The Design of a Test Protocol to Model the Degradation of Polyolefins During Recycling and Service Life

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ABSTRACT: In terms of the sustainable development for polymeric materials the recovery of plastic waste by means of mechanical recycling is a favorable technique. The largest part of the collected plastic municipal solid waste fraction consists of packaging materials, e.g., polypropylene (PP) and polyethylene. A major drawback to the increased use of recycled polymers is the lack of knowledge about the property changes and the overall quality of the recyclates, e.g., the degree of degradation, mixing, and contamination. This article presents a test protocol for description of the mechanical, physical, and chemical property changes during recycling and service life by combining several reprocessing cycles and thermooxidation. The test protocol was designed to mimic the degradation mechanisms potentially occurring in the materials during the service life and the reprocessing. Virgin PP and HDPE were multiply processed by injection molding. Service life of plastic materials was modeled by accelerated thermal degradation of one time processed materials. Tensile testing, MFR, HT-SEC, DSC, FTIR, and SEM were used to analyze material changes. In parallel, a set of industrially recycled PP and HDPE were also subjected to the same analyses. The results proved that recycled plastics maintain the majority of the material properties even when reprocessed several times. It was demonstrated that the mechanical and thermal properties of PP and HDPE were preserved also after several reprocessing steps. Initiation of degradation was observed for PP but not for HDPE. A decrease in M_w of PP from 240,000 to 190,000 (six times reprocessed) was established, this corresponds to an increase in MFR from 8 to 18 g/10 min. By FTIR, it was shown that the carbonyl index increased. The loss of stabilizers affects the properties of the final product. In comparison, industrially recycled PP and HDPE presented to some extent poorer mechanical properties than the materials subjected to model recycling. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 1835–1844, 2009

Key words: degradation; injection molding; polyolefins; recycling; structure-property relations

INTRODUCTION

Recycled polymeric materials are today considered as low-grade plastic products. In order for these materials to be a natural part of the sustainable development, new systems of recycling and product developments need to be established. In 2005, 4.5 million tonnes of the postconsumer plastic were recovered as material and feedstock recycling.[1] The mechanical recycling is increasingly considered as the preferred treatment option in the handling of postindustrial and postconsumer plastic waste. An obvious driving force is the developing legislation, but the underlying reason is that investigations show an environmental gain by the use of mechanical recycling in comparison with energy recovery and landfills. An important part of the gain is the reduced energy consumption when recycled plastic waste is used to make new products, compared with the energy needed to make products from raw petroleum.[2,3] Limitations in the material recycling are the difficulties in controlling the purity of the product, due to e.g., contaminations by undesirable material blends and/or varieties in soiling and degradation of the plastics.[4] Recent research on various techniques for simulation of plastic recycling that have been applied for several polymers [e.g., polyethylene (PE), polypropylene (PP), PVC, PC] have been presented in excellent reviews by La Mantia et al.[5] and Vilaplana and Karlsson.[6] During the mechanical recycling, the plastic material is subjected to grinding, remelting, and processing. Because of the high pressures, high temperatures, and shear forces applied, this leads to irreversible changes in the structure of the polymeric material as well as in its mechanical properties. One way of improving the mechanical properties of the postconsumer waste is restabilization by means of stabilizers or compatibilizers for mixed streams.[7]

The degradation of the plastic materials occurring during mechanical recycling can be divided into two main mechanisms, mechano-oxidative, and thermooxidative. It is likely that both of these occur
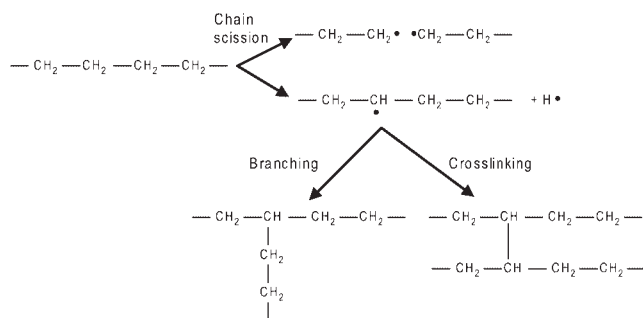
Scheme 1 Macroradicals generated in PE structure due to mechanical stress and possible recombination routes.[8,11]

