

Influence of Cleaning Conditions on the Degradation of Recycled HDPE

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ABSTRACT: One of the materials most commonly found in municipal plastic waste (MPW) is High Density Polyethylene (HDPE), which is used particularly for food packaging and cleaning product containers. Postconsumer HDPE is generally contaminated with other impurities and, therefore, a cleaning process is necessary before it can be reprocessed. The aim of this study was to investigate the influence of the cleaning conditions on the oxidative degradation of postconsumer HDPE. These plastic materials were washed in NaOH solution, liquid detergent (D), and a mixture of NaOH/D (1 : 1). Results for the melt flow rate (MFR) and capillary rheometry showed that

NaOH has a great influence on the oxidative degradation of HDPE. The HDPE treated with NaOH solution had a lower decomposition temperature, observed through Thermal Gravimetric (TG) analysis, and a lower the Oxidative Induction Time (OIT), obtained via Differential Scanning Calorimeter (DSC). Finally, the oxidative degradation of HDPE was verified through a higher carbonyl index. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1454–1460, 2009

Key words: oxidative degradation; postconsumer HDPE; plastic waste; cleaning process

INTRODUCTION

Since the introduction of food packaging, the plastic packaging industry has grown greatly, particularly the use of thermoplastic polymers, such as high and low density polyethylene (HDPE and LDPE), polypropylene (PP), polyethylene terephthalate (PET), polyvinyl chloride (PVC), and polystyrene (PS). The polyolefins are present in the highest proportion in municipal plastic waste (MPW). HDPE is the one of the most commonly found polyolefins in MPW, since it is used to make plastic bags and food product packaging.

The increase in the consumption of these products has led to a consequent increase in MPW volume, particularly due to food packaging^{1,2} which results in serious problems in modern society. These include environmental pollution and reduction of raw materials from renewable sources. Furthermore, the decomposition of plastic can take 100 years, since it is a nonbiodegradable material.^{3,4}

Implementing the reduction, re-use, and recycling (known as the 3Rs) of postconsumer plastics offers an alternative of solution. This involves a reduction in the consumption of products with excess packag-

ing. Re-use is sometimes applicable when careful design and material selection has produced a container that can not only withstand the treatment involved in multi-trip operations but also the rigorous cleaning required. Recycling of postconsumer plastic in its different forms (mechanical, chemical, and energetical) is the last, and least attractive, alternative, and mechanical recycling has to be an economically viable proposition. This means that recycled material must be competitive on the market and offered at prices lower than the virgin polymer.

Even though recycling has proved to be one alternative solution, the heterogeneity and incompatibility of the chemical nature of these polymer materials (caps, labels, printing, among others) present serious problems in the success of this process.^{5,6} Also, there is often the presence of different impurities impregnated on the packaging surfaces (organic and inorganic). These negative factors result in a low aggregated value of the processed product.¹

The recycler is thus faced with the dilemma of increasing production cost, by making use of ways to remove the contaminants, or developing a (usually) lower grade process that such containers can withstand. Returned plastic packaging is often contaminated with the original product or other foreign material. This is the major problem facing those seeking to recycle plastic to be used in food packaging. It is well-documented that certain chemical products can be absorbed by the plastic container and migrate into the new product at a later stage.^{7,8}

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Many unknowns are present here concerning the range of chemicals that are contained in plastic packaging, either originating from the original product or another product which the purchaser later stored in it. The effects of washing all such chemicals out of plastics are not sufficiently well-researched to satisfy the strict food legislation.^{8,9}

The cleaner the postconsumer plastic, the higher its added value, however, there is still the necessity to carry out in depth studies on the effect of the different products used for the removal of impurities from plastics. In the literature, use of caustic soda and some liquid detergents to remove impurities is commonly reported.^{2,6,10,11} Apart from being contaminating, the use of these products and cleaning conditions can lead to polymer degradation.

