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Study of the degradation mechanisms of polyethylene during reprocessing

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ABSTRACT

The present work aims at evaluating the behaviour of various grades of high and low density polyethylene subjected to continuous injection moulding operations. It is based on a wide range of experimental techniques that allowed the establishment of relationships between the observed property changes and the structural modifications developed in the polymers. The study confirmed the coexistence of two distinct degradation mechanisms, crosslinking and chain scission, that occur due to thermo-oxidative reactions arising during the different injection moulding stages. The relative importance of these two mechanisms depends on the material structure and on the processing conditions used. It was also possible to confirm that the polyethylenes with lower molecular mass show low sensitivity to degradation during reprocessing. Furthermore, the more branched polymers (as is the case of LDPE) also proved to be less sensitive to thermo-degradation phenomena. Overall, it was concluded that the primary recycling of polyethylene, if performed under well controlled conditions, will lead to only minor material property losses.

1. Introduction

Waste production has been increasing worldwide, owing to changes in economic activity, demography, technological innovation and production and consumption patterns. Due to their ubiquity and specific properties, plastics waste, namely from used packaging, has suffered most of the criticisms addressed to this environmental problem. Recent European legislation has stressed the need to solve it on the basis of a hierarchy of solutions [1]. Material recycling ranks high on that hierarchy. In particular, primary recycling seems to be an obvious answer to environmental concerns. Primary recycling of thermoplastics is done in industry using standard processing operations, and homogeneous, non-contaminated scrap to fabricate parts with properties similar to those of the products from which it is obtained [2]. The scrap is usually continuously introduced in the feed and replaces the equivalent amount of virgin polymer. Consequently, this process, often called reprocessing, is not only environmentally desirable, but also economically advantageous. This fact has been recognized and studied for more than 40 years. It is probably interesting to point out that the same ideas have been repeated many times over throughout these years: "As a result of rising material costs, plastics recycling is at present not only of great concern to the people involved in energy conservation programs but also to processors" [3]. The critical limitation to unrestrained use of primary recycling was, and is, the need to maintain the polymer properties above a minimum threshold. This limitation was often the object of the earlier reprocessing studies [3–8], some of which proposed algorithms to predict that minimum threshold [3,5,8]. These initial studies were mainly focused on more costly engineering polymers, such as polycarbonate. Due to its amorphous nature and generally interesting properties, namely high transparency and impact resistance, probably more primary recycling studies have been dedicated to polycarbonate than to any other polymer. A recent publication presents a short but rather comprehensive review of these studies [9].

Another thermoplastic whose reprocessing has been often studied is polyethylene, a semi-crystalline polymer with various isomeric forms. This was to be expected, as polyethylene is the most consumed general purpose polymer, prevalent in the packaging sector and is easy to reprocess. Earlier studies were dedicated to its degradation on reprocessing, and focused on the effect of specific stabilizers [10,11]. Often these studies covered different grades of polyethylene and polyolefins in general, and aimed at predicting the minimum amount of the virgin polymer that must be added to the feed in order to prevent significant loss of properties [12]. As polyethylene is relatively stable and industrial processing conditions are always optimized, degradation effects are frequently only significant after a minimum number of reprocessing cycles. This

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effect was confirmed in a study of high density polyethylene, polypropylene and HDPE/PP blends, which also found that the degradation increased with the severity of the successive processing conditions [13]. A significant amount of research has been devoted to the numerous functional groups generated under processing and reprocessing of polyethylene and their effect on the properties changes. In a series of studies, many of those groups formed on melt processing of LDPE in an open mixer were identified [14]. In some cases, rotational rheometry was found to be an extremely sensitive technique to detect those changes, namely the variation of the molecular mass and its distribution [15]. Other techniques commonly used in reprocessing studies are MFI measurements [6], tensile and impact tests and fibre length determination [12], as well as assessment of the oxidation induction time via chemiluminescence experiments [16].

The identification of the prevailing degradation mechanism during the reprocessing of polyethylene was also the object of many studies. An early investigation on a Phillips-based HDPE, compared the variation of the molecular weight distribution and the extrudate swell of the polymer as received and after three extrusion cycles at 240 °C [17]. At the time it was suggested that the successive extrusion processes caused preferential chain scission of the higher molecular weight fractions. A later study of reprocessing via multiple extrusions indicated that the main cause of properties loss in unstabilized Phillips HDPE (Cr-catalysts) was crosslinking, whereas that of unstabilized Ziegler HDPE (Ti-catalysts) was chain scission [10]. Although conflicting with the previous results, this investigation showed the importance that the remaining polymerization catalyst has on the reactions occurring during processing. A study of the effect of multiple extrusions on the properties of virgin homopolymer, virgin copolymer, natural post-consumer, and mixed colour post-consumer HDPE helped to clarify this problem [18]. It was possible to conclude by means of rheological, extrudate swell and sag measurements that the dominant degradation mechanism in the homopolymer was crosslinking and in the copolymer was chain scission. The polydispersity always decreased with reprocessing, the effect being less pronounced with the latter polymer. Thus, adding to the effect of residual components in the resin, the primary polymerization process also plays a role in determining the controlling degradation reactions. Another study of post-consumer HDPE also found that the polymer displayed crosslinking when reprocessed, indicating the need for stabilization to keep adequate properties [13]. However, an investigation that compared the behaviour on successive extrusions of high-density and low-density polyethylene, with and without stabilizers, concluded that the dominant mechanisms were chain scission for HDPE and chain branching and crosslinking for LDPE [19]. The tensile properties decreased for both but could be retained with the proper stabilizers, namely for LDPE. Supporting evidence for the prevalence of the chain scission mechanism for two types of HDPE, Phillips and Ziegler-Natta, was published shortly after [20]. The mechanical and thermo-oxidative degradation was measured in a twin-screw extruder using various processing conditions. The degradation begins with chain scission of the longer chains due to the higher probability of entanglements. Shorter chains are more mobile, and graft the macro-radicals formed in the melt, increasing the molecular weight via chain branching. Higher temperature profiles intensify these effects. The final result is the reduction of both longer and shorter chains, narrowing the polydispersity and increasing the average molecular weight.