Scheme 2 Macroradicals generated in PP structure due to mechanical stress.[8,11]

simultaneously during the mechanical recycling and affect the polymer properties such as molecular weight, molecular weight distribution, crystallinity and chain flexibility. The mechanical degradation occurs due to the shear forces applied during the grinding and processing. The molecular chains are degraded, cleaved or damaged, when ground against each other and/or the equipment in the presence of oxygen. The thermal degradation takes place when the polymer is exposed to oxygen at the high temperatures involved in melting and reprocessing of the plastics. Reactions with oxygen cause chain damages.[8,9] PP and HDPE have a semicrystalline structure with a randomly ordered amorphous phase and a highly ordered crystalline phase. During both the mechano-oxidative and thermo-oxidative degradation of the polyolefins, free radicals are formed, causing chain scission and as a consequence branching and/or crosslinking.[8,9] The extent of these coexisting reactions depend on the processing conditions, the availability of oxygen and, in case of HDPE, the catalyst type used during production of the polymer.[10] Oxidative chain reactions, autoxidations, take place resulting in free radical formations that through reaction with molecular oxygen form hydroperoxides, which in turn decompose causing the formation of new radicals.[11]

Schemes 1 and 2 show the mechanical degradation mechanisms for PP and HDPE. These mechanisms alone are very rare, rather oxygen is normally always present, resulting in the formation of carbonyl containing chains and also longer and shorter oxygen

containing fragments e.g., ketones. Scheme 3 presents the mechanisms for hydroperoxide formation in polyolefins, showing PP as a specific example.

The objective of this work was to design a test protocol which allows modeling of the PP and HDPE recycling. By dividing it into two parts, it is possible to explain in detail the macroscopic and microscopic material changes potentially occurring during the service life and the reprocessing. This type of data gives valuable input to a subsequent quality assessment of recycled polymeric materials. Comparison with industrially recycled polyolefins was performed, but taking into account that this comparison is very difficult as the industrially recycled materials are of unknown composition. The test protocol was designed to mimic the degradation mechanisms potentially occurring in the materials during service life and reprocessing. Commercial, virgin PP and HDPE were processed by injection molding, some material was removed for characterization, the rest was ground and injection molded again. The in-plant recycling procedure was repeated six times. PP was injection molded at 230°C and HDPE at 200°C. The service life of plastic materials was modeled by accelerated thermal degradation of one time processed materials. The procedure was executed in the presence of oxygen in a forced-ventilation oven. The samples were aged at 120°C for 5, 10, and 15 days. In parallel, a set of industrially recycled PP and HDPE were subject to the same analyses. Tensile testing, MFR, HT-SEC, DSC, FTIR, and SEM were used to analyze material property changes.
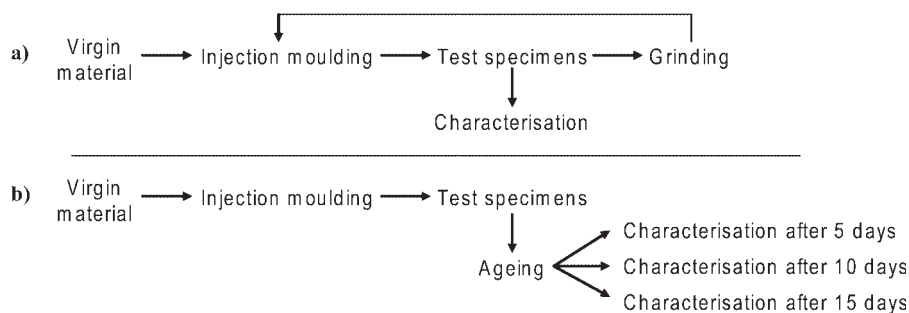
EXPERIMENTAL