Many studies have been carried out to investigate the influence of postconsumer plastic the processing conditions on the degradation of polymer.^{2,5,12–24} Polymer processing involves high temperatures, shearing, and the inevitable presence of small amounts of oxygen. Thus, the mechanisms of melt degradation involve both thermomechanical and thermo-oxidative reactions, with crosslinking and chain scission processes occurring simultaneously in the polymer melt. The relative contribution of these processes depends on the processing conditions and the polymer microstructure. Thermoplastic polymers undergo thermal-mechanical and oxidative degradation, however, some to a greater degree than others, when they are submitted to different reprocessing conditions.^{2,12–26}

In the case of HDPE, the occurrence of degradation has been mostly attributed to crosslinking, branching, and scission degradation reactions depending on the synthesis conditions. Polyethylenes are produced by many technologies involving different types of catalysts.^{14,16,21} Different chemical reactions occur in the course of processing polyethylene, which modify the structure of the polymer produced in the reactor. The overall kinetics of these reactions depends on the number of weak sites (branched, unsaturated, and oxygen-containing groups), the concentration of residual catalyst, and the processing conditions.

However, there is some variability in the role which scission plays due to the different types and concentrations of residues resulting from the polymerization method used to produce the virgin resin.¹⁴ Heat, shear, and oxygen are all sources of the initiation of these reactions, and the extent to which they influence the polymer is largely dependent on the processing method.^{14,17}

Moss and Sweifel¹⁴ evaluated the degradation of HDPE during five extrusions in a single screw extruder and concluded that HDPE undergoes scission and crosslinking reactions during the process. In the

case of Phillips-type HDPE, crosslinking is usually favored, showing an increase in the molecular weight, whereas Ziegler-Natta-type HDPE undergoes mainly chain scission during the melt processing.

Polymer degradation in the earlier stages of plastic reprocessing is not usually considered. However, the cleaning process of the material can have a great influence on HDPE degradation, as has been demonstrated for other polymers, such as PET, where the influence of caustic soda on the hydrolytic degradation has been verified.²⁷

According to Rex et al.,¹⁶ the deterioration of HDPE properties is referred to as degradation and is mostly attributed to the reground content of the feedstock that has experienced more than a single-pass processing history. In injection molding, high processing temperatures and shear are experienced by the polymer in an environment which is mostly anaerobic, except near the solids conveying zone of the plasticizing unit. However, due to the auto-catalytic nature of oxygen in polymer degradation, only a small quantity of oxygen needs to be present for significant damage to the chain structure to occur.

Therefore, thermomechanical and thermo-oxidative degradation are both potential contributors to changes in the polymer structure in this processing machinery. Incorporation of antioxidants in the polymer seeks to minimize the occurrence of degradation reactions. However, due to the high-cost and potentially negative influence of these chemical species on the processability and final properties, resin suppliers generally do not add sufficient concentrations to prevent all radical reactions from occurring.^{14,18,20,24}

Studies on HDPE degradation before its reprocessing are scarce in the literature. Therefore, the aim of this study was to evaluate the extent of HDPE degradation under different cleaning conditions, through monitoring the rheological, chemical, and thermal properties of the plastic.

EXPERIMENTAL

Bottles for milk products made from postconsumer HDPE were used in this study. This material was collected from a waste separation central office "Associação Ecológica Rubem Berta" in Porto Alegre, Brazil. NaOH (brand name Lipon) and liquid detergent (D) (brand name Max Clean Plus) were used as cleaning products.

First, PP caps and LDPE labels were separated from the postconsumer HDPE bottles. The HDPE containers were ground in a knife mill (Kie model MAK 250) to medium-sized pieces of ~ 5 cm. Solutions of NaOH, D, and NaOH/D (1 : 1) in concentrations of 0.1% by weight were prepared. The postconsumer HDPE pieces were divided into three

TABLE I
Turbidity and pH of Effluents After
Washing Post-consumer HDPE

Post-consumer HDPE	Effluent	Turbidity (NTU)	PH
	Water	0.6	7.9
HDPE _{NaOH}	NaOH	107.8	11.9
HDPE _D	D	71.0	7.7
HDPE _{NaOH/D}	NaOH/D (1 : 1)	73.0	11.9

lots of 3 kg each: HDPE_{NaOH}, HDPE_D, and HDPE_{NaOH/D} and then washed in NaOH (pH = 11.9), D (pH = 7.7), and NaOH/D (pH = 11.9) solutions, respectively, under the cleaning process conditions (mixing speed of 30 rpm for 15 min). Liquid effluents from each one were characterized using an Alkafit turbidimeter. The HDPE material was then dried in hot air at 50°C for 24 h in an air circulation stove. After drying, it was again ground, this time into flakes.