The effect of the polymer structure on the prevalent degradation mechanism was further investigated by single pass injection moulding of HDPE [21]. Again it was reported that crosslinking and possibly chain extension did occur and the effect increased with increasing temperature. To explain this large body of apparently conflicting evidence, it has to be admitted that not only residual components and the primary polymerization process play a role, but also that the (re)processing conditions can determine the main degradation reactions. In fact, a recent publication on the structural changes occurring during HDPE processing concluded that when the operational conditions promote scarce mobility of the macromolecular chains, branching is more favoured than chain scission. When the mobility of the chain increases, scission becomes progressively more important [22]. However in both cases, no crosslinking was detected. As heat, shear, and oxygen are the main initiators for the degradation reactions, it is obvious that the extent of their relative influence will largely depend on the operational conditions. It is also clear that more data is still needed to have a clear picture of this subject.

The mechanical properties of any polymer are a critical determining factor of its industrial applications. Thus, since the earliest published works, many primary recycling studies have focused on these properties, namely in their variation with multiple processing (for instance [6]). In the case of polyethylene, it was reported that the tensile and impact strengths of both LDPE and HDPE decreased exponentially with reprocessing [13]. In one of the aforementioned investigations a re-melting - stabilization technique was applied for the recycling of yellow-pigmented HDPE bottle crates. After multiple extrusion cycles of the stabilized and non-stabilized material both the tensile impact strength and the tensile strength of the non-stabilized HDPE increased significantly [11]. On the other hand, an investigation of the reprocessing of greenhouse films, virgin and recycled, showed that the elongation-at-break decreased with the number of cycles but the tensile strength much less so. In any case, the loss of properties of the latter film was much more pronounced than that of the former [23]. Other study reports that the stress-at-break increased and the strain-at-break decreased with the number of extrusion cycles [19]. In the same study, the tensile Young modulus increased with the number of extrusion cycles (for HDPE, since the first cycle; for LDPE only after the fourth cycle).

It is obvious that the changes in mechanical properties of polyethylene with reprocessing are the direct reflection of the changes in the polymer structure. If crosslinking reactions predominate, then the polymer becomes a harder and stiffer material, displaying an increase in modulus and a decrease in elongation-at-break. The opposite will happen when scission reactions predominate. When no clear trend is detected, either the two types of reaction cancel each other or possibly a third mechanism is controlling the process. Consequently the measured properties will depend on all the factors that determine these reactions, that is, the type and degree of ramifications, the processing conditions, the polymerization residues and stabilizers present. This means that it is practically impossible to derive general principles to relate the reprocessing conditions to the final properties of the recycled polyethylene. Instead, reprocessing – structure–properties relationships will have to be obtained for each specific situation.

The present study aims at elucidating the relative importance of the two distinct degradation mechanisms, crosslinking and chain scission, that occur during reprocessing of polyethylene. By studying different polymer types, with distinct structures, it may be possible to ascertain in what way they influence the resulting properties losses. Finally, an attempt is made to establish relationships between the mechanical properties of the polymers and the structural changes prevailing under the reprocessing conditions used.

2. Experimental procedure

2.1. Materials and methods

The characteristics of the six polyethylenes studied are presented in Table 1. All the polymers, except the recycled one, were

Table 1
Characteristics of the polyethylenes studied.[a]

Type	Commercial name	Reference	Density		Melt flow index (g/10min)	Crystallinity (%)	End-use
			Measured	Supplier			
HDPE	Stamylan 7731	HDPE 7731	0.9524	0.952	0.023	47.7	Blow-moulding
HDPE	Stamylan 7625	HDPE 7625	0.9468	0.954	0.154	54.2	Blow-moulding
HDPE	Stamylan 3H634	HDPE 3H634	0.9486	–	0.387	55.4	Injection
HDPE	Stamylan 9089U	HDPE 9089U	0.9567	0.963	6.789	63.6	Injection
HDPE	–	Recycled HDPE	–	–	0.064	40.8	–
LDPE	Stamylan 2304	LDPE 2304	0.9290	–	3.792	24.0	Injection

[a] All values were determined experimentally; for the density those provided by the supplier are also shown.

supplied by DSM (currently SABIC, Saudi Basic Industries Corporation).

The selection of the polymers was based on the following criteria: a) the four HDPE were chosen so that their molecular weights would cover the range used in most commercial applications; b) LDPE was chosen in order to study the effect of the larger number of side chains that lead to a lower crystallinity degree and expectably to differences in the degradation behaviour; c) the recycled HDPE, obtained from post-used large size containers, was selected in order to assess the consequences of ageing and the presence of stabilizers on the reprocessing behaviour.

2.2. Injection moulding and recycling procedures

A DEMAG D 100 NCIII injection moulding machine was used to produce normalized test pieces according to the ISO 3167 (1983) standard. The operating conditions were optimized for each polyethylene using the Moldflow modelling software. A Kistler DAS 16-2851 data acquisition system, based on a piezo-electric sensor, was used to monitor the process by registering the temperature and pressure profiles in the mould.

For two materials a second series of injection mouldings was done choosing a higher temperature profile along the cylinder. Although these conditions are untypical of normal industrial injection moulding operations, they were selected to enhance the degradation effects. The operational conditions of all the injection moulding processes are presented in Table 2, where the acronyms HDPE 7731-T and HDPE 9089U-T, represent those performed under aggressive (higher temperature) conditions.

The reprocessing protocol was done without and, in some cases, with addition of virgin polymer (50% w/w) between the processing operations. After each processing, some samples were collected for properties' determination and the remainder material was shredded in a Broyeur FR 16-18 granulator, mixed with virgin polymer (if applicable) and processed again. This sequence of operations is usually named a "cycle". In all cases the injection conditions were kept constant along the same cycle.

2.3. Determination of the general properties of the mouldings

The evolution of the colour with successive reprocessing was measured by inspection of optical photographs of the samples collected at the end of each cycle. The original polymer was white and translucent, so that the appearance of coloration with increasing intensity would be an indication of the occurrence of degradation reactions. In fact, the colour observed depends on the relative importance the transmission/absorption phenomena that take place as the light passes through the material, which in turn are determined by the characteristics and spatial arrangements of its molecular chains.

