit of 40–50 μm for transmission mode [82].

Size Exclusion Chromatography (SEC)

Molar mass analyses were performed at 150 °C in a high temperature Viscotek HT-GPC size exclusion chromatograph from Malvern Panalytical with main and auxiliary pump flow of 1 mL/min. Shodex HT-806 M columns were used, with exclusion limit of 20,000,000 g/mol (permeation range between about 500 g/mol and 10,000,000 g/mol). The guard column used was Shodex HT-G (particle size 13 μm). The samples were solubilized at 150 °C for 3 h in 1,2,4-trichlorobenzene (TCB) solvent pre-stabilized with 2,6- di-*tert*-butyl-4-methylphenol (BHT) at a concentration of 1 g/L. SEC analyses were carried out on the same samples subjected to infrared spectroscopy (50-min processing in the torque rheometer).

Results and Discussions

Monitoring of PE processing in the torque rheometer was conducted by means of torque and temperature measurements and the results are shown in Fig. 1. In the first 20 min of processing, torque and temperature of the samples neat P, MnSt 0.06 and MnSt 0.35 are approximately equal. Analysis of neat sample P throughout the entire test shows that both torque and temperature increase slightly between about 10 and 25 min, maintaining relative stability between approximately 25 and 35 min and afterwards both decrease slightly
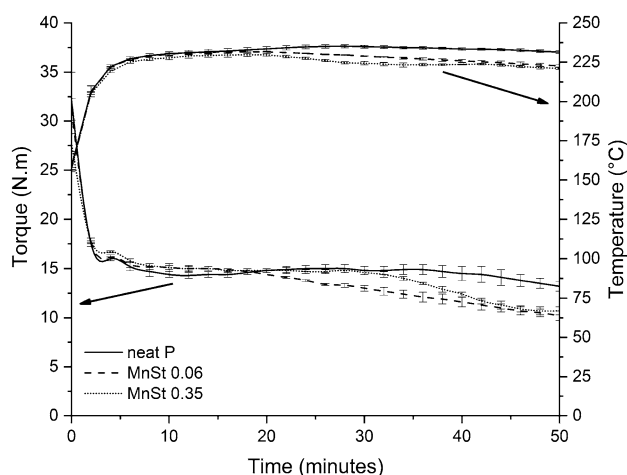

Fig. 1 Torque and temperature of the polymer versus processing time: neat P (line), MnSt 0.06 (dashed line) and MnSt 0.35 (dotted line)

until the end of the test (50 min). This behavior indicates that between about 10 and 25 min of processing, HDPE degradation in the neat sample P may predominantly have been driven by branching and/or crosslinking reactions, whereas after approximately 35 min degradation may predominantly have been conducted by HDPE chain scission. The recombination reactions between free radicals, and consequent increase in polymer molar mass, are favored by the relatively reduced viscosity of the HDPE melt, which facilitates caging of the free radicals, thus keeping them close to each other and thereby facilitating recombination [36, 47, 48, 52–56, 58–61, 63–68]. Since ROOH is the main chemical species formed at the beginning of the polyethylene auto-oxidation process during processing, it will also be the main precursor of the different oxygenated organic functional groups generated during the oxidative thermomechanical degradation of the polymer [44–68]. In the presence of oxygen, thermomechanical degradation of PE is mainly driven by reactions involving free radical pairs (alkyl, alkoxy and peroxy) confined in a cage and these pairs can be generated from mono or bimolecular decomposition of ROOH. The decomposition of the different ROOHs is the main reaction of the degradation processes of PE, from which a series of products can be formed such as carbonyl groups (acids, aldehydes, esters, γ-lactones and, mainly ketones), hydroxyls (free and associated hydroperoxides, and especially alcohols) and unsaturated groups (vinyl, vinylidene and *trans*-vinylene) [44–48, 52–68]. Scheme 1 shows some possible branching and/or crosslinking (Scheme 1k, n, o), oxidation with molecular scission (Scheme 1b, e, g, j, l) and oxidation without significant change in average molar mass of the PE molecule (Scheme 1a, c, d, f, h, I, m) during thermomechanical oxidative degradation [52, 55, 60, 63–65, 83–87]. It should be mentioned that the HDPE used in this study was synthesized with the Phillips supported chromium catalyst, which promotes significant formation of vinyl groups in HDPE molecules during polymerization. This characteristic might have contributed to the predominance of branching and/or crosslinking during thermomechanical degradation of the polymer [38, 39, 41, 42, 68].

Formulations MnSt 0.06, MnSt 0.35, and the neat formulation P showed different behavior after approximately 20 min in the rheometer. Nevertheless, at the end of the assay both stearate-containing formulations reached statistically equal torque and temperature values, which were significantly lower than the values of the neat formulation P, indicating that after approximately 20 and 33 min of testing, HDPE chain scission predominated in MnSt 0.06 and MnSt 0.35 formulations, when compared to the neat formulation P. This behavior can be explained by the prodegrading action of MnSt which, through the decomposition of hydroperoxides, may have conducted the degradation process towards oxidative degradation with chain scission and consequent

reduction in viscosity and in torque, according to the reactions in Scheme 1b, e, g, j, l [17, 18, 52, 55, 60, 63–65, 83–87].