The HDPE flakes were characterized according to their rheological, chemical, and thermal properties. The melt flow rate (MFR) of the flakes was determined in a Microtest 4105 plastometer, at 190°C using 2.16 kg load, based on the ASTM 1238-95 standard. The viscosity and shear stress were evaluated with the use of a Galaxy III Capillary Rheometer, model 9052, at 200°C and the shear rate was measured from 100 to 1000 s⁻¹. The carbonyl index of HDPE after cleaning was determined using a Perkin-Elmer Spectrum 1000 FTIR spectrometer, from 4000 cm⁻¹ to 400 cm⁻¹, at 1740 cm⁻¹ with a reference peak of 840 cm⁻¹. It was necessary to prepare the samples in the form of a film of 300 μm thickness, obtained by thermal compression molding at 190°C, with 3 tons of pressure and 3 min of residence time.

Thermal characterization was performed with a heat flow differential scanning calorimeter (DSC—model 2920, TA Instruments). The analysis was carried out either in a nitrogen or oxygen atmosphere using a heating rate of 10°C/min. Using the same instrument, oxidative induction time (OIT) was determined according to ASTM D3895-80, with an isothermal temperature at 200°C. Thermogravimetric analysis (TGA) was carried out at 20°C/min in a nitrogen atmosphere using the DSC mentioned earlier.

RESULTS AND DISCUSSION

Cleaning efficiency

Table I shows the turbidity values of the three liquid effluents evaluated, which, as expected are all higher than that of water. On comparing the effluent tur-

bidity values for the same concentration of cleaning product it can be observed that the NaOH effluent has the highest value. This result indicates the efficiency of NaOH (caustic soda) in the removal of impregnated impurities from plastic packaging, transferring these impurities, usually organic waste (milk and derivatives), from the postconsumer plastic to the washing solution.

The turbidity of effluent D indicates that the concentration used was not efficient in removing impurities and, therefore, needs to be increased. On the other hand, it can be seen that D and NaOH/D effluents have similar turbidity values. This is because even though the NaOH/D effluent contains caustic soda in the mixture, its efficiency was low due to its lower concentration (0.05 wt %) in this solution and to the presence of the liquid detergent (D).

On the other hand, the NaOH and NaOH/D solutions had a high pH after washing due to the highly alkaline nature of caustic soda, whereas the D solution had a neutral pH. Generally, the liquid detergents used in postconsumer plastic cleaning processes are mixtures of tensoactive agents: sodium dodecylbenzene sulfonate and sodium lauryl ether sulfate, whose function is to reduce the water surface tensile strength, allowing oils and fats to be emulsified.

Rheological properties

To investigate the effects of the polymer structure, under the cleaning conditions, on the nature of the polymer degradation reactions, results from rheological measurements of shear strength, viscosity (capillary rheometry), and melt flow were related to changes in the chemical functional groups (unsaturated, carbonyl) during chemical treatment.

In Figure 1, the apparent viscosity profile of post-consumer HDPE after cleaning with different

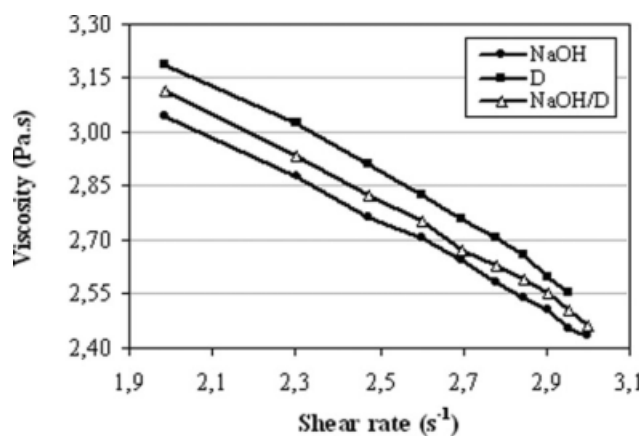


Figure 1 Log Viscosity profile of postconsumer HDPE after cleaning as a function of log shear rate.