To monitor and control the reproducibility of the injection process, 25 test specimens were weighted at the end of each cycle in a Mettler AE 200 balance with a precision of 0.1 mg. Only those specimens whose weight was within the average ± 1 standard deviation, σ, were used for further testing. A small absolute value of σ, as well as a small variation of the weight for the same reprocessing cycle, was taken as indicating appropriate control of the operation conditions. Density determinations were made using a Mettler Toledo AG 204 analytical balance, with a precision of 0.1 mg, according to the ASTM D 792-8 standard.

The rheological behaviour of the polymers was determined in a Rosand RH8-2 capillary rheometer, according to the ASTM D 3835-79 standard, using 2 dies, 2 mm in diameter, and an aspect ratio of 16 and 3.8. Temperatures of 190 °C and 170 °C were chosen to test the four HDPE and the LDPE, respectively. The Rabinowitsch and Bagley corrections were applied to the data in order to correct for the shear rates and shear stresses. The Melt Flow Index (MFI) was determined in a Zwick Z4101 extrusion plastometer, according to the ASTM D 1238-04 standard, at 190 °C and a load of 2.16 kg.

The mechanical properties (tensile strength, $\sigma_{\max}$, elongation-at-break, ϵ_{rot}, secant modulus at 1% elongation, $E_{1\%}$) were determined from tensile tests in an Instron 4505 testing machine with a 50 kN load cell and an Instron 2630 resistivity extensometer. The tests were performed at 23 °C and 50% humidity, at a 50 mm/min crosshead speed, according to the ASTM D-638M-87b standard. The

Table 2
Injection moulding conditions.

Machine	Temperature (°C)						Hydraulic pressure (MPa)[a]			Time (s)				Screw speed (rpm)
Polymer	Mould	Cylinder					Injection	Holding pressure	Back pressure	Injection	Cooling	Holding	Cycle	
		Entry	Zone 1	Zone 2	Zone 3	Nozzle								
HDPE 7731	40	80	180	220	230	235	10.3	7.8	0.63	2	20	2.5	20.5	20
HDPE 7625	50	80	160	190	210	230	10.1	8.1	0.38	5.5	20	5	60	30
HDPE 3H634	40	70	150	190	210	230	6.4	5.8	0.63	1.5	9.5	8.5	24.0	63
LDPE 2304	30	80	140	205	210	215	4.5	3.5	0.38	5.5	12	5	60	35
HDPE recycled	40	70	160	200	217	230	3.8	3.8	0.38	1.5	15	10	65	20
HDPE 7731U-T	40	105	205	245	255	260	10.3	7.8	0.63	2	20	2.5	25.5	20
HDPE 9089U-T	40	70	180	220	237	240	3.8	3.2	0.38	5.5	9.5	8.5	60	20

[a] The pressure values refer to the machine hydraulic system.

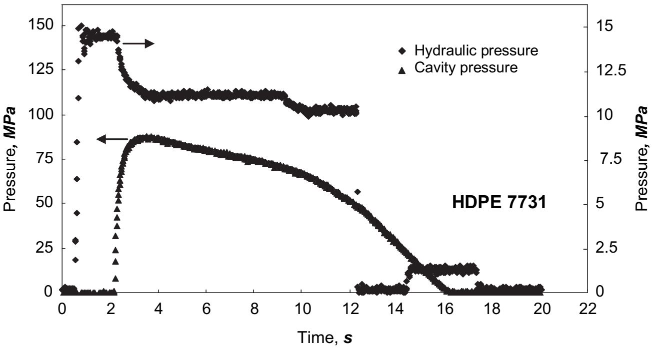

Fig. 1. Evolution of the pressure profiles with process time.

LDPE 9089U test pieces did not break under these conditions so the crosshead speed was increased to 100 mm/min.

Morphological modifications were assessed via the observation of the fracture surfaces of test pieces in a Leica Cambridge S-360 Scanning Electron Microscope. Typically 10–40 μm microtomed slices were observed in an Olympus BH2 Polarized Light Microscope to determine the level of residual stresses in the polymer samples. A Setaram 131 Differential Scanning Calorimeter (DSC) operating under N_2 at 200 kPa (20 cm^3/min) and with a 10 °C/min heating rate was used to measure the melting enthalpy of the different polymers. The degree of crystallinity, χ_c, was determined from $\chi_c = \Delta H_m / \Delta H_{m100}$, where ΔH_m and ΔH_{m100} represent the melting enthalpy of the polymers tested and that of a 100% crystalline polyethylene, respectively. The latter value was taken as 296 J/g [24].

3. Results and discussion

3.1. Monitoring and control of the injection moulding process

The reproducibility and control of the operational conditions are necessary requirements to guarantee that the variation of polymer properties observed in successive injection mouldings truly reflects a structural change and not a processing effect. Fig. 1 represents the profiles of the evolution of the hydraulic and the cavity pressures during the first processing of one of the polymers studied (the ordinates stand for the hydraulic – right – and cavity pressures – left, respectively). The shape of these profiles and its reproducibility were used to assess the process and, namely, the change-over to the pressurization stage of the injection moulding operation. The data is representative of that obtained in the first processing of all the polymers studied, with the variations resulting from their structural differences.

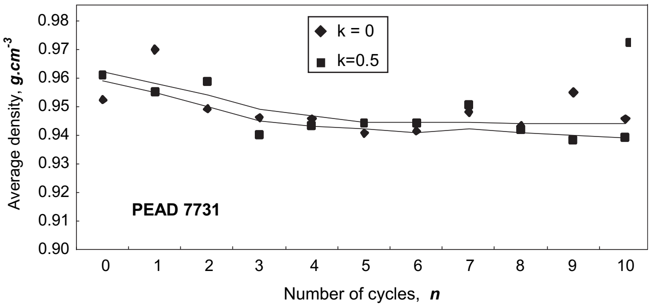

Fig. 2. Density of the mouldings versus number of processing cycles.