Between approximately 20 and 40 min, formulations MnSt 0.06 and MnSt 0.35 presented statistically different torque values and this behavior may be related to the competition between the prodegrading and lubricating effects of manganese stearate, since metal stearates can be used as lubricants in the processing of polyolefins [88, 89]. Whereas the prodegrading action of manganese may accelerate HDPE's auto-oxidative process via hydroperoxide decomposition, the lubricating action of stearate may reduce the shear stress in the system, hence, reducing the amount of alkyl radicals, which are the most important reactive species at the initiation stage of HDPE's auto-oxidative process [17, 18, 52, 55, 63–65, 88, 89]. Based on this hypothesis one can explain the distinct behavior between formulations MnSt 0.06 and 0.35 in the interval between 20 and 40 min in which formulation MnSt 0.06, with less pro-oxidant, shows reduction in torque (oxidative degradation with chain scission) at an earlier stage than formulation MnSt 0.35. The torque results indicate predominance of the prodegrading effect of manganese stearate in formulation MnSt 0.06, anticipating oxidative degradation with chain scission. However, for formulation MnSt 0.35 the results indicate, in this time interval, predominance of the lubricating effect of manganese stearate, inhibiting the formation of reactive species (alkyl radical) and retarding the oxidative degradation process with chain scission, and consequently retarding the reduction in torque. Nevertheless, after approximately 33 min of testing the torque of formulation MnSt 0.35 decreases, indicating that, from this time on, the prodegrading effect of manganese stearate becomes predominant in the system, promoting auto-oxidation with chain scission. The torque reduction rate of formulation MnSt 0.35, compared to formulation MnSt 0.06, is higher, which may be due to the accumulation, up to this time, of the hydroperoxide species and of the relatively high amount of manganese stearate (approximately six times greater) [14–17, 45, 47]. After approximately 40 min, and until the end of the test, both formulations (MnSt 0.06 and 0.035) show statistically the same torque and temperature values, and these results indicate after 50 min of testing, no difference between 0.06 and 0.35% manganese stearate in the thermomechanical degradation of HDPE. It is important to note that in the time interval between approximately 20 and 33 min the MnSt 0.35 formulation experienced a discrete but noticeable reduction in temperature and this phenomenon also reflects the lubricating effect of manganese stearate, which on reducing friction reduces the viscous dissipation, promoting reduction in polymer melt temperature in that time interval [88, 90–94]. It should also be mentioned that the reduction in temperature contributes to the increase in melt viscosity and consequently this effect contributed to delaying the decrease in torque of formulation MnSt 0.35 in that time interval [88, 89, 94]. Up to approximately 20 min of testing the torque and temperature values of formulations MnSt 0.06 and 0.35 are statistically the same, but this result does not mean that there was no distinct lubricating effect of the manganese stearate in the respective formulations. It may mean that in this time interval the difference between the lubricating effects of manganese stearate in each formulation could not be detected by the equipment, due to equipment sensitivity. The final average torque (at the end of the test) of neat formulation P was approximately 26% higher than the final average torque of the MnSt formulations 0.06 and 0.35. It should be mentioned that for all formulations the effective temperature exceeded the nominal temperature (190 °C) during approximately the entire test and this result is associated with the heat generated in the system, as part of the mechanical energy was transformed into thermal energy through viscous dissipation, which is inherent in fluid flow processes. Another feature is the absence of a cooling mechanism to assist the temperature control system [69, 88–94].