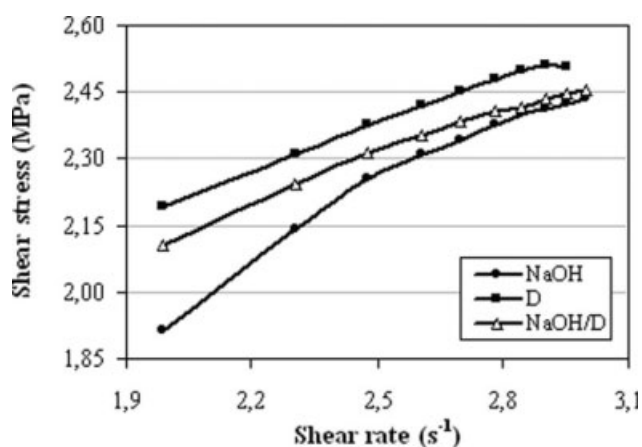


Figure 2 Log Shear stress profile of postconsumer HDPE after cleaning as a function of log shear rate.

washing solutions as a function of shear rate is presented. It can be observed that the viscosity of HDPE_{NaOH} is significantly lower when compared with the other HDPE samples cleaned in D and NaOH/D solutions, particularly for a low shear rate.

These results may indicate that the caustic soda, as well as the washing and drying conditions, influenced the oxidative degradation of HDPE, resulting in the formation of functional oxygen species. It also appears that when these samples are submitted to the rheological tests carried out at high temperatures, macromolecule chain scission occurs and, probably, the molecular weight distribution becomes broader.^{14,22}

This is reflected in a change in the rheological properties, that is, in a decrease in the viscosity. This behavior is in agreement with that described by Moss and Zweifel,¹⁴ where the HDPE undergoes chain scission and crosslinking reactions during its reprocessing. The Phillips-type HDPE generally undergoes crosslinking; whereas the Ziegler-Natta-type HDPE mainly undergoes chain scission and the molecular weight distribution becomes broader.

In Figure 2, the shear stress profiles of postconsumer HDPE samples after cleaning with different washing solutions, as a function of shear rate, are shown. It can be observed that the shear stress of the postconsumer HDPE_D sample is higher than that of the other samples at the shear rate interval evaluated. This result indicates that the higher viscosity of the polymer is related to its higher molecular weight leading to a greater shear stress. Also, the high viscosity indicates that HDPE cleaned in this solution does not undergo significant degradation (scission chain), as confirmed by its viscosity profile shown in Figure 1.

It is known that during thermal and mechanical treatment of a polymer, the degradation phenomena take place, mainly chain scission and branching.

These two processes are usually responsible for an increase or decrease in the MFR.^{14,19}

Figure 3 shows the MFR of postconsumer HDPE samples treated in different solutions. The MFR values for the HDPE_{NaOH} samples are higher than those of the other samples (40–50%). These results may reveal a significant degradation of HDPE samples cleaned in NaOH solution when compared to the other samples. This decrease in the HDPE viscosity may indicate a decrease in the molecular weight through the scission chain. In relation to the other samples cleaned in D and NaOH/D solution, the influence was lower, although the degradation mechanism was also via chain scission.

The fact that the rheological behavior indicates a molecular weight decrease for the different treated samples is further evidence of the participation of the cleaning product in the system. This suggests that the induction period for hydroperoxide generation is greater than that for oxygen in the open system.