Table 3 presents the variation of the average weight (determined on 25 test pieces) of the mouldings with the number of processing cycles and the corresponding standard deviation, σ. The weight remains practically constant and the values of σ are significantly smaller than 1%, reflecting the good control of the operational conditions.

3.2. Structural changes with reprocessing

As mentioned before, the structural variations of the polymers with reprocessing were assessed by means of colour change, density, MFI, rheometry, thermal analysis, SEM, and polarized light microscopy determinations. The initial HDPE and LDPE mouldings were translucent and clear. With successive processing their colour became progressively more yellow, albeit not in a very marked way. This effect was clearly more pronounced on the injection moulding operations performed under more aggressive conditions. This change in colour reflects the degradation of the polymer and quite probably the formation of conjugated double bonds, as in the case of PVC [25]. In the case of the recycled HDPE the initial colour was light brown, and the yellowing effect, although noticeable, was more difficult to follow.

The variation of the density of the mouldings with the number of processing cycles, n, is represented in Fig. 2 for HDPE 7731.

In the figure, as in all the subsequent ones, the full line is just a guide for the eyes. For comparison, the same protocol was repeated admitting 50% (w/w) of the virgin polymer at the beginning of each cycle. This is indicated in the figure as $k = 0.5$. In this case, the density for $n = 0$ was estimated using a law of mixtures and the values corresponding to the virgin polymer and to the sample with one processing. A similar behaviour is observed for both compositions: a slight but continuous decrease in density as the number of cycles increases. This is quite probably a consequence of a reduction in the crystallinity degree of the polymer. For all the other polymers studied the observed variations were qualitatively similar.

Table 3
Evolution of the mass of the mouldings (in grams) with the number of cycles.

Polymer	N. of cycles									
	1	2	3	4	5	6	7	8	9	10
HDPE 7731	11.4205 $\sigma = 0.0116$	11.4244 $\sigma = 0.1289$	11.4267 $\sigma = 0.0280$	11.4366 $\sigma = 0.0171$	11.4164 $\sigma = 0.0037$	11.3911 $\sigma = 0.0056$	11.3586 $\sigma = 0.0116$	11.3418 $\sigma = 0.0235$	11.3827 $\sigma = 0.0283$	11.1844 $\sigma = 0.0730$
HDPE 7625	11.4931 $\sigma = 0.0187$	11.4974 $\sigma = 0.0528$	11.4289 $\sigma = 0.0107$	11.5047 $\sigma = 0.0590$	11.4992 $\sigma = 0.0057$	11.5143 $\sigma = 0.0066$	11.5007 $\sigma = 0.0069$	11.5288 $\sigma = 0.0137$	11.5026 $\sigma = 0.0116$	11.4975 $\sigma = 0.0051$
HDPE 3H634	11.4258 $\sigma = 0.0066$	11.4415 $\sigma = 0.0200$	11.4184 $\sigma = 0.0237$	11.3675 $\sigma = 0.0184$	11.3539 $\sigma = 0.0371$	11.3777 $\sigma = 0.0199$	11.3886 $\sigma = 0.0397$	11.3434 $\sigma = 0.0299$	11.3836 $\sigma = 0.0238$	11.3728 $\sigma = 0.0216$
HDPE 9089U	11.2513 $\sigma = 0.0116$	11.3882 $\sigma = 0.0880$	11.4428 $\sigma = 0.0697$	11.4179 $\sigma = 0.0350$	11.4015 $\sigma = 0.0477$	11.4158 $\sigma = 0.0356$	11.3831 $\sigma = 0.0388$	11.4136 $\sigma = 0.0433$	11.3974 $\sigma = 0.0302$	11.4083 $\sigma = 0.0423$
LDPE 2304	11.0920 $\sigma = 0.0133$	11.0918 $\sigma = 0.0256$	11.1286 $\sigma = 0.0362$	11.1033 $\sigma = 0.0223$	11.062 $\sigma = 0.0075$	11.1155 $\sigma = 0.0108$	11.0456 $\sigma = 0.2072$	11.0820 $\sigma = 0.0133$	11.0826 $\sigma = 0.0140$	11.0805 $\sigma = 0.0081$

Table 4
Evolution of the MFI with the number of cycles

Polymer	N. of cycles										
	0	1	2	3	4	5	6	7	8	9	10
HDPE 7731	0.023 $\sigma = 0.002$	0.023 $\sigma = 0.002$	0.023 $\sigma = 0.002$	0.022 $\sigma = 0.003$	0.021 $\sigma = 0.001$	0.017 $\sigma = 0.001$	0.011 $\sigma = 0.002$	0.007 $\sigma = 0.000$	0.005 $\sigma = 0.001$	0.004 $\sigma = 0.001$	0.004 $\sigma = 0.001$
HDPE 7625	0.154 $\sigma = 0.004$	0.140 $\sigma = 0.006$	0.123 $\sigma = 0.004$	0.081 $\sigma = 0.002$	0.052 $\sigma = 0.002$	0.039 $\sigma = 0.001$	0.038 $\sigma = 0.004$	0.028 $\sigma = 0.004$	0.021 $\sigma = 0.001$	0.015 $\sigma = 0.001$	0.015 $\sigma = 0.001$
HDPE 3H634	0.387 $\sigma = 0.018$	0.406 $\sigma = 0.010$	0.375 $\sigma = 0.003$	0.279 $\sigma = 0.013$	0.216 $\sigma = 0.009$	0.171 $\sigma = 0.002$	0.132 $\sigma = 0.001$	0.110 $\sigma = 0.001$	0.078 $\sigma = 0.004$	0.070 $\sigma = 0.001$	0.063 $\sigma = 0.001$
HDPE 9089U	6.789 $\sigma = 0.045$	6.768 $\sigma = 0.160$	6.843 $\sigma = 0.415$	7.187 $\sigma = 0.199$	7.301 $\sigma = 0.480$	6.945 $\sigma = 0.748$	6.417 $\sigma = 1.149$	7.349 $\sigma = 2.258$	6.968 $\sigma = 0.361$	7.261 $\sigma = 0.052$	7.008 $\sigma = 0.041$
LDPE 2304	3.792 $\sigma = 0.102$	3.580 $\sigma = 0.618$	3.020 $\sigma = 0.004$	2.443 $\sigma = 0.013$	1.724 $\sigma = 0.071$	1.475 $\sigma = 0.055$	1.269 $\sigma = 0.041$	1.205 $\sigma = 0.036$	1.131 $\sigma = 0.011$	1.100 $\sigma = 0.025$	1.121 $\sigma = 0.151$
HDPE recycled	0.064 $\sigma = 0.004$	0.069 $\sigma = 0.005$	0.067 $\sigma = 0.002$	0.065 $\sigma = 0.002$	0.06 $\sigma = 0.003$	0.055 $\sigma = 0.003$	0.042 $\sigma = 0.004$	0.039 $\sigma = 0.002$	– –	– –	– –
HDPE 7731-T	6.789 $\sigma = 0.045$	6.068 $\sigma = 0.027$	6.179 $\sigma = 0.287$	6.098 $\sigma = 0.017$	5.996 $\sigma = 0.0301$	– $\sigma = 0.017$	5.553 $\sigma = 0.116$	– $\sigma = 0.008$	5.277 $\sigma = 0.008$	– $\sigma = 0.050$	5.210 $\sigma = 0.035$
HDPE 9089U-T	0.023 $\sigma = 0.002$	0.031 $\sigma = 0.002$	0.026 $\sigma = 0.004$	0.022 $\sigma = 0.004$	0.021 $\sigma = 0.004$	– $\sigma = 0.004$	0.015 $\sigma = 0.004$	– $\sigma = 0.004$	0.013 $\sigma = 0.005$	– $\sigma = 0.004$	0.013 $\sigma = 0.003$

