Mechanical Degradation of Polypropylene Solutions Under Large Pressure Drops

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ABSTRACT: The degradation of polypropylene (PP), dissolved in *n*-alkanes at high temperatures and pressures, during the solution discharge to ambient conditions was experimentally studied. Molecular weight distributions (MWD) of the solubilized PP were measured by gel permeation chromatography. The MWD curves of PP obtained after discharge of the polymer solution shift to the low molecular weight side of the distribution and the polydispersity is reduced. In this work, a systematic study on the discharge products was performed to elucidate the degradation mechanism and the effects of temperature and concentration on this phenomenon. Initially, pure polymers, PP and polystyrene (PS) were studied varying the solution temperature. In a second stage, the effect of polymer concentration on chain scission was assessed using experiments on physical blends of PP/PS. In all cases, thermal and oxidative degradation were previously analyzed. Mechanical degradation was found to be the main chain scission mechanism. A negative linear functionality of the chain scission was found in both temperature and polymer concentration. To analyze the relationship between polymer degradation and molecular weight, the chain scission distribution function was calculated. On this basis, a critical molecular weight for the beginning of chain scission was obtained. This value is a function of temperature but remains constant with concentration. ©2007 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 45: 455–465, 2007

Keywords: chain scission; high shear stress; mechanical degradation; polypropylene

INTRODUCTION

The polypropylene (PP) chains have tertiary carbons very susceptible to oxidation and degradation. In the case of oxidative processes, the products formed depend on a variety of factors, including oxygen availability, impurities, residual catalyst form, radiation exposures, etc. The polymer degradation involves chain scission (particularly the unimolecular β-scission of tertiary carbon); consequently, both the average molecular weight ($\overline{M_w}$) and the molecular weight distribution (MWD) change. There are several causes of PP degradation and they could act by themselves or combined. Some of these are thermal actions, chemical agents additions (i.e. peroxides), applications of high shear strains, etc.[1,2]

In particular, mechanical degradation refers to the chemical process in which the activation energy of polymer chain scission is exceeded by the mechanical action on the polymer chain, causing a bond rupture to take place.[3] The processes that involve the mechanochemistry of commercial polymers are principally comminution, mixing, and extrusion. Polymer mechanical reactions can be induced purely by the storage

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Table 1. Characteristics of Different Mechanisms of Polymer Degradation Reactions[4]

	Mechanical	Thermal	Chemical
General effect	Highest molecular weights react	Broad range of effects	
Reaction products	Large chain segments, generally no monomer	Monomer and/or small chain fragments	
Reaction specificity	Moderate, related to mechanical and polymer properties	Depolymerization and/or decomposition	Highly specific
Reaction temperature coefficient	Negative	Positive	Positive

of elastic energy due to chain extension. However, in many cases, multiple-reaction mechanisms operate. For example, in polymer processing at elevated temperatures, competitive polymer reactions caused by heat and oxygen as well as mechanical forces may be involved. In this regard, Table 1 presents the principal characteristics of the more important polymer degradation reactions. From the point of view of the present study, it is useful to distinguish mechanochemical degradation reactions from other types of degradation. Shear forces can induce temporary (shear thinning) as well as permanent (molecular weight) changes in the viscoelasticity of polymer systems. Increasing the shear forces leads to the destruction of supermolecular structures through the disruption of molecular interactions of ever stronger inter- and intrachain forces. However, if shear forces are sufficient to store elastic energy equal to the strength of the main chain, bonds are distorted, bond angles and distances are extended, and the rupture of bonds takes place. The general process is thus one of sequential energy store, with mechanically induced reactions being the "highest gate," in electronic terminology, for the dissipation of elastic energy. In general, bond rupture in mechanochemistry takes place by homolytic cleavage with the fate of the generated radicals not always being known.[3]

The magnitude of the stored internal forces depends mainly on the degree of deformation and on the local molecular topology. Entangled chains may slip, extend, or rupture depending on the relaxation rates. In melts, disentanglement and degradation are competitive processes that depend on composition (entanglement density) and polymer bulk viscosity. This viscosity is a function of temperature and of polymer molecular weight, molecular weight distribution, and chemical structure (effective cross-section area of the polymer chain and presence of side groups). Chain scission generally takes place more readily at lower temperatures when a macromolecule is subjected to shear.[4]

If the process is carried out in a solution, the mechanochemistry can also be influenced by the polymer concentration and the nature of the solvent medium. The rupture of chains is followed by structural changes such as molecular weight reduction, molecular weight distribution change, branching, crosslinking, and new functional group formation.[4] However, for PP, the most common rupture mechanism is β-cleavage, which modifies average molecular weight and molecular weight distribution.[5]

In a previous work,[6] a selective separation of PP/polystyrene (PS) blends was carried out by using n-pentane at high pressure and high temperature. In this process, the PP dissolved was collected by rapid expansion of the superheated n-alkane throughout a narrow valve (diameter $\approx$ 0.2 mm). The pressure drop in the valve was about 30 MPa. When the soluble fraction was analyzed by gel permeation chromatography (GPC), a diminution of the $\overline{M}_w$ and changes in MWD were observed. Taking into account the high levels of shear rate and temperature to which the polymer is exposed during discharge, mechanical degradation could be the cause of the $\overline{M}_w$ reduction.