Chemical properties

With the aim to evaluate the oxidative degradation level of postconsumer HDPE, the carbonyl indexes of the three samples were obtained by FTIR analysis (Fig. 4). The carbonyl groups developed through the oxidative degradation of the HDPE can be observed in the IR-region of 1900 cm⁻¹ to 1600 cm⁻¹, where the characteristic bands of carbonyl groups are found. Choudhury et al.²³ also observed a gradual increase in the absorbance of the carbonyl bands at 1740, 1727, 1714, and 1682 cm⁻¹ attributed to the carbonyl (CO) stretching vibrations of the ester (COOR), aldehyde (CHO), ketone (CO), and unsaturated ketone groups, respectively. Such an increase in the absorbance value of the ester carbonyl group

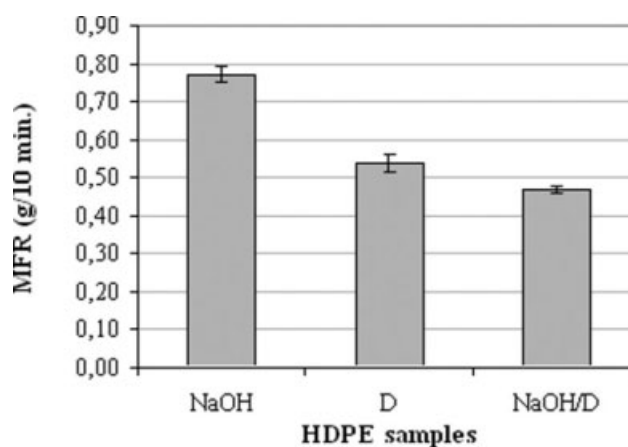


Figure 3 Melt flow rate of postconsumer HDPE flakes treated in different solutions.

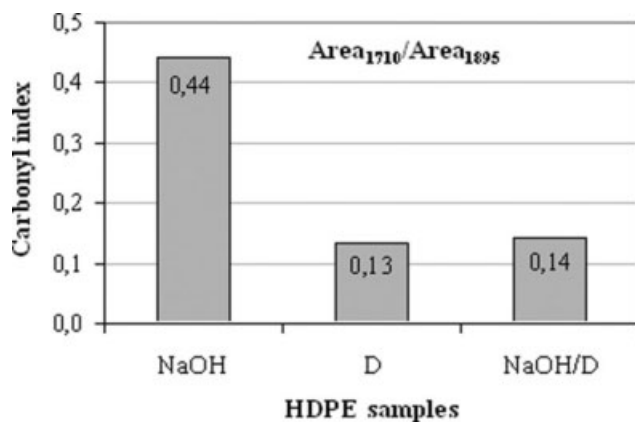


Figure 4 Carbonyl index of postconsumer HDPE samples treated in different solutions.

is clearly due to molecular enlargement reactions occurring during a series of thermo-oxidative reactions in the presence of air.

For this analysis, the peak area at 1740 cm^{-1} was compared with the reference peak at 840 cm^{-1} . In Figure 4, it can be seen that there is a significant difference in the carbonyl index of $\text{HDPE}_{\text{NaOH}}$ when compared with the other solutions, in fact, it is approximately three times higher than the others.

These results indicate that for catalyst residues of the Ziegler-Natta type,^{6,14,19,22} in the presence of NaOH at the test concentration HDPE degradation occurred via the oxidation pathway (appearance of carbonyl and hydroxyl groups, among others) under the cleaning process conditions. This result was not as pronounced for the sample treated with D solution.

As previously mentioned, polyethylenes are produced using various technologies involving different types of catalysts. Although the excess catalysts are often removed in the polymerization process, these are not totally eliminated, and their presence may initiate premature oxidation. Hoang et al.,²¹ detected the presence of metal catalyst residues in polyethylenes using inductively coupled plasma (ICP) analysis, and concluded that the HDPE was of the Phillips-type, containing chromium catalyst residues, although at very low levels. Small traces of aluminum and titanium residues were also detected.

Despite the large number of studies in the literature dealing with the effect of catalyst residues on the oxidative stability of polyolefins, the exact nature of the pro-oxidant effect of these residues is still not fully understood. However, it is generally accepted that the effect of catalyst residues in Phillips polymers is more pronounced than in products prepared with Ziegler-Natta catalysts.