The data on Fig. 2 was confirmed by crystallinity degree determinations. In the case of HDPE 7731 and 7625, for instance, it decreased 29% to 33.9% and 26% to 40.3%, respectively, from the original polymer to the 10th cycle. The other polyethylenes, including the LDPE, followed a similar pattern, although the decrease was less pronounced in the case of the less viscous polymer, HDPE 9089U.

Table 4 presents the Melt Flow Indices of all the polymers, together with the corresponding standard deviations, σ. Each value is the average of 7 determinations. All polymers were reprocessed 10 times, except the recycled HDPE that was injection moulded only 7 times.

The MFI data shown in Table 4 is represented in Fig. 3, normalized by the initial values ($n = 0$) of the virgin polymers. This representation is quite usual in reprocessing studies, namely those dedicated to the development of predictive algorithms [26]. It is observed that, in general terms, the Melt Flow Indices decrease with reprocessing, indicating a predominance of the crosslinking mechanism in the degradation processes.

It should be noted that the complex information displayed in the figure is difficult to interpret. The first thing to consider is that, to better represent the evolution of the property, the normalized representation of-sets the differences in the MFI of the original polymers. It should also be noted that it comprises different subsets of data that should be analyzed separately. These are, the four HDPE (un-recycled), the two HDPE processed in normal and aggressive conditions, the LDPE and the recycled HDPE. The four HDPE have very distinct initial MFI values, ranging from 0.023 to 6.789 g/10 min, the limits corresponding to HDPE 7731 and HDPE 9089U, respectively. Those of HDPE 77625 and HDPE 3H634 are closer to the former, 0.154 and 0.387 g/10 min, respectively. In general terms, it can be said that the decay pattern of the 3 more viscous polymers is similar; after an initial period in which the MFI does not significantly decrease, or even increases, it drops significantly. This behaviour has been observed before for properties such as MFI [12] and the modulus [19]. As in previous studies, a possible explanation for this effect is the simultaneous occurrence of two competitive degradation mechanisms, scission and crosslinking. Apparently, the rate of the former is significant in the first two cycles but decreases markedly thereafter and can no longer compete with crosslinking. There is thus an initial equilibrium or even predominance of scission, but crosslinking eventually becomes rate controlling. However, this change in controlling step does not occur in the case of the less viscous polymer, HDPE 9089U, in which the MFI always increases, albeit slightly, with the number

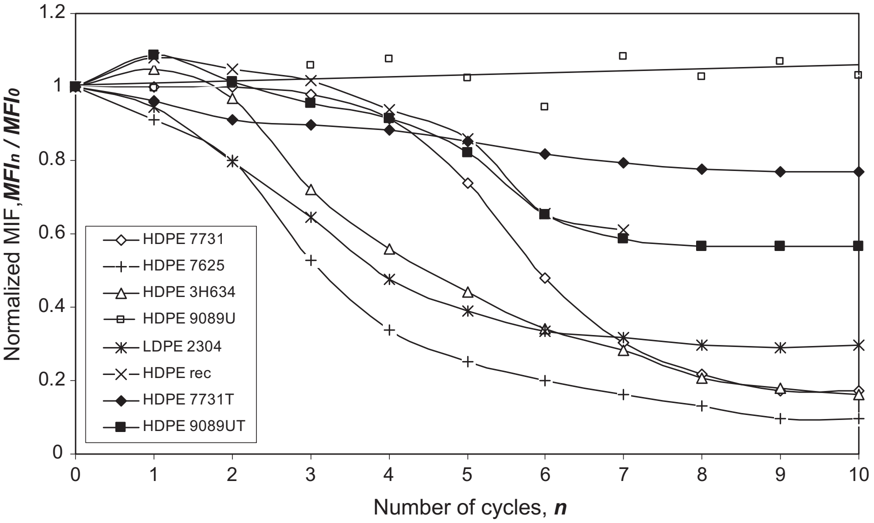

Fig. 3. Evolution of the MFI with the number of cycles.