The competition between crosslinking and chain scission is inherent in abiotic degradation processes of PE, and determination of gel content is therefore important to assess the degree of crosslinking in the polymer. Timóteo et al. investigated the presence of polycarbonate cross-linking, subjected to the combination of photodegradation and stress cracking, using UV–Visible spectroscopy by turbidity measurements [95]. However, the chemical (mainly solubility) and physical (mainly melting temperature) properties of HDPE and the limitations of UV–Visible spectrometers preclude the use of this technique in the investigation of crosslinking in degraded HDPE [1, 96, 97]. On the other hand, investigation of polyethylene crosslinking has been performed by determining the gel content according to ASTM D2765 [98–100]. Gel content in neat NP, neat P, MnSt 0.06 and MnSt 0.35 samples are presented in Fig. 2 and show that after 50 min of processing, the gel contents in neat NP, neat P, and MnSt 0.06 samples are statistically the same, indicating that even when crosslinking occurred, chain scission was predominant and crosslinking may have been reversed when oxidation became more intense by the presence of the pro-oxidant. However, compared to the neat NP sample, the MnSt 0.35 sample showed an increase of about 240% in the average gel content. This indicates that the pro-oxidant action of manganese stearate may have generated, through decomposition of hydroperoxides, a significant amount of free radicals (alkyl, peroxyl and alkoxy). These radicals, in addition to promoting oxidation reactions with chain scission (Scheme 1b, e, g, j, l), may promote crosslinking reactions shown in Scheme 1 (reactions k, n, o) and Scheme 2,
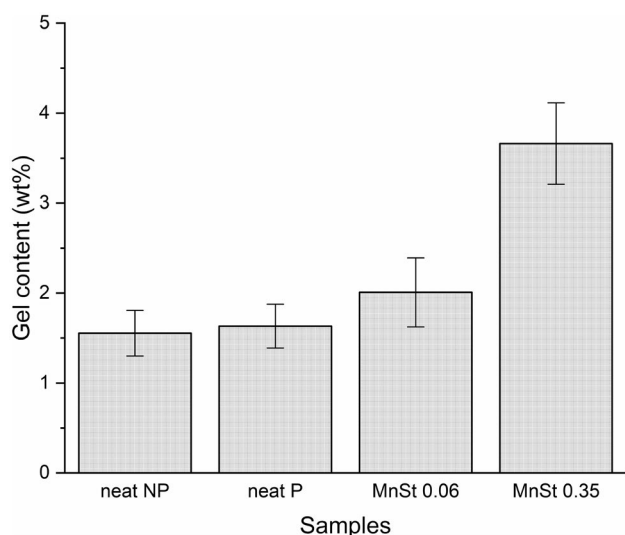
Fig. 2 Effect of MnSt concentration on gel content of HDPE samples subjected to 50 min of oxidative thermomechanical degradation (120:80 rpm and 190 °C)
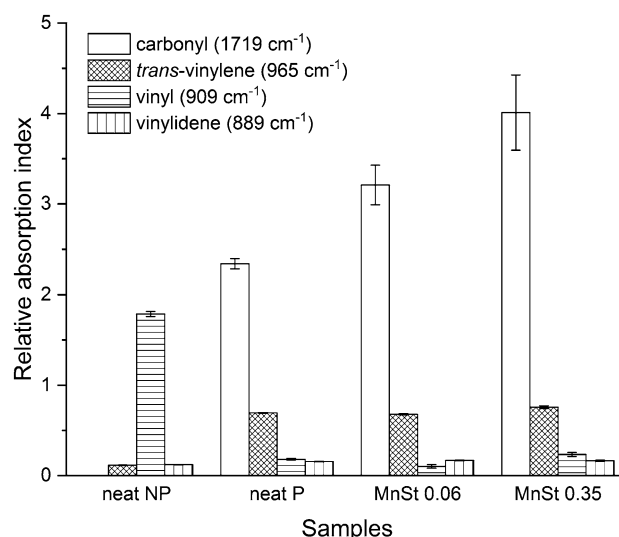

Fig. 3 Relative absorption index of carbonyl (1719/2019) and of the unsaturated groups in samples neat NP, neat P, MnSt 0.06 and MnSt 0.35
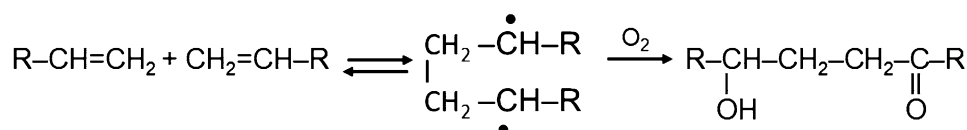
contributing to the relatively intense gel formation in the MnSt 0.35 sample, mainly after 33 min of processing. It should be mentioned that FTIR analysis proved that the residues inside the stainless-steel cages were HDPE gel.

Conclusions regarding the thermomechanical degradation of HDPE should not be drawn based solely on the results of torque rheometry. Therefore, infrared spectroscopy and size exclusion chromatography results may be used to contribute to the understanding of the thermomechanical HDPE degradation process. The results obtained by these last two techniques, as well as the results of the rheological test, will be discussed according to the main organic functional groups associated with the oxidative abiotic degradation process of HDPE, i.e., carbonyl and unsaturated groups [44, 73, 74]. FTIR results are presented in Figs. 3, 4, 5, 6. Figure 3 shows the evolution, in relation to the neat NP sample, of the investigated functional groups in HDPE after 50 min processing. In the reference sample (neat NP), the relative carbonyl index (1719 cm^{-1}) was not detected at the test conditions, however all processed samples showed a significant amount of carbonyl at the end of processing, indicating that all HDPE processed samples underwent oxidative degradation. This result was expected because of the relatively large amount of oxygen (air) in the rheometer chamber (approximately 24% of the free volume of the chamber) [16,

48]. The results (Fig. 3) also show that, in the investigated concentration range, the pro-oxidant accelerates the oxidative degradation of HDPE as MnSt concentration increases. In addition to ketone, the main carbonyl product of the thermomechanical oxidative degradation of PE, aldehydes and carboxylic acids are also formed. Therefore, the relative ketone carbonyl content might not represent, relative to the carbonyls, the effective level of oxidative thermomechanical degradation of the polymer [52–54, 58, 59, 62–66, 68].