In the present work, a systematic study on the discharge products was performed to elucidate the kind of degradation that had taken place and the effects of temperature and concentration on chain scission. Initially, pure polymers (PP and PS) were studied varying the solution temperature. Subsequently, the effect of polymer concentration on degradation was assessed using experiments on physical blends of PP/PS. In all of the cases, thermal and oxidative degradation were previously analyzed.

BACKGROUND AND THEORY

In degradation processes, there are molecular weight averages ($\overline{M_w}$) and MWD changes. In general terms, if the degradation is carried out by chain scission the curve shifts towards the lower molecular weight side. The curve shifts to the higher molecular weight side when the degradation proceeds through crosslinking. Because of the presence of hydrogen linked to a tertiary carbon in the backbone chain, PP degrades mainly by β-chain scission with an overall shift of the molecular weight distribution curve towards lower values.[7]

As explained in the introduction, when sufficient energy is concentrated in a portion of the polymer chain, mechanical rupture of primary bonds takes place with the consequent release of the stress of broken fragments. These stresses are related to the entanglements, viscosity, and shear rate. The tension exerted (F_0) on the chains depends on these factors according to the Bueche theory,[8] through eq 1

$$F_0 \simeq \left(\frac{\eta \dot{\gamma}}{\rho}\right) M_e^{1/2} \tag{1}$$

where η is the viscosity, $\dot{\gamma}$ is the shear rate, ρ is the density, and M_e is the molecular weight between entanglements.

A very interesting and useful method for degradation analysis was developed by Canevarolo.[7] He studied the melt degradation of PP during multiple extrusions and proposed the use of a chain scission distribution function (CSDF) to follow the polymer degradation. His methodology allows for a better understanding of the relationship between polymer molecular weight and chain scission probability. One of the conventional ways to analyze polymer degradation has been to calculate the average number of chain scissions (n_s) that occurred during the polymer thermal history. It is a single and average value, obtained from the ratio between the initial $\overline{M_{n_o}}$ and final $\overline{M_n}$ number–average molecular weight as given in eq 2

$$n_s = \frac{\overline{M_{n_0}}}{\overline{M_n}} - 1. \tag{2}$$

If the probability of scissioning of a chain could increase by shearing during mechanical degradation as the length of chains increase (higher amounts of entanglements), the average value n_s would not be enough to characterize the whole spectrum. Starting from this conclusion, this author extended the number average of chain scission n_s (a single value) to a complete CSDF curve. Equation 2 can schematically be extended to eq 3 as:

$$N_S = \frac{\mathrm{MWD_i}}{\mathrm{MWD_f}} - 1 \tag{3}$$

where the original average values were substituted by the whole initial ($\mathrm{MWD_i}$) and final ($\mathrm{MWD_f}$) molecular weight distribution curves, before and after degradation, to calculate the distribution number of chain scission.

To calculate the N_S, a correlation rule between each pair of values of $\mathrm{MWD_i}$ and final $\mathrm{MWD_f}$ must be set. For this purpose, a three-step procedure is applied. First, the curves are calibrated to obtain the same area under the each curve (same polymer concentration injected). Second, the magnitude (intensity) of each point of the distribution curve $d_w/(\log(M_w))$ is linearly shifted so that both curves have the same maximum value. Finally, in the correlation rule, two points were considered corresponding when they are at the same side in each curve and have the same intensity. The CSDF was defined as eq 4:

$$\mathrm{CSDF} = \log\,(N_s + 1). \tag{4}$$

In this work, the methodology proposed by Canevarolo was used to study the polymer degradation during the discharge of the separation process. The CSDF for the samples obtained was calculated from pure PP processed at different temperatures, and from PP/PS blends with diverse concentration of PP.

EXPERIMENTAL

Materials

Polystyrene Lustrex HH-103 ($\overline{M_w}$: 270600 g/mol, $\overline{M_n}$: 136000 g/mol), and polypropylene (PP) Cuyolen 1102 HX ($\overline{M_w}$: 345500 g/mol and $\overline{M_n}$: 69800 g/mol) were used as base commodity materials for blending. n-Pentane (T_c: 196.5°C, P_c: 33.7 bar) was the solvent, with purity higher than 99 wt %.

Blending

Blending was performed under nitrogen atmosphere, in a polymer batch mixer (Brabender Plastograph W50) at 190°C and 60 rpm for 24 min. The mixing procedure included the initial softening of polystyrene (PS) and subsequent incorporation of PP. Also, pure PP was subjected to the same process. The relative content of each polymer was varied to obtain physical blends. All blends prepared are summarized in Table 2.

Extraction Procedure

A polymer sample of about 30 mg in film form (0.7 mm of thickness) was confined in a holder with a Teflon microporous filter (porous diameter minor than 0.2 μm), and was introduced into a stainless steel 316 cylinder of about 10 cm^3 (full volume) as explained in detail in a previous work.[6] The cylinder was pressurized up to 30 MPa and heated to the desired temperature (T_f). The extraction time was 3 h, and the soluble fractions were collected by rapid expansion of the superheated *n*-alkane. Both samples, soluble fractions (SF) and insoluble fractions (IF), were collected and analyzed. The experimental extraction cell is illustrated in Figure 1. The mass solubilized was determined by gravimetric analysis.