Materials

Commercial virgin PP (HD120MO) provided by Borealis, Stathelle, Norway and commercial virgin high density PE, HDPE, (MG9621) provided by Borealis, Stenungsund, Sweden were used. According to
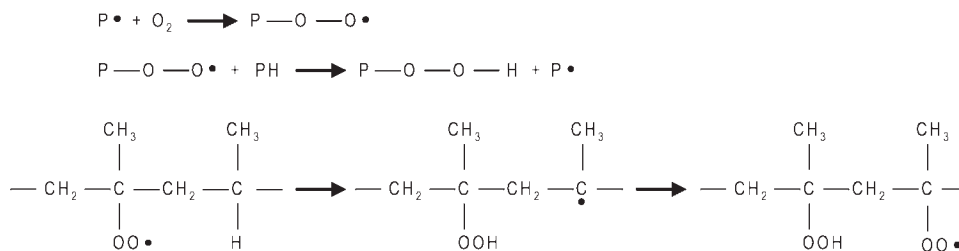
Scheme 3 Oxidation mechanisms for PP, P is an abbreviation for a polyolefin chain.[11]

Scheme 4 Sample preparation: (a) modeling second life of plastics; (b) modeling service life of plastics.

specification given in the data sheet, PP contains small amount of stearates. Generally, PP and HDPE contain UV-stabilizers of hindered amine type and antioxidant systems. Recycled PP and HDPE were provided by Plastkretsen AB, Stockholm, Sweden. The recycled materials were received as flakes from various packaging applications and had to be homogenized for further analysis. It can be anticipated that the PP and HDPE grades of the recycled materials are of different sources and thus their properties such as melt flow rate, molecular weight and type of additives vary. These materials were extruded at 200°C barrel temperature, at a speed of 10–15 rpm and then ground.

Material processing

Virgin PP and HDPE were processed by injection molding, in a Battenfield PLUS 250/50 injection molding machine (Wien, Austria) with a single screw (diameter of 22 mm and an L/D ratio of 16), some material was removed for characterization, the rest was ground and injection molded again. The procedure was repeated six times, as shown in Scheme 4(a). The dimensions of the mold used were chosen according to ASTM standard D 638M-89. PP was injection molded at 230°C and HDPE at 200°C. Service life of plastic materials was modeled by accelerated thermal degradation of one time processed materials, performed following the guidelines of ASTM standard D5510-94, the test temperature and the exposure times were, however, chosen from experimental data on the effect of temperature on the materials. The procedure was executed in the presence of oxygen in a forced-ventilation oven. The samples were held at 120°C for 5, 10, and 15 days [Scheme 4(b)]. The recycled materials were also injection molded, at the equivalent temperatures, for further analysis.

Characterization techniques

To investigate the changes in mechanical, physical, and chemical properties of the polymers, all proc-

essed, recycled, and aged materials were characterized by the following techniques.

Tensile testing

The tensile tests were performed by means of Instron 5566 universal electromechanical testing machine (Instron Corp., High Wycombe, UK) with a gauge length of 50 mm and a 10 kN load cell at a crosshead speed of 50 mm/min. The specimens were prepared according to ASTM Standard D638M-89. The average values of modulus, stress at upper yield, and strain at upper yield from five samples were selected as the representative values.

Melt mass-flow index

The melt flow measurements were carried out on a Melt Indexer CFR-91 (Campana S.R.L., Italy). All experiments were performed according to European Standard ISO 1133 : 1997. PP and HDPE were analyzed at 230 and 190°C, respectively, and 2.16 kg as nominal load. Five samples of each material were tested and an average value was calculated. The melt mass-flow rate was calculated using eq. (1), were m is the average mass (in grams) of the cut-offs; t is the cut-off time-interval (in seconds), and t_{ref} is 600 s.

$$MFR = \frac{m \cdot t_{ref}}{t} \qquad (1)$$

High temperature SEC

The molecular weight analysis was performed by Rapra Technology Ltd, Shawbury, United Kingdom. The analysis of five multiple processed PPs and five multiple processed HDPEs was carried out by high temperature SEC equipped with one PLgel guard column in series with two 10 μm mixed B columns, length 30 cm (Polymer Labs, Chruch Stretton, UK). 1,2,4-Trichlorobenzene was used as the solvent at 160°C and the flow rate was 1.0 mL/min (nominal). Spectra were recorded with refractive index and

Viscotek differential pressure (viscosity) detector and the data were collected and analyzed using Viskotek "Trisec 3.0" software. The measurements were carried out as duplicates. The SEC system was calibrated with polystyrene standards and a mathematical procedure involving the use of literature viscosity constants was applied to the calibration to compensate for differences in molecular shape between the samples and the calibrants.