Figure 4 shows the infrared spectra in the region between 1760 and 1680 cm^{-1} for the processed samples (neat P, MnSt 0.06 and MnSt 0.35) and for the neat NP sample. The results show quantitative and qualitative differences between the spectra as pro-oxidant concentration increases. With increasing MnSt concentration, absorptions at approximately 1735 cm^{-1} (aldehydes) and 1719 cm^{-1} (ketones) increase significantly, whereas the absorption at approximately 1700 cm^{-1} (carboxylic acids) increases slightly. To quantify and qualify each of the carbonyl absorptions in the region between 1760 and 1680 cm^{-1}, Fityk version 0.9.8 was used, a program for data processing and nonlinear curve fitting. This program enabled deconvolution of the FTIR spectrum, facilitating identification and quantification of the respective absorptions, individually. Figure 5 shows the deconvolution, in the region of interest, of the infrared spectrum of a sample

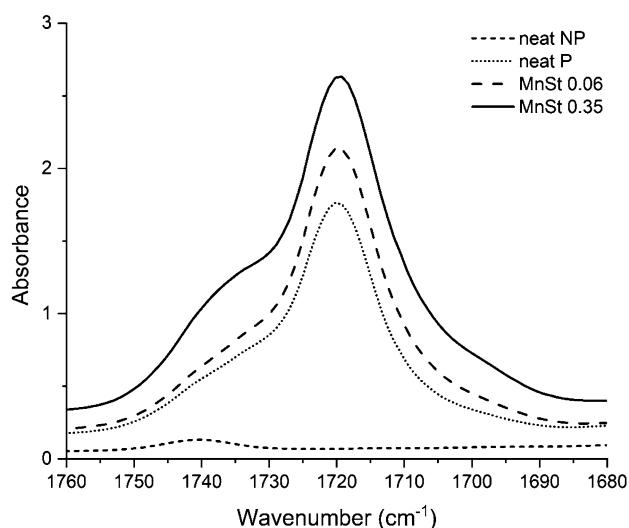**Scheme 2** Molecule size increase via dimerization reaction [60, 101]

Fig. 4 IR spectra of the reference and processed samples (50 min) in the region comprising the absorption of the carbonyl and CH$_2$ groups
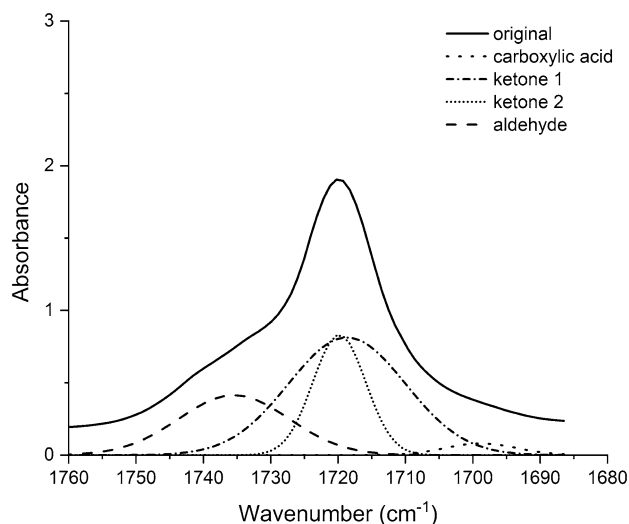

Fig. 5 Deconvoluted curves of the carbonyl absorptions between 1760 and 1680 cm^{-1} of one of the neat P samples (Gaussian fit of the Fityk program version 0.9.8)

Fig. 6 Effect of MnSt concentration on the production of different carbonyl groups after processing in closed-chamber torque rheometer

of the neat P formulation. The Gaussian mathematical model presented the highest precision regarding curve fitting. Figure 6 shows the relative index results of the carbonyl groups from ketones, aldehydes and carboxylic acids, which were quantified using the ratio between the carbonyl absorption intensity, determined by the deconvolution program for each organic function, and the absorption intensity of the reference CH band (at approximately 2019 cm^{-1}).

The main formation reactions of ketone, i.e., the main carbonyl product of the thermomechanical oxidation of HDPE, are shown in Scheme 1a, c, i, m [52–55, 65, 68, 86]. The ketones may be formed either at a constant rate, as soon
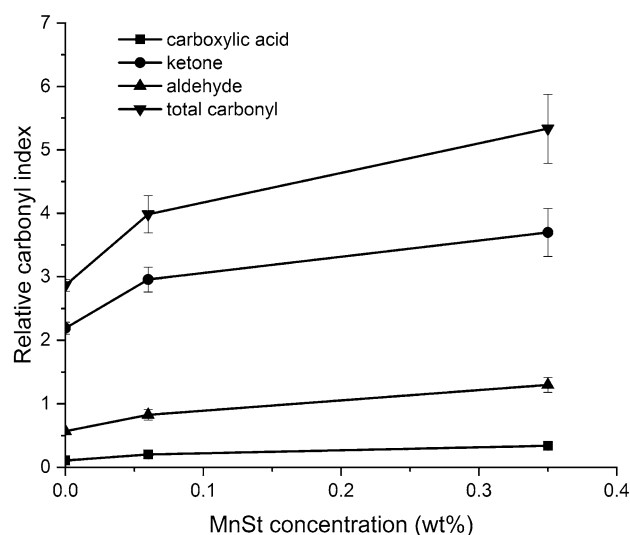
as processing starts (Scheme 1c), or at an increasing rate (Schemes 1a, m), after an induction time that increases as melt temperature decreases. The reactions are based on the decomposition of hydroperoxide and the entrapment (cage) of free radicals, characteristic of relatively high-viscosity liquids with consequently limited mobility. As with total carbonyls, the amount of ketones formed during HDPE processing increased with increasing pro-oxidant concentration. The production of ketones in formulations MnSt 0.06 and 0.35 was, respectively, approximately 35% and 69% higher than the amount of ketones produced in the neat sample P. Most of the major reactions that produce ketones in the thermomechanical oxidation of PE do not result in significant alteration in average polymer molar mass, except for the α-γ-ketohydroperoxide decomposition reaction, which produces, after chain scission, a carboxylic acid and a methyl ketone (Scheme 1d). It should be mentioned that the α,γ-ketohydroperoxide species is produced in the propagation stage of the thermomechanical oxidative degradation of HDPE [52–55, 65, 68, 86].