Two kinds of experiments were performed. Initially, PP degradation was studied on a wide range of temperatures (from 120 to 220°C), following the procedure explained earlier. It was determined that the entire PP sample was solubilized at temperatures higher than 150°C (temperature where the PP is melted). PS was completely insoluble with *n*-pentane at this temperature range.[6] From these results, the experimental conditions to carry out the PP/PS blend separation were chosen. In this way, the polymer blend separation was performed at $T_f = 180°C$ in *n*-pentane, following the same procedure, varying the PP content in the PP/PS blends.

Table 2. Physical Blends Prepared

Blend	PP (wt %)
PB 05/95	5
PB 15/85	15
PB 25/75	25
PB 40/60	40
PB 50/50	50
PB 65/35	65
PB 80/20	80
PB 95/05	95

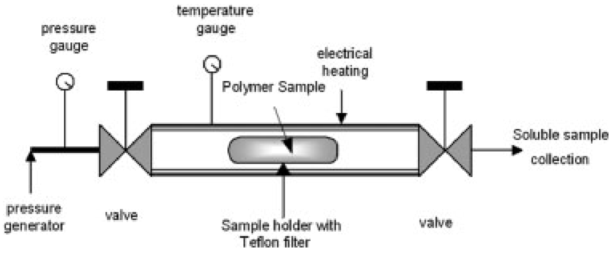

Figure 1. Schematic diagram of the experimental equipment used to perform high pressure–high temperature solvent extractions.

Characterization

Gel Permeation Chromatography

Gel permeation chromatography (GPC) chromatograms of virgin and processed PP, and all the extracted fractions and residues were obtained in a Waters Science Chromatograph, model 150-CV. The different samples were dissolved in 1,2,4 trichlorobenzene using 0.0125 wt % butylhydroxytoluene (BHT) as antioxidant, at the same initial concentration, and then injected at 135°C. The measurement was done in duplicate and sequentially to reduce the effect of changing the calibration curve. Furthermore, the measurements were repeated twice for each sample. Molecular weight distributions (MWD) were assessed by using the Millenium software. From this, the average molecular weights, number-based $\overline{M}_n$, weight-based $\overline{M}_w$, and polydispersity index ($PDI = \overline{M}_w/\overline{M}_n$) were calculated.

Scanning Electron Microscopy

Micrographs on physical blends, fractured under liquid nitrogen, were obtained. The electron microscope used was a JEOL JSM-35 CF equipped with secondary electron detection. The samples were coated with Au in a sputter coater PELCO 91000. Analysis PRO^{TM} software was used for processing the particle size data.

Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) spectroscopy was used to analyze the possible oxidative polymer degradation and to quantify the relative polymer contents in blends. The typical carbonyl region oxidative absorption peak, at about 1700 cm^{-1}, was followed on all the samples.

Table 3. $\overline{M_n}$, $\overline{M_w}$, and Polydispersity Index of Soluble PP at Different Temperatures

Sample	$\overline{M_n}$ (g/mol)	$\overline{M_w}$ (g/mol)	PDI
Virgin PP	69800	345500	4.9
PP 140°C	58600	160600	2.7
PP 160°C	70200	169000	2.4
PP 180°C	64400	185300	2.9
PP 200°C	69400	192300	2.8
PP 220°C	72800	210700	2.9

RESULTS AND DISCUSSIONS

Chain scission during discharge process was studied along with a wide range of solutions temperatures and PP concentrations, following changes either in average molecular weight or in MWD. Results of PP MWD, both for a solution of pure PP and for a soluble phase of a physical blend (with 80% of PP), in comparison with virgin PP are shown in Figure 2. The experiments were performed at 180°C following the procedure explained in the Experimental section. A shift to lower molecular weight with respect to the virgin PP can be observed in the last two samples. This shifting occurs on the entire curve in solubilized PP from PP/PS blends. But in the pure PP samples, only a reduction of M_w is observed in the zone of higher molecular weight. Both soluble PP curves show a narrowing of the M_w spectrum (lower PDI). It is clear that the PP molecules are shorter after the process. A complete characterization on all the samples analyzed is shown in Tables 3 and 4. These tables summarized the $\overline{M_n}$, $\overline{M_w}$, and PDI for pure PP solubilized at different temperatures (Table 3), and for soluble fractions of physical blends with different PP concentrations (Table 4).

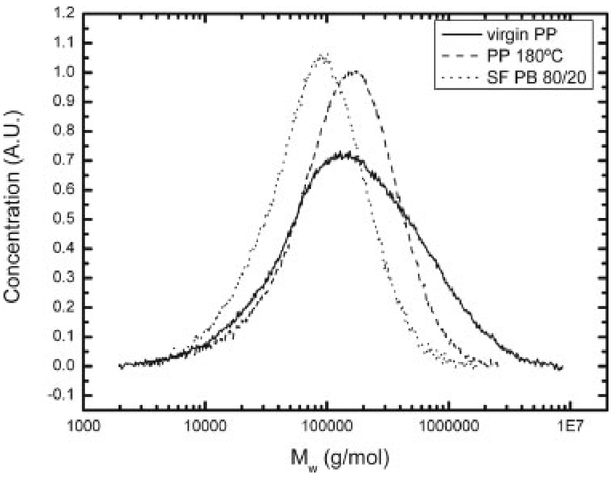

Figure 2. GPC chromatogram of the soluble phase of pure PP extraction at 180°C and soluble fraction of PB 80/20 in comparison with the GPC chromatogram of virgin PP.