Scanning electron microscope (SEM)

The morphology of the injection molded samples was examined by means of a JEOL (Tokyo, Japan) JSM-5400 scanning electron microscope using acceleration voltage of 10 kV. Three samples from each material were prepared by cutting square pieces from a randomly chosen part of the injection molded sample. The pieces were mounted on metal studs and sputter-coated with gold/palladium (60/40%) using a Denton Vacuum Desk II (Moorestown, NJ) cold sputter etch unit operated at 45 mA for 3×15 s. Surface analysis of each sample was performed.

Differential scanning calorimetry (DSC)

The changes in the melting temperature (T_m) and polymer crystallinity were determined using a Mettler Toledo DSC820 calorimeter (Schwerzenbach, Switzerland) calibrated with indium standard. Approximately 5 mg of each sample were placed in a standard 40 μL aluminum crucible in N_2 atmosphere. Both the first and the second heating runs were recorded and the heating/cooling rate used was $\pm 10°C/min$. The results were obtained from the second heating run as an average value of three samples.

The crystallinity was calculated using eq. (2), where ΔH_{100} for PP was 190 (J/g) and ΔH_{100} for HDPE was 290 (J/g):

$$X_c = \frac{\Delta H}{\Delta H_{100}} \cdot 100 \qquad (2)$$

The oxidation temperature (T_{ox}) was reached by heating the samples from 25 to 300°C at a rate of 10°C/min in oxygen atmosphere. The T_{ox} was obtained from the onset point of the resultant curve. The results were determined as an average value from three samples. The oxidation induction time (OIT) measurements were performed in accordance with ISO 11357-6:2002 standard. The samples were heated rapidly from 30 to 180°C for PP and 195°C for HDPE at a rate of 20°C/min and held at that temperature for 5 min in N_2 atmosphere. The atmosphere was thereafter instantly switched to oxygen at a flow of 50 mL/min and the oven temperature was held at 180 and 195°C, respectively. The OIT was

calculated as the difference between the instant when the atmosphere was switched to oxygen and the onset of the oxidation signal at thermograms. The results were determined as an average value from three samples.

Infrared spectroscopy (FTIR)

The changes in the carbonyl region during oxidation were monitored by a FTIR spectrometer Spectrum 2000 from Perkin–Elmer (Waltham, MA) equipped with a golden gate attenuated total reflection (ATR) holder with a diamond FTIR crystal. The ATR technique was used since the specimens were too thick for the transmission mode. Each spectrum was based on 16 scans with a resolution of 4 cm^{-1}. The results are based on measurements carried out in triplicate.

The peaks were identified and the carbonyl index was calculated as the relationship between the peak height of the absorption peak at 1742 cm^{-1} for PP and 1744 cm^{-1} for HDPE (the maximum of the carbonyl peak) and the absorption for each materials internal standard peak, 1454 cm^{-1} for PP and 1472 cm^{-1} for HDPE. These bands are due to the CH stretching, deformation, and rocking vibrations.[12]

RESULTS AND DISCUSSION

The mechanical properties of recycled materials are desired to be in equivalence with those of virgin polymers. Strain at break was monitored, but here the Young modulus and strain at upper yield are presented as being more relevant for the future applications. Figure 1(a,b) show the Young modulus and strain at upper yield of reprocessed PP and HDPE. Decreases up to 12% with increasing number of processing cycles were observed for PP modulus, which is a sign of polymer degradation. In the corresponding curve for HDPE, no significant changes in the Young modulus could be detected, Figure 1(b). In general, the degradation is heterogeneous,[13–16] which gives difficulties interpreting the analyses results. In Figure 1(b), this is significant, as a wide spreading in the measured modulus is observed for all reprocessed samples.

The strength of PP, i.e., the stress at upper yield, does not change with reprocessing. The results indicated that the material sustains its strength and ductility even though thermomechanical degradation occurs. For HDPE, the stress at upper yield does not alter throughout the reprocessing. The material sustains its strength, stiffness, and ductility.