Despite their relatively low concentrations, aldehydes and carboxylic acids are quantitatively important products in the thermomechanical oxidative degradation of HDPE [62–66, 68]. The results show that the production of aldehydes and carboxylic acids in HDPE processing was relatively significant and, just as in the case of the ketones, the production of these species increases with increasing manganese stearate concentration. The production of aldehyde in formulations MnSt 0.06 and 0.35 was, respectively, approximately 45 and 128% higher than the amount of aldehydes produced in the neat sample P. The main aldehyde formation reaction during HDPE processing is β scission of secondary alkoxyl radicals

(Scheme 1j), which are formed mainly via bimolecular decomposition of hydroperoxides at the initial processing stage and/or bimolecular decomposition between an alcohol and a hydroperoxide at long processing times [63–65, 68]. Aldehydes can also be formed at significant amounts from the acid catalyzed decomposition of allylic hydroperoxides, producing two aldehydes for each decomposed hydroperoxide, and in this case, the reaction depends on the accumulation of carboxylic acids in the system (Scheme 1g). The aldehydes can also be formed by other oxidative reactions, but the quantitative contribution to the thermomechanical degradation process is relatively less than the aforementioned reactions [63–65, 68]. Aldehyde formation reactions result in HDPE chain scission, which significantly reduces the average polymer molar mass.

As to the carboxylic acids, the production of this chemical species in formulations MnSt 0.06 and 0.35 was, respectively, approximately 89 and 217% higher than the amount of carboxylic acids produced in the neat P sample. Like the aldehydes and ketones, the acids can also be formed at a constant rate at the start of the oxidative thermomechanical degradation process and at an increasing rate in the advanced processing stages [63, 65, 66]. The main carboxylic acid formation reactions during PE processing are presented in Schemes 1d, e, h, l. At relatively high temperatures (above 200 °C), the main carboxylic acid formation reaction at the beginning of the oxidative thermomechanical degradation is the decomposition of the α,γ-ketohydroperoxide species (Scheme 1d), which also contributes to the increase in the amount of ketones introduced into the HDPE molecule [52–55, 63–65, 68]. Another reaction that produces a significant amount of carboxylic acids at constant rate is the reaction of unsaturated peracids (Scheme 1h) [63, 65]. A probable carboxylic acid formation reaction at increasing rate in the advanced stages of the oxidative thermomechanical degradation of HDPE is the peroxidation of caged aldehyde pairs that are close enough to favor the reaction shown in Scheme 1e [66]. The aldehyde pairs are generated mainly from the decomposition of allylic hydroperoxides (Scheme 1g). The peroxidation reaction of the aldehyde pairs (Scheme 1e) depends on the concentration of oxygen in the system and this condition occurred in the thermomechanical tests carried out in the current investigation (free volume of approximately 24%) [63, 66]. The decomposition of α, β-ketohydroperoxide also contributes to the formation of carboxylic acids and aldehydes, especially when the concentration of ketones increases in the polymer melt (Scheme 1(l)) [66]. The aldehydes are considered the main precursors of carboxylic acid formation; however, temperature and shear conditions of the oxidative thermomechanical degradation of PE do not favor the transformation of free aldehydes, but rather the peroxidation of caged aldehyde pairs [63, 66]. Like aldehydes, the production of carboxylic

acids promotes, through molecular scission, reduction in HDPE average molar mass. Several other reactions may produce ketones, aldehydes and carboxylic acids, however at much lower amounts [52–55, 62–66, 68, 86].

The results regarding carbonyl production indicate that manganese stearate accelerated the oxidative process of HDPE during processing. This is in agreement with the Haber–Weiss mechanism, as the main carbonyl production reactions (Scheme 1) are based on the decomposition of hydroperoxides into alkoxyl and peroxyl radicals, which propagate the oxidative degradation reactions of HDPE [52–55, 62–66, 68, 86]. It should be mentioned that all the carbonyl groups assessed by infrared spectroscopy (Fig. 6) present, at the end of 50 min of processing, a significant increase in relative intensity as manganese stearate concentration increases. This is especially true for the carboxylic acids, which, although possess lower absolute amount of carbonyls, exhibit the highest increase (89 and 217% for MnSt 0.06 and 0.35, respectively) in the amount of carbonyl relative to the neat P sample when compared to aldehydes (45 and 128% for MnSt 0.06 and 0.35, respectively) and ketones (35 and 69% for MnSt 0.06 and 0.35, respectively). These data agree with the oxidative thermomechanical degradation reactions of neat PE, i.e., without pro-oxidant (Scheme 1). This shows that carboxylic acids may be formed from additional peroxidation of other organic functional groups that accumulate during PE processing (liquid melt state) as for example, aldehydes, ketones and alcohols. Since the decomposition of hydroperoxides is the main step of these reactions, the presence of manganese stearate is essential in the acceleration of the auto-oxidative process (reactions A and B) and formation of carboxylic acids and other oxygenated organic groups [36, 52–55, 62–66, 68, 86]. Hence, the amount of carbonyl groups (ketones, aldehydes and carboxylic acids) is expected to increase as manganese stearate concentration increases (Figs. 3, 4, 5, 6), indicating the effective prodegrading performance of the additive in oxidative thermomechanical degradation processes.