In the experiments performed on pure PP at different temperatures, all the PP mass was solubilized at temperatures above 150°C. This fact was verified by gravimetric analysis. In this sense, the data in Table 3 show changes in $\overline{M_w}$ and PDI with respect to the virgin PP. The $\overline{M_w}$ also changes with the temperature used in the experiment. However, the $\overline{M_n}$ values remain almost constant for all the temperatures analyzed and match with those of virgin PP. In the case of solubilization of the PP phase from physical blends with different concentrations, the changes are either in $\overline{M_n}$ as in $\overline{M_w}$ and PDI (Table 4).

To analyze the mechanism of degradation suffered by PP during the separation experiments, a systematic study of different variables influencing the PP degradation was performed. The first step was the determination of the existence of oxidative reactions by checking the presence of carbonyl group by FTIR. No oxidation peak (1700 cm^{-1}) appears in the spectra of all samples prepared, evidencing the absence of oxidative reactions during the discharge process.

The other variable analyzed was the pressure–temperature combination effect during the

Table 4. $\overline{M_n}$, $\overline{M_w}$, and Polydispersity Index of Soluble Fractions of Physical Blends

Sample	$\overline{M_n}$ (g/mol)	$\overline{M_w}$ (g/mol)	PDI
SF PB 15/85	54300	94800	1.7
SF PB 40/60	35600	93200	2.6
SF PB 50/50	49100	108000	2.2
SF PB 65/35	47600	110200	2.3
SF PB 80/20	49700	118400	2.4
SF PB 95/05	36600	117300	3.2
SF PP 180°C	64400	185300	2.9

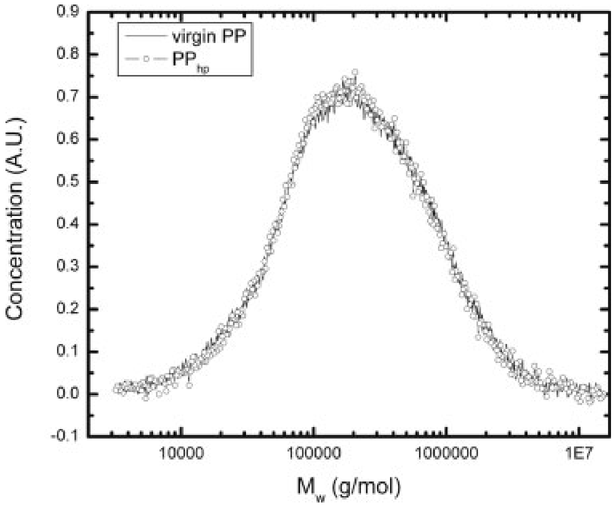

Figure 3. GPC chromatogram of pure PP subjected to high pressure–high temperature solubilization and without discharge process (PP$_{hp}$) in comparison with the GPC chromatogram of virgin PP.

solubilization process. In this regard, samples of pure PP were subjected to the high pressure–high temperature process during the same time and after that, the camera was depressurized and cooled to room temperature. The PP became insoluble under these conditions and a sample of it was analyzed by GPC. Figure 3 shows the chromatogram of this sample and that of virgin PP. The match between both curves is evident, demonstrating that the degradation that occurs after the discharge process is not due to the high pressure–high temperature combination used during the solubilization process.

Excluding the effects of thermal degradation and oxidation, the present work assumes that mechanical degradation is a reasonable mechanism to explain the chain scission that takes place during the discharge process. This assumption is also based on the results found by other authors. Several studies show that mechanical degradation is present in the flow of polymer solutions[2,9–11] when a shear field is applied.

In the case under study, the polymer solution flows through a capillary tube subject to a high pressure and temperature drops. The discharge tube has ~0.2 mm of diameter and 1 mm of length (L/D = 5) and the pressure drop is of 29.9 MPa. Because of this, a very high wall shear stress (τ_w) in flow process can be estimated ($\cong$15 MPa).[12] The polymer solutions are subjected to this high strain rate and this is the main cause of the chain rupture. Yu et al.[10] found that diluted polystyrene and polyisobutylene solutions with similar concentrations and molecular weight ($\overline{M}_w$) suffer from mechanical degradations even with stresses as low as 4×10^{-3} MPa.

Temperature Effect

The effect of temperature on mechanical degradation of pure PP during the polymer solution discharge process can be understood if mechanical degradation is considered as the only source of chain scission. Even if the influence of temperature on mechanochemistry is accepted, it may act in a variety of ways. The main effects include changes in the physical state of the polymer, in the flow properties (viscoelasticity and viscosity), and in the mechanism of bond rupture in polymer chain. First, temperature determines the polymer state, that is, whether it is predominantly glassy, crystalline, elastic, or fluid. The effect of temperature of a polymer system depends on composition and molecular weight. The softening of a polymer system with temperature results in lower stress and a lower rate of energy input at a given shear rate. In consequence, there is a reduction in chain rupture and an increase in the critical molecular weight (M_{W_c}). This value represents the molecular weight from which the degradation takes place. At lower temperatures, thermal motions are reduced, relaxation processes are slower, and chain disentangling processes are longer. As a result of these features, the extent and reaction rate for mechanochemistry are generally higher. In fact, a negative temperature coefficient is a prime criterion of the existence of a mechanical reaction. This has been experimentally confirmed by many researchers for a variety of reaction conditions, polymers, and instruments.[4]