Drelich et al.,²⁷ studied the separation of PVC from PVC/PET by flotation. They found that a highly alkaline solution of sodium hydroxide (4–

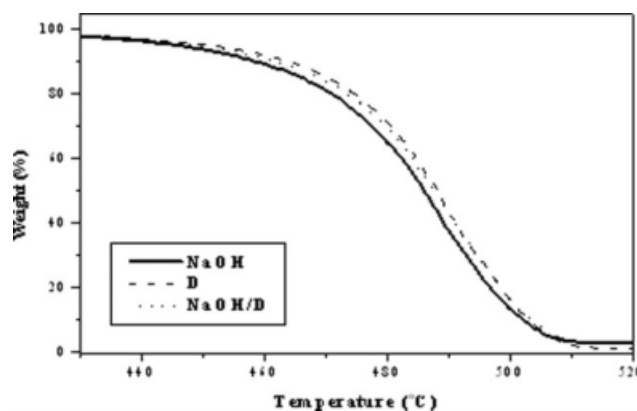


Figure 5 Thermogravimetric curves of postconsumer HDPE samples treated in different cleaning solutions.

10 wt %) is able to destroy the hydrophobicity of PET, whereas the hydrophobic properties of the PVC surface remain only slightly affected by these solutions. Also, large water contact angles were verified for PVC and PET plastic. A large contact angle indicates a greater number of functional groups (CO, OH, COO, among others) on the sample surface.

On the other hand, the HDPE_{D} and $\text{HDPE}_{\text{NaOH/D}}$ samples had a carbonyl index lower than that treated with NaOH solution. This may be due to the anionic detergent used having a low level of influence on the polymer degradation and also to the chemical nature of the solution, i.e., pH close to that of water and low concentration used.

Thermal properties

The influence of the chemical treatment during the cleaning process on the thermal stability of the postconsumer HDPE was assessed by TGA, DTG, and DSC analysis. In Figure 5, the thermograms collected in nitrogen for all HDPE samples show one

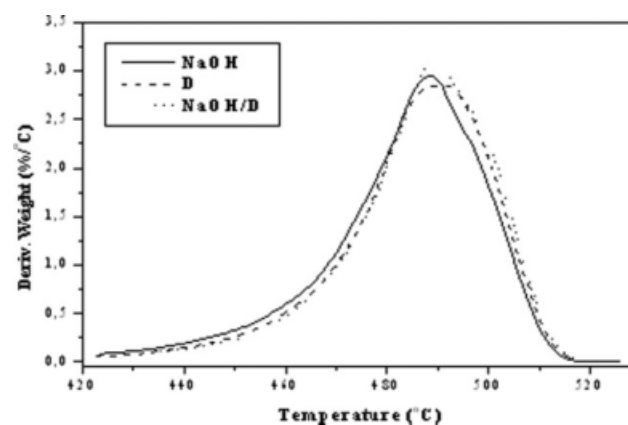


Figure 6 Derivative thermogravimetric curves of postconsumer HDPE samples treated in different cleaning solutions.

TABLE II
Thermal Properties of the Post-consumer HDPE Samples Measured by TGA, DTG, and DSC Analysis

HDPE sample	TGA		DTG		DSC		
	T_i (°C)	Residue (%)	T_p (°C)	T_m (°C)	ΔH_m (J/g)	X_c (%)	OIT (min.)
HDPE _{NaOH}	380.3	3.12	488.3	132.9	174.9	60.02	4.38
HDPE _D	395.5	3.86	489.3	134.7	182.8	63.25	8.14
HDPE _{NaOH/D}	390.1	1.47	491.0	132.9	174.9	60.02	5.76

decomposition step, between 380 and 490°C, which is due to the complete oxidation of the polymer.

On comparing the different HDPE samples, as expected, the initial decomposition temperatures (T_i) of HDPE_{NaOH} are shifted toward a lower temperature when compared with the other samples (HDPE_D and HDPE_{NaOH/D}). This may be due to the oxidative degradation of shorter molecules produced by the chain scission being more significant in HDPE samples treated with sodium hydroxide solutions, consistent with results for the rheological properties given earlier.