Many reactions of the oxidative thermomechanical degradation of PE, such as the reactions in Scheme 1b, e, g, j, l), promote simultaneously molecular oxidation and scission, and consequently, the reduction in average molar mass of the polymer [64–66]. Figure 7 shows the weight-average molar mass (Mw) of the samples after 50 min of processing. SEC results show that Mw of HDPE decreases with increasing manganese stearate concentration. It should be mentioned that the gel fraction in the respective formulations did not contribute to the determination of the average molar mass, since the guard column retains particles larger than 13 μm. Associated with infrared spectroscopy results, this indicates that at the end of the processing, the reactions that promote oxidation and scission of the polymer molecule (Scheme 1b, e, g, j, l) are more relevant when compared to
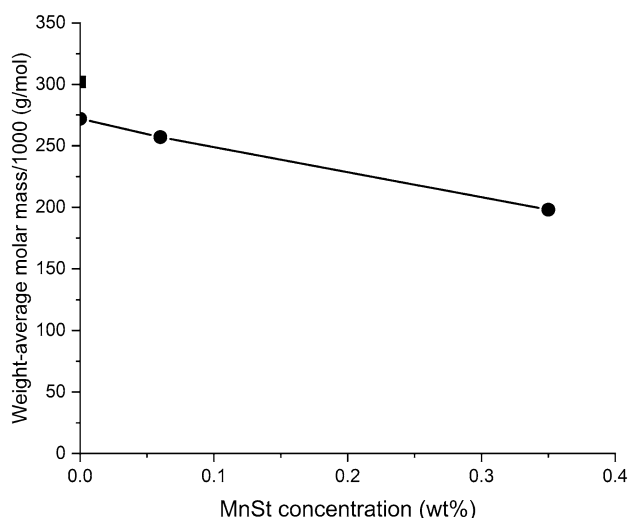
Fig. 7 Effect of MnSt concentration on the weight-average molar mass of HDPE after 50 min processing in a closed-chamber torque rheometer (closed square-neat NP; closed circle-processed samples)

the branching and/or crosslinking reactions (Scheme 1k, n, o) and the oxidation reactions without molecular scission (Scheme 1a, c, d, f, h, i, m). One cannot conclude, based on infrared spectroscopy and SEC results at the end of the processing, whether oxidation reactions with molecular scission predominated throughout the processing, but torque results (Fig. 1) throughout the assay may contribute to this discussion. Correlating the results of the three techniques, used to monitor the thermomechanical degradation of HDPE in the rheometer, supports the discussion of the previously described torque results on the "competition" between chain branching and/or crosslinking and the oxidation reactions with and without chain scission. The results of torque, infrared spectroscopy and SEC indicate that the intensity of the oxidation reactions without and with molecular scission exceeded the intensities of the branching and/or crosslinking reactions of the HDPE molecule after 50 min of processing. The reduction in HDPE Mw in the neat samples P, MnSt 0.06 and MnSt 0.35 were about 10, 15 and 34%, respectively, relative to the reference sample (neat NP). It is important to note that, compared to the reference sample (neat NP), all processed samples showed oxidative thermomechanical degradation. However, as manganese stearate concentration increases, CI values, related to the several compounds formed, increase and Mw decreases, indicating that oxidation reactions with molecular scission play an important role in the oxidative thermomechanical degradation of HDPE at the test conditions.

SEC results reveal that significant differences (about 60,000 g/mol) in Mw may not be detected by the torque of the rheometer, since, at the end of the 50-min test, the torque of the MnSt 0.06 and 0.35 were statistically equal. The results of torque, carbonyl content and SEC reveal significant changes in the physicochemical properties (reduction in average molar mass and increase in oxygenated organic functional groups) of HDPE. On the one hand, these changes may promote the biotic degradation of the polymer. On the other hand they may compromise the primary or secondary recycling of the polymer, since the oxidative thermomechanical degradation introduced in a first processing can become more intense in a possible processing inherent to primary and secondary recycling. This requires special attention such as for example the addition of sufficient amount of processing stabilizer to guarantee the properties during recycling but without compromising the biodegradability of the material when discarded in the environment after use [26].