In the case under study, the mechanochemistry of the degradation can be analyzed by following the molecular weight change of the solubilized PP with respect to the virgin PP at a given temperature ($\Delta\overline{M}_w = M_w^{\mathrm{virginPP}} - M_w^{\mathrm{Ti}}$). The $\Delta\overline{M}_w$ parameter allows following the degree of chain scission. For temperatures higher than the melt temperature of PP,[6] these values show a linear negative variation with temperature (Fig. 4). As explained earlier, the negative coefficient of variation with temperature confirms the mechanical

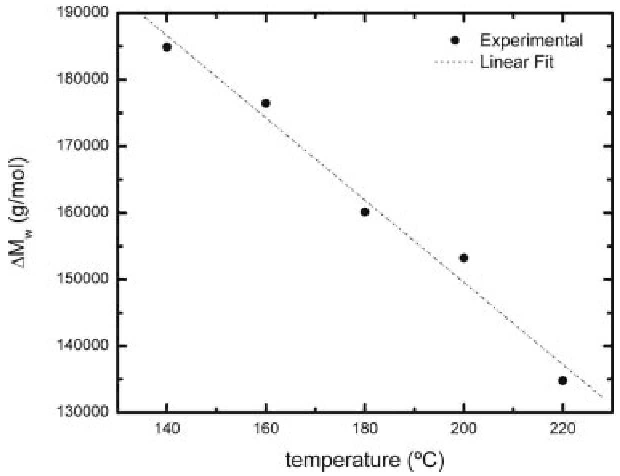

Figure 4. Polypropylene molecular weight diminution with the extraction temperature.

reaction. The equation fitting the variation of the $\Delta\overline{M_w}$ with temperature is as follows:

$$\Delta\overline{M_w}\ (\mathrm{g/mol}) = -617T(^\circ\mathrm{C}) + 273000. \qquad (5)$$

The Bueche relation between the tension exerted (F_0) on the chains and the viscosity, density, and M_e (eq 1) gives a phenomenological reason for understanding the effect of the temperature on the scission. For polymer solutions, the effect of temperature on viscosity (η) can be described with Andrade's equation:[13]

$$\eta = B\exp(E_\eta/RT) \qquad (6)$$

where B is a constant, E_η is the activation energy of viscous flow, R is the gas constant, and T is a temperature. High temperatures result in lower polymer solution viscosity. Further increments in temperature result in a relatively large decrease in viscosity. The changes in ρ and M_e are less important. Consequently, a decrease in temperature causes an increment in tension exerted (F_0) on the chains, and then, the final molecular weight of the degraded material is lower. Therefore, an increase in temperature at constant stress causes an opposite dependence with respect to chemical reactions, that is, the thermal coefficient (used to measure the activation energy) is negative.

Solution Concentration Effect

The PP solutions were obtained from PP/PS physical blends with different relative contents. In this regard, the blends have very different phase morphology depending on the PP/PS relative concentration. When PP is the major phase, very small particles of PS are dispersed in PP matrix. Most of the particles are spherical and homogeneously dispersed in the matrix. When the content of PS is greater than 50 wt %, the blend has a similar morphology but the particles are of PP and the matrix is PS. However, in the blends with around 50 wt % of PP, the morphology is very different. In these blends, phase cocontinuity is observed. Although only a few very small particles of one phase are dispersed in the other, in general, there are zones of one polymer and of the other. Figure 5 shows the morphology of three blends with different PP/PS contents obtained by SEM microphotographs of fracture surfaces. These differences in morphology influence the PP extraction and the blend separation, resulting in decreasing extraction efficiency with the increment of PS in the blend. The entire phase of PP was extracted in a 80/20 blend as well as in a 95/05 blend. As the fraction of PS in the blend increases, it is not possible to completely extract the PP fraction because there is a high mass transfer resistance to PP diffusion, and this polymer cannot diffuse totally throughout the PS phase. At an extraction temperature of 180°C, PS molecules are far above their glass transition temperature ($T_g = 105^\circ\mathrm{C}$), and they are only softened and swelled (not dissolved) by the hydrocarbon solvent. Therefore, when PS is in the continuous phase, it hinders the diffusion of the PP molecules. Nevertheless, the extraction efficiency is not so small, in the worst case (major PS concentration, PB15/85 blend), about 85% of the PP was extracted.[6]