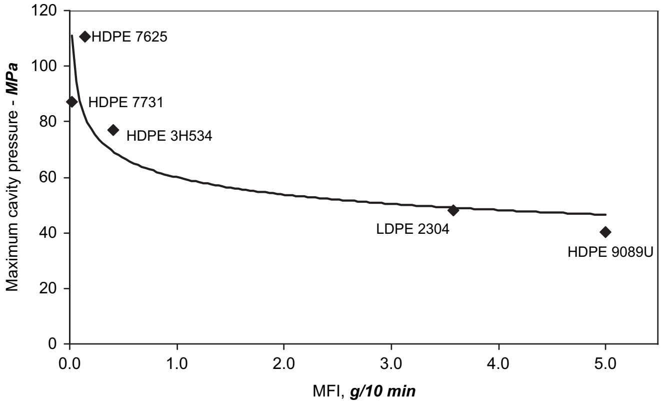

Fig. 4. Maximum pressure versus initial MFI of the various polyethylenes.

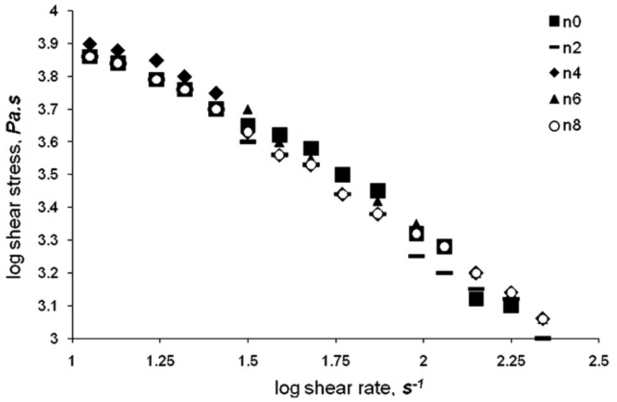

Fig. 5. Shear stress versus shear rate for various processing cycles (HDPE 7731).

of cycles. The increasing importance of the scission reaction with enhanced mobility of the polymer chains has already been reported [22]. Nevertheless, when the processing is done in aggressive conditions, that is, at higher temperature, the flow behaviour is altered and crosslinking seems to predominate again, as can be observed for HDPE 9089U-T. There is no clear explanation for this significant change in behaviour as, in principle, higher temperature would favour chain mobility. Conceivably, it can be due to asymmetric temperature effects on the kinetics of the scission and the crosslinking reactions.

The degradation behaviour of the Low Density Polyethylene, LDPE 2304, in spite of the larger number of side chains and concomitant lower degree of crystallinity, is similar to that of the HDPE of much smaller MFI. This evidence, although in line with the reported predominance of crosslinking reactions in multiple reprocessing [19], directly contradicts the same study that concluded that different mechanisms were rate controlling in the case of LDPE and HDPE. Also interesting to note is the decay behaviour of the recycled HDPE, qualitatively similar but smaller than that of the virgin ones, of comparable MFI, processed in the same conditions. Although, in qualitative terms, this behaviour has been reported before [15], the small value of the property decay is noteworthy. It may be due to the presence of stabilizers added by the recycler, partially inhibiting the crosslinking reaction. Another possibility is the concomitant good control of the processing conditions, which may also be partially responsible for the behaviour of the LDPE.

Globally, the MFI results confirm the crystallinity degree determinations, obtained via DSC measurements, which showed a continuous decrease in the property values with reprocessing. The development of a crosslinked network with the increase in the number of processing cycles hinders the mobility of the macromolecules and thus the possibility of the material to organize itself in large crystalline domains.

Given the effect of the operation conditions on the structural changes and the consequent flow behaviour of polyethylene, it is useful to be able to easily determine their optimum for each specific polymer. This can be done by correlating the above MFI data with the operational conditions such as those in Fig. 1, namely the maximum mould cavity pressure. This correlation is presented in Fig. 4, showing the expected pressure decrease with increasing MFI.

Capillary rheometry was performed to further elucidate the rheological changes occurring during reprocessing. The variation of the shear stress with the shear rate for one of the polymers, HDPE 7731, is presented in Fig. 5.

In the figure, the symbols n_0, n_1, n_2 … n_8, represent the values measured for the original polymer and those determined at the 1st, 2nd , …8th cycles, respectively. With small variations, the behaviour portrayed is representative of all the other polymers studied, in that there is no marked difference from cycle to cycle. It is possible that a more profound analysis of the rheometric data could have provided more information. For instance, a study of the thermorheological behaviour of various Ziegler-Natta LLDPE and LDPE samples using relaxation functions demonstrated a strong dependence of the properties on the branching density [27]. However, this type of analysis is outside the scope of the present work.

SEM observations of the samples revealed that the texture of the fracture surfaces became less ductile as the number of cycles increases. This observation agrees with the progressive crosslinking hypothesis formulated from the MFI results. The effect is less pronounced for the lower molecular weight (higher MFI) polymers, such as LDPE 2304.

The morphological changes were also studied by polarized light microscopy. Fig. 6 depicts micrographs of HDPE 7731 processed one and 10 times. For brevity, only the results for this polymer are shown as they are representative of most of the observations.

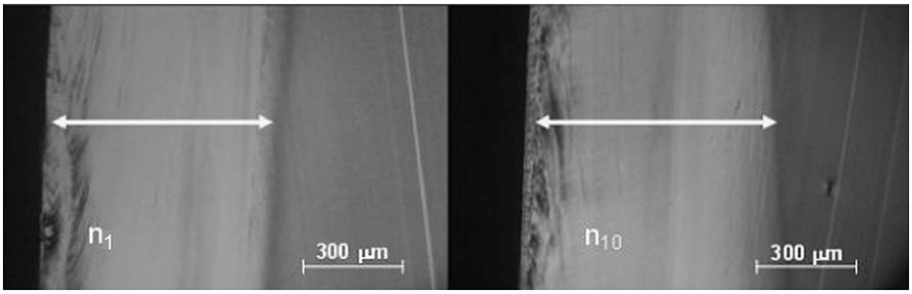

Fig. 6. Polarized light micrographs of HDPE 7731 samples at the 1st (n_1) and 10th (n_{10}) cycles.

Table 5
Mechanical properties determined for HDPE 7731 and HDPE 7731-T.