Table I presents results for the changes in the mechanical properties for thermo-oxidized PP, HDPE, and industrially recycled material. PP exposed to an accelerated thermal oxidation showed a slight
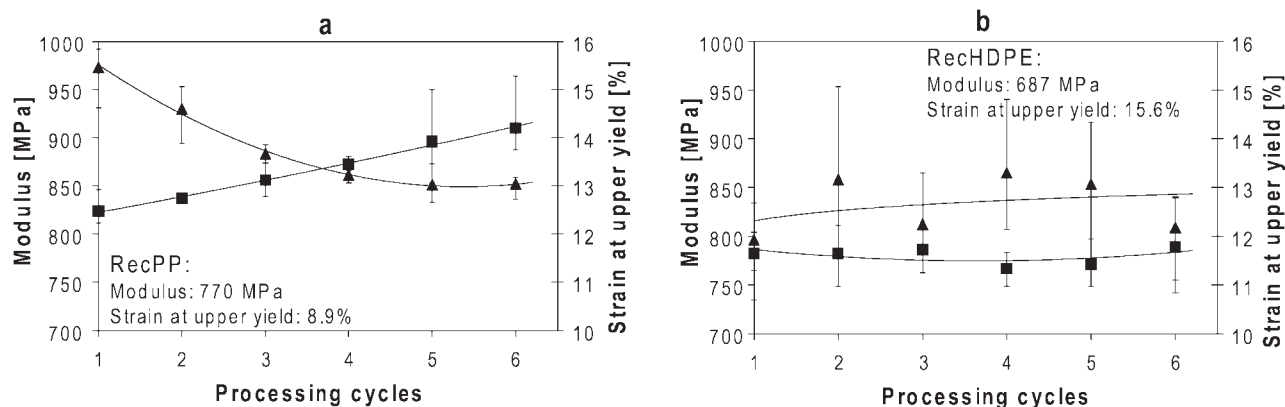
Figure 1 Young modulus (▲) and strain at upper yield (■) during multiple processing (a) PP and (b) HDPE. The respective values of industrially recycled materials are included.

increase in the Young modulus. The strength of the material remained constant. A minor decrease in the strain at upper yield occurred. However, the strain at break shows that the ductility decreases substantially, from $\sim$ 300 to 30%. Similar data was also presented in another study of recycled polyolefins.[17] It is notable that the ductility of the polymer is greatly affected without any substantial effect on the toughness. The results could be explained by a large increase in the crystallinity of the polymer, but this is not supported by DSC measurements. On the other hand, thermo-oxidation of polyolefins usually results in a varying values of the crystallinity during the ageing period, increasing and decreasing as the degradation proceeds primarily in the amorphous parts and secondly also in the crystalline parts.[18] Other causes for this behavior could be that PP has started to degrade by chain scission in the amorphous part,[15] which results in a gradual change in the chemical composition which in turn could effect the elongation.

A considerable increase in the Young modulus and the stress at upper yield has been observed during accelerated thermal degradation of HDPE when compared with the initial processed material, with a modulus of $\sim$ 800 MPa. The elevated temperature in the oven allows the polymer chains to be arranged in more favorable energetic states and as a consequence the stiffness and strength can be increased. These property changes can also occur due to crosslinking or molecular enlargement caused by physical and chemical degradation.[19] The ductility of the material does, however, decrease from $\sim$ 850 to 40% for HDPE.

The industrially recycled materials, RecPP and RecHDPE, showed lower values in material toughness and strength. Figure 1 includes values of the Young modulus and strain at upper yield for industrially recycled polymers in comparison with the influence of reprocessing on the material properties. The brittleness of the materials was observed during tensile testing. The elongation at break was much lower than for the one time processed material. The results indicated negative effects on the mechanical properties of the material after recycling, however, the reduction can to some extent be explained by the fact that this sample contains a mixture of different polyolefins, which is supported by DSC analysis, and is not a homopolymer as the reference sample is. In reality, recycled PP and HDPE will consist of a

TABLE I
Mechanical Properties of Aged PP, Aged HDPE, and Industrially Recycled Material