The PP concentration in the solution depends on the blend concentration. Although the mass of the blend subject to extraction was kept constant in all the experiments, the mass of PP to be extracted varies with its proportion in the blend. Thus, a lower mass of PP in the blend increases the solvent/solute mass ratio. Figure 6 shows the molecular weight changes between the PP from the blend soluble phase with respect to the virgin PP ($\Delta\overline{M_w} = M_w^{\mathrm{virginPP}} - M_w^{\mathrm{Ci}}$) as a function of PP concentration in the blend. These experiments were performed at a constant temperature (180°C). The higher the PP concentration, the lower the chain scission. This tendency is almost linear and can be fitted with eq 7:

$$\Delta\overline{M_w}\ (\mathrm{g/mol}) = -343\mathrm{c} + 258000. \qquad (7)$$

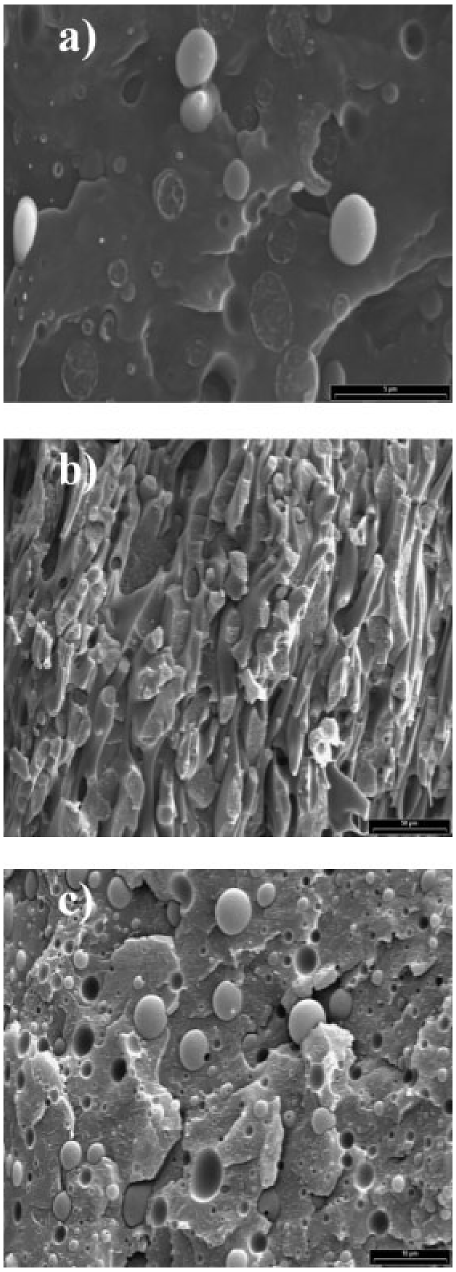

Figure 5. SEM micrographs of blends: (a) PB 80/20, (b) PB 50/50, and (c) PB 15/85.

It is important to note that, although the entire mass of PP was not extracted in the PB15/85 blend, the molecular weight of the mass extracted follows the general linear behavior.

Yu et al.[10] also observed degradation with negative concentration dependence for dilute polymer solutions. If the entanglements are the only factor involved in shear degradation, the degradation effectiveness should always show positive concentration dependence. Therefore, there must be some other factors besides entanglements involved in shear degradation. "Stretching" of the individual molecules could be one other factor involved since "stretching" has negative concentration dependence. At higher concentrations, molecular extensions are inhibited by surrounding molecules. Therefore, degradation is limited at higher concentrations. However, other authors have found no concentration dependence[14] and positive coefficients for shear degradation. No obvious trend of the effect of concentration on polymer degradation is apparent in these reports. These conflicting results could be explained by the coexistence of two competitive processes: molecular entanglements and inhibition of molecular extension by surrounding molecules. Depending on the experimental conditions, either process may be the dominant one. The conditions that determine which mechanism is dominant are polymer concentration, polymer nature, molecular weight, solvent-solute affinity, and type and intensity of the shear field.[10] The results in this work are in agreement with the reasons explained earlier and particularly with the results shown by Yu et al.,[10] who found a negative concentration dependence working with diluted polymer solutions in a thermodynamically good solvent.

In Figure 6, an important difference can be observed between the $\Delta\overline{M}_{\rm w}$ values of pure PP extracted at 180°C, and the soluble fractions of the blends processed at the same conditions (see also Fig. 2). The main difference between these samples is the thermomechanical history before the extraction. Pure PP samples were films of virgin PP prepared by compression

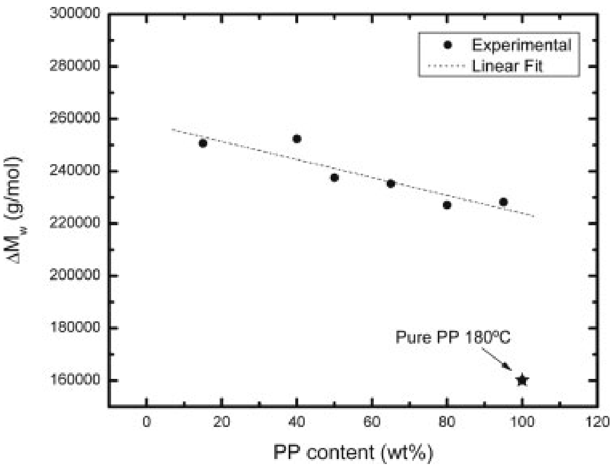

Figure 6. Polypropylene molecular weight diminution with the content of PP in the blend extracted.