In infrared spectroscopy carbonyl is the organic functional group commonly used to monitor the oxidative abiotic degradation of polyolefins [7, 10, 14, 17–20, 22–26, 32, 34–36, 38, 39, 41, 44, 48, 52, 62, 67, 78, 81, 84], but monitoring of unsaturated groups may also be useful [37–39, 41, 44, 56, 57, 60, 61, 68, 84]. The ethylene polymerization process is a very important issue in the PE degradation processes, especially in the thermo-mechanical oxidative degradation during polymer transformation processes. The catalytic residues, the degree of crystallinity, the amount of branching, the presence of heteroatoms and the amount of unsaturated groups, which are the main characteristics defined in the synthesis of the polymer, may affect the degradation processes of polyethylenes [1]. HDPE, for example, produced by the Phillips system (relatively more vinyl groups inherent in the synthesis process) exhibits a tendency of increasing average molar mass (crosslinking and/or branching) during processing when compared to HDPE produced by the Ziegler–Natta system. However, both are susceptible to oxidative degradation processes [38, 39, 41, 42, 68]. The results of the unsaturation index of the major unsaturated groups (*trans*-vinylene, vinyl and vinylidene) present in PE are shown in Fig. 3.

The vinyl group is apparently formed and consumed during the oxidative thermomechanical degradation process. Formation occurs preferentially in the early processing stage of PE mainly from the decomposition of secondary hydroperoxide groups in the α position relative to the branch of a methyl group [57]. However, due to the synthesis process, the HDPE used in this work (Fig. 3, neat NP formulation) presents significant amount of vinyl groups and the results (Fig. 3) show that, after 50 min of processing, consumption of the vinyl group predominated in the oxidative thermomechanical degradation of HDPE [68]. The reduction (relative to the neat NP formulation) of vinyl groups was significant in all processed formulations (approximately 90, 94 and 87% for neat P, MnSt 0.06 and MnSt 0.35, respectively). Consumption of the vinyl group may occur during the entire processing time, but the main reactions of vinyl

consumption occur in the early processing stages, including dimerization reactions, addition of alkyl macroradicals and reactions with peroxy radicals, molecular oxygen, hydroperoxide and peracids [60]. Some of the vinyl consumption reactions (molecular oxygen, hydroperoxide and peracid) do not significantly alter the average molar mass of the polymer, but promote oxidation of the molecule and can therefore lead to chain scission in the advanced processing stages. On the other hand, other reactions such as dimerization, shown in Scheme 2, and the addition of macroradicals (Scheme 1k, n, o) promote molar mass increase [60, 101]. As a result of the relatively high temperature and shear in the PE transformation processes, the dimerization and the addition of macroradicals are the main consumption reactions of the vinyl group in the thermomechanical degradation process [60, 101]. Thus, at the early stages the predominance of dimerization reactions and macroradical addition may explain the torque results during processing, which remained constant (MnSt 0.06 and 0.35) or showed a slight increase (neat P) up to approximately 20 min of processing, indicating an increase in polymer molar mass. At the end of processing (50 min) the formulations presented a decrease in torque. This behavior may be due to the predominance of chain scission oxidation reactions (Scheme 1b, e, g, j, l), which may have occurred in the intermediate and final stages (after 20 min of processing) of the oxidative thermomechanical degradation process. As a result weight-average molar mass is reduced and oxygen groups are introduced in the HDPE molecule. IR spectroscopy results (relative carbonyl content) and SEC (weight-average molar mass) also support this hypothesis. Despite the fact that the results were statistically not equal, consumption of the vinyl group, at the end of the test, was significantly intense and approximately the same for all formulations. This indicates that manganese stearate did not influence the consumption of the vinyl group after 50 min of thermomechanical degradation testing. Importantly, the PE oxidation induction time in the oxidative thermomechanical degradation decreases with increasing vinyl concentration, indicating that the oxidation process starts through the molecular oxygen attack of the allylic hydrogen of the PE molecule and, from this reaction, other oxidative degradation reactions occur [47, 48, 57–60, 64].

FTIR results (Fig. 3) show a significant increase of the *trans*-vinylene group, after 50 min of processing, in all processed formulations, which was similar for the different formulations (approximately 610, 596, and 665% increase for neat P, MnSt 0.06, and MnSt 0.35 respectively). The formation of the *trans*-vinylene group, as well as other functional groups, occur mainly at the early processing stages through several hydroperoxide decomposition reactions, which are also responsible for the formation of other ketone and alcohol functional groups. The decompositions of these groups generate free radicals which lead to the formation of the *trans*-vinylene group. For example, the direct decomposition reaction of the peroxy radical (Scheme 1f), at relatively high processing temperatures (210 to 300 °C), accounts for significant amount of the *trans*-vinylene group formed [56]. On the other hand, the consumption of the *trans*-vinylene group, as well as the vinyl group, may occur through reactions with peroxy radicals, hydroperoxides and peracids. However, the main consumption reaction of the *trans*-vinylene group in the oxidative thermomechanical degradation process is the reaction with molecular oxygen, forming allylic hydroperoxides, which, by means of acid catalysis, decompose in pairs of aldehydes (Scheme 1g) [45, 48, 53, 54, 56, 58, 59, 61–68]. In PE containing no pro-oxidant the concentration of *trans*-vinylene increases with processing time and reaches a stable level in the more advanced stages. This stabilization is related to the "competition" between the formation and consumption of the functional group during processing, since the *trans*-vinylene group is an important intermediate in the formation of oxygenated functional groups, such as aldehydes [56, 61]. The results (Fig. 3) agree with the literature [56, 61] and show that the formation reactions of the *trans*-vinylene group are predominant during processing, presenting similar values for all processed formulations. This indicates that after 50 min of processing, the concentration of manganese stearate did not influence the production of the *trans*-vinylene group. Nevertheless, this does not mean that during the thermomechanical degradation test the pro-oxidant did not exert influence, since the "competition" between the formation and the consumption of the *trans*-vinylene group and the relatively long test time may have contributed to the stabilization of the functional group at approximately equal concentration levels for all processed formulations. Thus, a possible influence of manganese stearate during the test may have been concealed. The influence of the pro-oxidant is expected, since this species promotes the decomposition reactions of the hydroperoxides, which may form the *trans*-vinylene group. Therefore, the higher the pro-oxidant concentration, the higher the *trans*-vinylene concentration will be. However, as the *trans*-vinylene concentration increases, so does its consumption and therefore the final concentration of the species tend to equalize in all processed formulations, regardless of pro-oxidant concentration. On the other hand, the concentration of functional groups formed from the consumption of the *trans*-vinylene group should increase with the increase in pro-oxidant concentration. Hence, the influence of manganese stearate on the thermomechanical degradation process will be perceived through the variation in the concentration of the functional groups formed from the *trans*-vinylene group. Within this context, the carbonyl groups are the main indicators of the influence of the pro-oxidant, as shown in the results (Figs. 2, 3, 4, 5) of the carbonyl index discussed previously.