Polymer	HDPE 7731			HDPE 7731-T		
Property N. of cycles	σ_{max} (MPa)	$E(\epsilon = 1\%)$ (MPa)	ϵ_{break} (%)	σ_{max} (MPa)	$E(\epsilon = 1\%)$ (MPa)	ϵ_{break} (%)
n_1	25.79	691.6	80.02	25.57	719.9	74.92
	$\sigma = 0.43$	$\sigma = 46.9$	$\sigma = 0.25$	$\sigma = 0.12$	$\sigma = 117.6$	$\sigma = 62.92$
n_2	25.57	664.8	98.06	25.94	757.8	71.48
	$\sigma = 0.04$	$\sigma = 21.3$	$\sigma = 0.37$	$\sigma = 0.1542$	$\sigma = 132.3$	$\sigma = 4.88$
n_3	25.27	684.0	73.60	25.82	789.9	72.12
	$\sigma = 0.48$	$\sigma = 25.2$	$\sigma = 0.11$	$\sigma = 0.18$	$\sigma = 55.5$	$\sigma = 11.69$
n_4	26.36	693.6	60.48	27.26	763.6	62.10
	$\sigma = 0.28$	$\sigma = 13.2$	$\sigma = 0.21$	$\sigma = 1.80$	$\sigma = 150.8$	$\sigma = 14.75$
n_5	28.77	732.9	57.46		–	–
	$\sigma = 0.45$	$\sigma = 21.0$	$\sigma = 0.20$			
n_6	31.92	776.8	45.14	–	–	–
	$\sigma = 0.23$	$\sigma = 49.2$	$\sigma = 0.32$			
n_7	35.00	840.2	32.05	27.43	774.8	68.44
	$\sigma = 0.51$	$\sigma = 38.7$	$\sigma = 0.08$	$\sigma = 0.36$	$\sigma = 17.7$	$\sigma = 7.23$
n_8	37.69	869.5	33.04	27.44	793.4	60.36
	$\sigma = 1.26$	$\sigma = 26.4$	$\sigma = 0.13$	$\sigma = 0.16$	$\sigma = 71.4$	$\sigma = 8.57$
n_9	36.83	863.7	32.80	–	–	–
	$\sigma = 0.77$	$\sigma = 18.1$	$\sigma = 0.16$			
n_{10}	35.63	850.3	36.81	27.31	769.2	54.35
	$\sigma = 1.87$	$\sigma = 14.0$	$\sigma = 0.18$	$\sigma = 0.33$	$\sigma = 183.2$	$\sigma = 2.95$

The micrographs reveal a laminated structure typical of semi-crystalline polymers, with a highly birefringent external skin (resulting from the molecular orientation) and a spherulitic core. The fine granular structure of this core reflects the spherulites' small dimensions which is also characteristic of polyethylene. It can be observed that the thickness of the oriented skin increased approximately 10% from the first to the tenth cycle. Although the effect is not very pronounced it was consistently observed in all polymers studied, once again supporting the hypothesis of the predominance of the crosslinking mechanism. In fact, if this mechanism predominates, the average molecular weight and the viscosity will increase, making molecular relaxation more difficult and inhibiting the development of large spherulitic structures.

3.3. Changes in the mechanical properties with reprocessing

The relevant mechanical properties, tensile strength, σ_{max}, secant modulus (at 1% elongation), $E_{1\%}$, and Strain at break ϵ_{break}, determined in a minimum of 7 tensile test specimens are presented in Table 5 for HDPE 7731 at the two processing conditions. The table also shows the corresponding standard deviations, σ.

Confirming previous studies [11,23], it is evident from the data that both the tensile strength and the modulus increase and the ultimate elongation decreases with the number of processing cycles. That is, the material becomes progressively stronger, stiffer and less ductile. These observations can be explained by the formation of an increasing number of crosslinks. It can be argued that the thermo-oxidative phenomena that occur during processing can originate other type of macromolecular changes, such as the formation of double bonds, leading to a similar effect on the mechanical properties. Although this is also a possibility, the consistency of these results with those obtained for the other properties strongly supports the hypothesis of the predominance of the crosslinking mechanism. These conclusions are representative of those obtained for the other polymers studied, including the LDPE, albeit with small differences. For instance, for HDPE 9089U the change in the mechanical

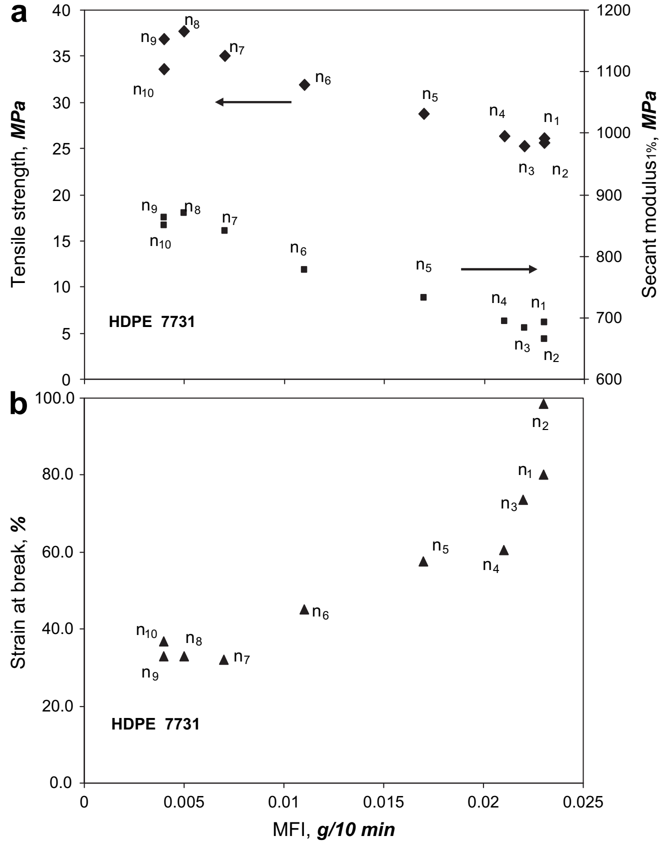

Fig. 7. Variation of the mechanical properties of HDPE 7731 with MFI and the number of cycles. a) σ_{max} and secant modulus at 1%; b) Strain at break.