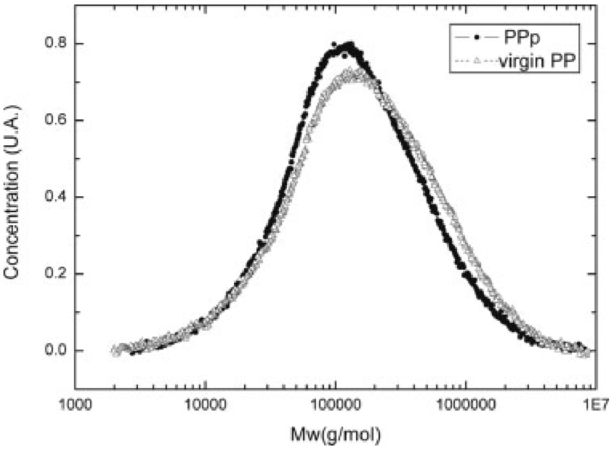

Figure 7. GPC chromatogram of the processed PP (PP_p) compared with that of virgin PP.

(180°C, 5 min). Blend samples were also compressed films prepared at the same conditions as pure PP. However, the blends were previously processed in a polymer batch mixer. This processing could induce a preliminary degradation, which could be thermal or mechanical in nature. To verify this hypothesis, pure PP was processed under the same conditions of the blends and its MWD was measured. The results are shown in Figure 7 in comparison with pure PP. It is clear that, although the "blend" process was performed under nitrogen atmosphere, thermal scission is present. The final molecular weight averages are $\overline{M}_w$ = 295,000 g/mol and $\overline{M}_n$ = 66,900 g/mol and the PDI = 4.4, which are lesser than the initial values.

The $\Delta\overline{M}_w$ values, for blends in Figure 6, were recalculated using the $\overline{M}_w$ of processed PP and the results are shown in Figure 8. These results correlate very well with the $\Delta\overline{M}_w$ value for PP at 180°C. The last data give additional evidence that also in the blends separation the cause of the decrease in the PP molecular weight is the high shear deformation during the discharge process.

Chain Scission Distribution Function

The chain scission distribution function (CSDF) curve can represent the average number of chains cleaved in each molecular weight fraction of the initial polymer. Figure 9 shows CSDF curves calculated for pure PP extracted at different temperatures. From these data, some observations can be made. First, the mechanical degradation of PP is only due to chain scission (CSDF > 0). Second, the occurrence of negative values in the low molecular weight region, as well as the scattered data at very low and very high molecular weights, should be taken with care because the low concentration of chains in these regions increases the uncertainty of the calculations. Furthermore, degradation is not present (CSDF = 0) in the range of low molecular weight up to a critical value called M_{W_c}. From this value, it becomes a preferential process dependent on the M_w (slope > 0). Longer chains are more prone to entanglements and so chains with molecular weight above a critical value ($M_w > M_{W_c}$) show a greater probability of being cleaved due to the ease of coupling of shear energy to the highly viscous solution.[15]

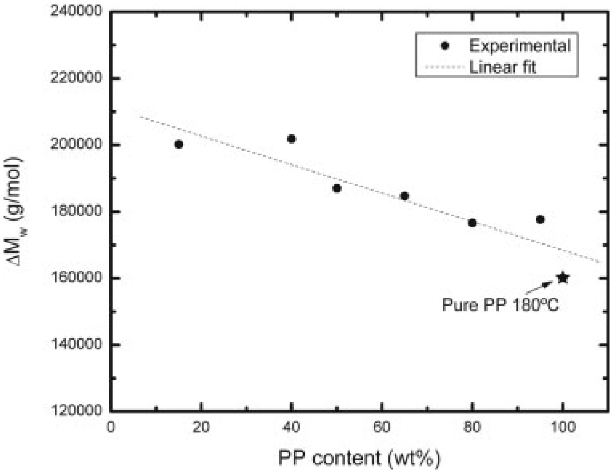

Figure 8. Polypropylene molecular weight diminution with the content of PP in the blend extracted, with respect to that of processed PP.

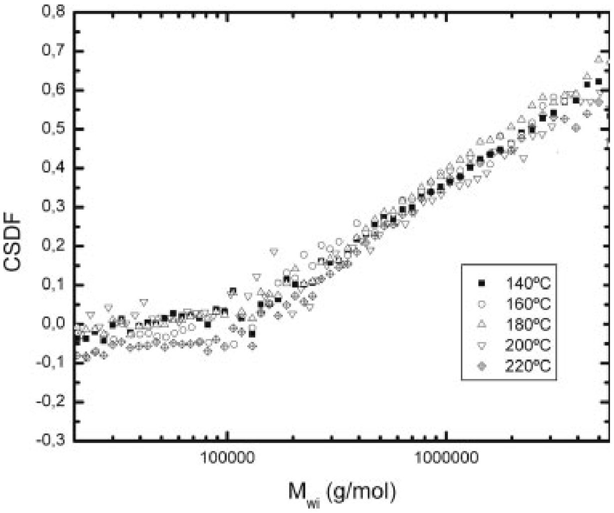

Figure 9. CSDF curves for soluble PP obtained at different temperatures.