	Stress at upper yield (MPa)		Strain at upper yield (%)		Young modulus (MPa)		Young modulus (SD)	
	PP	HDPE	PP	HDPE	PP	HDPE	PP	HDPE
Accelerated thermal degradation								
5 days	33.55	30.72	13.39	8.61	963	1091	26.08	94.78
10 days	33.45	30.79	13.11	9.39	952	1098	23.86	63.98
15 days	33.90	31.07	12.42	8.83	982	1082	9.15	96.46
Industrially recycled								
	22.57	26.98	8.89	15.58	770	687	31.99	20.32
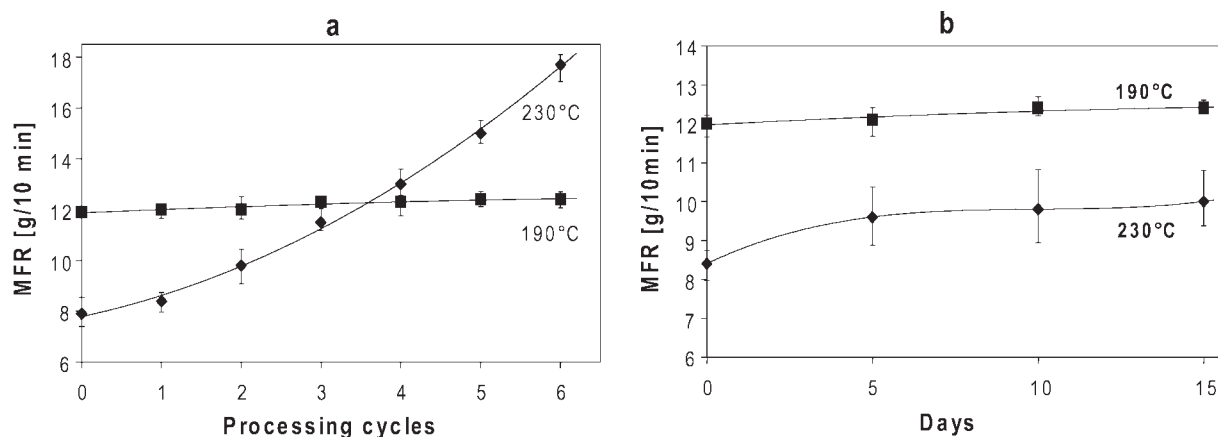
Figure 2 Melt index of PP (◆) and HDPE (■) during (a) multiple processing and (b) accelerated thermal degradation. PP and HDPE were analyzed at 230 and 190°C, respectively, and 2.16 kg as nominal load.

range of PP and HDPE qualities with varying properties. It can therefore be predicted that real recyclates should demonstrate poorer properties than corresponding laboratory modeled recycled samples.

Figure 2(a) presents the MFR for multiple reprocessed PP and HDPE. The results clearly show that melt index of PP increases with each processing cycle, which indicates that polymer degradation occurred. The molecular weight of the homopolymer is reduced by chain scissions, which enhance the melt index, lowering the viscosity of the polymer. These results are supported by analysis with SEC, Table II, where a substantial decrease in the molecular weight of PP is observed. In general the SEC peaks became slightly narrower, as demonstrated by the decrease in PDI, indicating a degradation of the less ordered, amorphous parts. The continuous reduction of the width of the SEC peaks together with the reduction in molecular weight indicates progressive polymer degradation during the reprocessing of PP. The decreasing PDI show, that degradation has occurred to a larger extent in chains with higher molecular weight, which was also observed by Jansson et al. and Canevarolo.[17,20]

The results from accelerated thermal degradation of PP also show a melt index increase, although it

does not increase as much as after processing, Figure 2(b). That indicates that thermo-oxidation alone has a lower influence on polymer degradation than thermomechanical degradation which takes place during processing, this is opposite to the results acquired for styrenic polymers.[21] A plausible cause for a larger influence on the melt properties in the initial stage of thermal oxidation is that due to the high temperature the additives close to the surface of the material leave the matrix, followed by subsequent stabilization by the additives incorporated in the bulk of the material.