These results are also confirmed by the derivative thermogravimetric curves (DTG) shown in Figure 6. The presence of one peak (T_p) for each sample, characteristic of HDPE, is observed, where the peak temperature of HDPE_{NaOH} is lower than that of the other solutions. This may be due to a slight reduction in the molecular weight produced by oxidative degradation, indicating faster decomposition kinetics, displacing the peak to lower temperatures. The results of the TGA and DTG measurements can be better visualized in Table II.

The melting temperatures (T_m) of all samples, their enthalpy of fusion (ΔH_m) and crystallinity degree (X_c) obtained by DSC measurement are reported in Table II. There was no significant difference between the T_m values obtained, except for HDPE_D which had a value of 134.7°C for the second heating. This difference is more pronounced for the ΔH_m values of the samples.

The HDPE degree of crystallinity (ratio between the measured enthalpy of fusion and the value of 289 J/g¹⁵ reported in literature for 100% crystalline), also presented the same behavior as the T_m and ΔH_m results, which raises two hypotheses. First, the low crystallinity of HDPE_{NaOH} and HDPE_{NaOH/D} could be attributed to the creation of structural irregularity through the formation of short branches in the backbone chain and groups such as hydroxide, hydroperoxide, carbonyl, aliphatic vinyl, etc., which reduces the close packing ability of the polymer chains, and hence decreases the polymer crystallinity.²³ Second, the chemical nature of the D cleaning product (organic compounds such as salts of mono and polycarboxylic acids) could be acting as nucleating agents²⁸ in the HDPE_D, resulting in a high degree of crystallinity.

Also, measurements of the oxidation induction time (OIT) confirmed the reduction in the stability of the HDPE treated with NaOH solution when compared with the other samples. There was a decrease from 8.14 min (HDPE_D) to 4.38 min (HDPE_{NaOH}) as shown in Table II.

These results, clearly seen in Figure 7, indicate that the NaOH solution and washing conditions used (wash time, mixing speed, and drying with hot air at 50°C for 24 h in an air circulation stove) exerted a strong effect on the HDPE oxidative degradation, due to the presence of functional groups, particularly on the polymer surface, created during the chemical treatment.

CONCLUSIONS

The extent of the degradation which occurs as a result of the cleaning of postconsumer HDPE was observed in this study. The modification of the molecular structure of postconsumer HDPE has a strong influence on its MFR and viscoelastic behavior. Results of the rheological analysis indicated an increase in the MFR and decrease in the viscosity of HDPE treated with NaOH.

The higher value of the carbonyl index and lower OIT of the HDPE treated with NaOH confirmed the results for the rheological properties. A significant source of this degradation is the possible generation of functional groups during the cleaning/drying

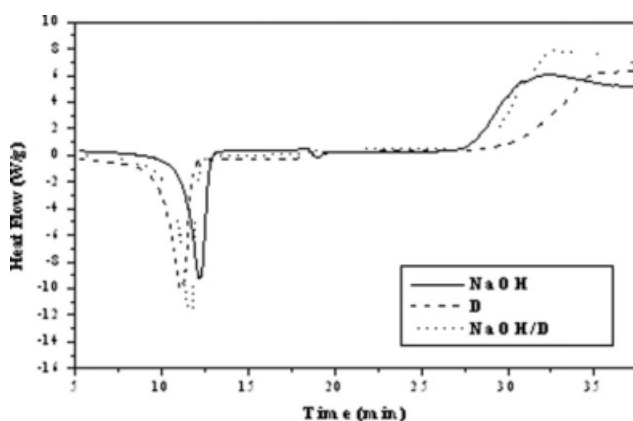


Figure 7 Isothermal curves of postconsumer HDPE treated in different solutions as a function of the time.

process where HDPE samples were submitted to oxidative, mechanical, and thermal degradation, due to the alkaline solution, mixing speed, and drying temperature, respectively. A low degree of thermal degradation was observed for the HDPE_{NaOH} sample, because the polymer was not submitted to high temperatures as it would be in normal processing.

Finally, all of the results obtained confirm that the HDPE degradation occurred through chain scission, characteristic of Ziegler-Natta-type HDPE.

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