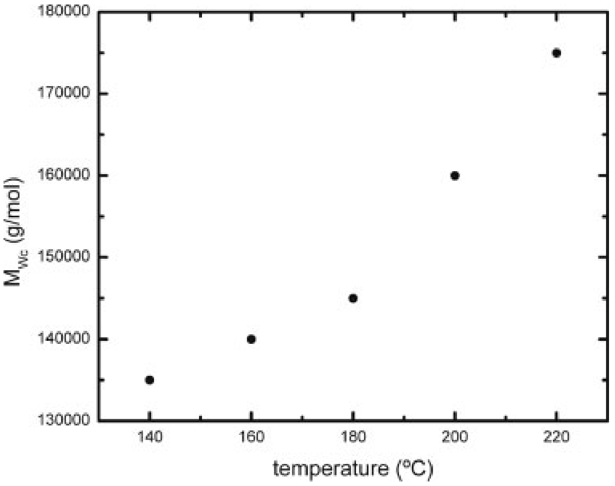

Figure 10. M_{W_c} observed at different temperatures.

The effect of temperature cannot be appreciated from the general form of this curve due to data superposition. The slopes of the CSDF are similar for all the temperature ranges but the values of M_{W_c} increase with the temperature as shown in Figure 10. For a given molecule with $M_w > M_{W_c}$, the chain scission (measured by CSDF) is similar for all the temperatures analyzed (the curves are superposed). Nevertheless, at higher temperatures, the molecules' cleavage is carried out over bigger molecules, providing differences in the MWD. The molecules affected by chain scission decrease as the temperature increases. As a consequence, the final $\overline{M}_w$ increases with temperature.

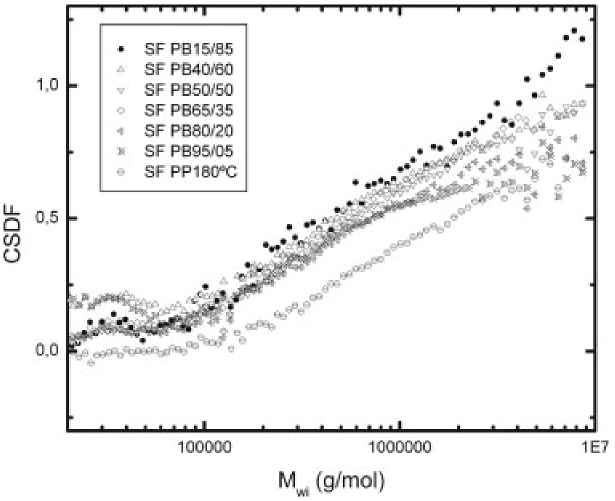

Figure 11. CSDF curves for soluble fractions obtained from physical blends with different content of PP.

Table 5. M_{W_c} Observed for Soluble Fractions of Physical Blends

Sample	M_{W_c} (g/mol)
SF PB 15/85	105000
SF PB 40/60	108000
SF PB 50/50	113000
SF PB 65/35	111000
SF PB 80/20	111000
SF PB 95/05	106000
SF PP 180°C	145000

The CSDFs for the soluble fractions obtained from the separation of the physical blends are shown in Figure 11. Degradation is observed in the low molecular weight region because CSDF is positive. This degradation process seems to be random (slope $\cong$ 0) up to the critical value M_{W_c}. In this case, M_{W_c} represents the value at which the degradation under study took place. The selective chain scission process of molecules with $M_w > M_{W_c}$ begins at this value. This process seems to be similar in all the blends' soluble phases, because both the slope and the M_{W_c} values (listed in Table 5) are similar. The deviations from slope zero in some samples in the first region ($M_w < M_{W_c}$) are due to the increment in short fragments generated by the preferential scission of the longest chains.

Furthermore, we can observe that the scission for all soluble fractions obtained is higher than the scission observed for the pure PP processed at the same temperature. In particular, scission is observed in the low molecular weight region, in zones, where the pure PP does not suffer degradation. This observation agrees with the conclusion obtained in the analysis of the $\Delta\overline{M}_w$, and also indicates the possibility of a previous degradation in the blend process (Fig. 7).

The effect of blend composition on polymer degradation explained earlier is observed by shifts to lower values of CSDF at a molecular weight when the content of PP in the blend decreases. However, the M_{W_c} observed for all blends were similar and lower than that of the M_{W_c} observed in the pure PP processed at the same temperature (180°C). These values are shown in Table 5.

CONCLUSIONS

Pure PP and PP phases from PP/PS blends solubilized in *n*-pentane at high pressure and high temperature degrade during the discharge process. In the present work, a systematic analysis of the chain scissions process led to the following conclusions:

- The consequence of the degradation process was always a chain scission. No oxidative reactions were detected.
- The main degradation mechanism is mechanical cleavage due to the high shear rates during the discharge process.
- The high pressure–high temperature combination effect during the solubilization process does not produce any kind of degradation.
- The chain scission linearly decreases as solution temperature increases because of the decrease in solution viscosity.
- The degradation linearly decreases with higher content of PP in the blend (increment in solution concentration). The negative concentration effect can be explained by the "stretching" of the individual molecules. At higher concentrations, molecular extensions are inhibited by surrounding molecules.
- The $\mathrm{M}_{\mathrm{W}_c}$ for all the samples is determined by CSDF. It changes with solution temperature but remains constant with concentration.
- The degradation is hardly dependent on the molecular weight. All samples show positive slope of the CSDF from $\mathrm{M}_{\mathrm{W}_c}$.
- No degradation occurs for pure PP when $M_w < \mathrm{M}_{\mathrm{W}_c}$. However, random degradation occurs for blends in the same region.

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