Regarding the vinylidene group, the results (Fig. 3) show a discrete increase in the concentration of this functional group, for all processed formulations, after 50 min processing. This in in agreement with results reported in the literature of HDPE containing no pro-oxidant [57, 60]. Like the vinyl group, it appears that the vinylidene group is also formed and consumed during the oxidative thermomechanical degradation and its formation also occurs primarily at the initial stage of PE processing, mainly by the decomposition of secondary hydroperoxide groups in the α position relative to a quaternary carbon [57]. The consumption of the vinylidene group occurs chiefly through reactions with hydroperoxide and peroxy radicals; reactions that propagate the oxidative process and promote the formation of oxygenated functional groups [60]. The amount of vinylidene and vinyl, formed in the oxidative thermomechanical degradation of PE, is relatively small. Associated with the consumption and the relatively small amount of this species in HDPE (Fig. 3, neat NP formulation) the amount of the vinylidene group after 50 min of processing is relatively discreet and approximately equal for all processed formulations, as a result of a slight increase in the functional group concentration as compared to the reference formulation (neat NP). As for the other unsaturated functional groups, the concentration of manganese stearate does not seem to influence the results. However, as to the *trans*-vinylene group, the influence may have been camouflaged, because as the group is formed it is also consumed and generates oxygenated functional groups, which indirectly reflect the influence of the pro-oxidant, as discussed previously.

Conclusion

The oxidative thermomechanical degradation of HDPE melt containing manganese stearate was monitored via torque rheometry, gel content determination, SEC and FTIR. Degradation increased with increasing manganese stearate concentration after 50 min of processing in a closed-chamber torque rheometer. Torque rheometry results indicate that, during the test, manganese stearate may have acted both as a lubricant, reducing shear stress and generating fewer alkyl radicals, and as a pro-oxidant, enhancing hydroperoxide decomposition and propagating auto-oxidation reactions. The lubricating effect of manganese stearate may predominate in the early processing stages, especially for the MnSt 0.35 sample, whereas in the final stage the pro-oxidant effect may predominate, significantly reducing the torque of the samples containing manganese stearate. Manganese stearate, at a concentration of 0.35 wt%, increases the amount of HDPE gel after 50 min of processing, indicating that the pro-oxidant action of the additive (hydroperoxide decomposition) promotes significant formation of free radicals (alkyl, peroxyl and alkoxyl), which may promote oxidation reactions with both chain scission and crosslinking. FTIR and SEC results agree with the results of torque rheometry and show that, after 50 min of processing, oxidative thermomechanical degradation of HDPE increases with increasing manganese stearate concentration, resulting in an increase in the number of oxygenated functional groups, mainly ketones, aldehydes and carboxylic acids, and in reduction in the weight-average molar mass of HDPE. After 50 min processing the reduction in the amount of vinyls and the increase in the amount of *trans*-vinylene groups in the processed samples (neat P, MnSt 0.06 and MnSt 0.35) were significant compared to the neat NP reference sample. Nevertheless, the results indicate that the presence and variation in manganese stearate concentration does not significantly influence the reduction in the amount of vinyl and, mainly, the increase in *trans*-vinylene groups. The amount of vinylidene groups did not show significant variation in the processed samples, indicating that the test conditions, presence and concentration of manganese stearate did not interfere with the final amount of the vinylidene group after 50 min testing. The results of the oxidative thermomechanical degradation of manganese stearate-containing HDPE indicate that, when products manufactured with this composition are disposed of in the environment, polymer biodegradation may be favored if oxidative abiotic degradation produces oxygenated fragments that can be assimilated as a substrate (carbon source) by the microorganisms present in the environment. However, the effects of the oxidative thermomechanical abiotic degradation may impair mechanical recycling, whether primary or secondary, requiring special care in the subsequent transformation processes. This includes the addition of processing stabilizers at adequate concentration, so as to guarantee the physicochemical condition of the polymer prior to recycling and to not compromise the biodegradability of the polymer in any future disposal in the environment.

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