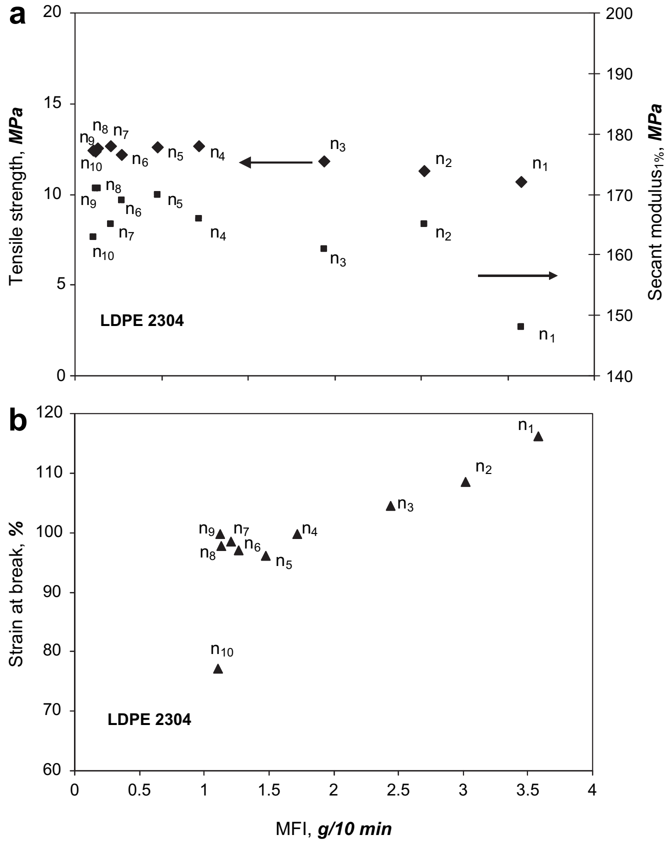

Fig. 8. Variation of the mechanical properties of LDPE 2304 with MFI and the number of cycles. a) σ_{max} and secant modulus at 1%; b) Strain at break.

properties from cycle to cycle is substantially smaller. This is again consistent with the behaviour detected with other properties in which the polymers with higher MFI (lower molecular mass) are less sensitive to the reprocessing effects.

When HDPE 7731 was processed at high temperatures the variation of the mechanical properties followed the same trend, but the observed changes from cycle to cycle were smaller. This indicates that the crosslinking mechanism does not predominate so clearly in this situation, in agreement with the MFI behaviour of HDPE 7731 /HDPE 7731-T in Fig. 3, but in contrast with that of HDPE 9089U /HDPE 9089U-T. Again there is no obvious explanation for such difference, unless to conclude that the effect of temperature is complex, possibly affecting differently polymers with quite distinct molecular masses.

3.4. Processing-structure–properties relationships

Fig. 7a and b), obtained from Tables 4 and 5, depict the correlation between the mechanical properties and the MFI of HDPE 7731 from cycles 1 to 10.

Considering that the MFI reflects the structure of the polymer, namely its molecular mass, then the figures portray processing-structure–properties relationships. To the best of the authors' knowledge, such relationships are not often represented in reprocessing studies.

The curves clearly show that as the number of cycles increases, the MFI decreases, that is, a crosslinking network develops, leading to an increase of both the tensile strength and the modulus and to a decline of the strain at break. On the other hand, the MFI can also be related to the processing conditions, as shown in Fig. 4.

The behaviour portrayed in Fig. 7 was again generally similar for the other polymers, albeit with the specificities of each one. Namely, as stated before, for the less viscous ones, LDPE 2304 and HDPE 9089U, the variation of the properties with reprocessing was significantly smaller. This situation is represented in Fig. 8a and b for LDPE 2304.

4. Conclusions

It is not possible to definitely demonstrate the existence or predominance of a given polymer degradation mechanism without using chemical and spectroscopic methods that are outside the scope of the present work. However, the literature survey presented in the introduction unquestionably demonstrates that the two mechanisms that have been most used to explain the degradation of polyethylene during reprocessing are crosslinking and chain scission. In this framework, the results reported herein, based on seven different experimental techniques, clearly indicate that crosslinking is the dominant mechanism for the injection moulding conditions used. Following the norm in industry, those conditions were optimized to obtain the best possible parts. It was also possible to relate them to the original MFI of the various polyethylenes, namely the maximum mould cavity pressure, and to establish processing-structure relationships.

The main consequence of optimizing the processing conditions is that properties do not degrade substantially with reprocessing, even when no virgin material is added to the feed between cycles. This is even true for the reprocessing of post-used HDPE, although in this situation certain properties, like the colour, were substantially affected. In any case, the change in properties was more marked for the polyethylenes with the highest molecular mass, such as HDPE 7731, and much less so for the low molecular ones, (HDPE 9089U) and those with higher degree of branching (LDPE 2304). Consequently, HDPE 7731 was selected as the example in the most of the figures shown.

Some properties were more sensitive to reprocessing than others. As in previous studies, the MFI [6] and the tensile properties [12] were found to be critical properties. The former not only reflects the structural changes occurring along the processing cycles, but also displays substantial differences in behaviour from polymer to polymer. The latter replicates quite adequately those changes. In fact, both the tensile strength and the modulus increased and the ultimate elongation decreased when the MFI decreased (and crosslinking progressed). This converging structure–properties information was quite clearly demonstrated in the MFI - mechanical properties curves.

Typically, properties do not decay up to the second cycle, and eventually stabilize after the seventh or eight. In some cases there was even a different slope in the initial cycles, indicating the possible occurrence of two competing degradation mechanisms, scission and crosslinking. When the processing was done in non-optimized conditions, namely at higher temperatures, there were substantial differences in the degradation behaviour. In this case, even for the polymers with lower molecular mass, such as HDPE 9089UT, the evidence of progressive crosslinking with reprocessing, and possibly a change in controlling mechanism, was clear.

Although the polyethylenes with higher molecular mass were more sensitive to reprocessing, this effect was not drastic in any of the polymers studied. This confirms the notion that primary recycling of polyethylene, if performed under well controlled conditions, will lead to minor material property losses.

Acknowledgements

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