The results in Figure 2 show that melt index of HDPE increases slightly with each processing cycle, which was also pointed out by Luzuriaga et al.,[22] suggesting chain scission as a cause. The change is, however, not significant enough for the alteration of the mechanical properties. This is supported by the tensile testing and the analysis of the changes in molecular weight by SEC, Table II, where insignificant alteration in the molecular weight of HDPE was shown. The very small change in M_w indicates crosslinking, this was, however, not confirmed by the analysis. According to Bernado et al. and Cruz and Zanin,[23,24] the degradation mechanism of HDPE consists of simultaneous crosslinking and chain scission

TABLE II
SEC Analysis of Molecular Weight Changes in PP and HDPE Due to Multiple Processing

Processing cycles	PP			HDPE		
	M_w	M_n	PDI	M_w	M_n	PDI
0	240,000	60,000	4.0	60,000	14,400	4.2
1	220,000	55,000	4.0	61,000	14,300	4.3
3	200,000	53,000	3.8	61,000	13,500	4.5
5	195,000	55,000	3.5	60,000	13,600	4.4
6	190,000	54,000	3.5	60,000	13,500	4.4
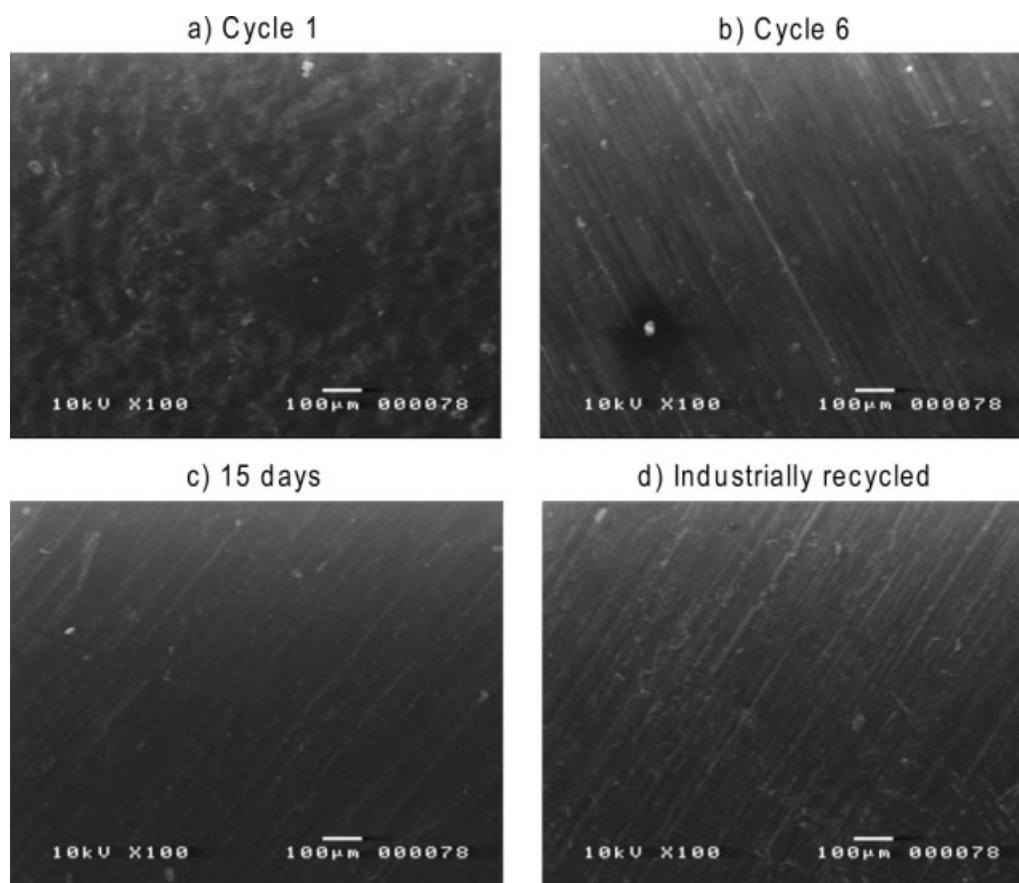
Figure 3 SEM micrographs of (a) one time processed, (b) multiprocessed (cycle 6), (c) aged (15 days), and (d) industrially recycled PP.

which might explain the insignificant changes observed by SEC. However, the form of the SEC peak became somewhat wider during degradation, indicating that crosslinking takes place, thus supporting the latter hypothesis. The thermal oxidation of HDPE does not influence the melt index. The polymer retains its viscosity. This implies that no decrease in molecular weight due to thermo-oxidation occurs.

The industrially recycled PP has high MFR, 15.3 g/10 min, as a result of the polymer degradation during its processing, exploitation life-time, recycling technique and reprocessing. However, the samples tested consisted of a mixture of PP grades which also may influence the melt index depending on the materials original viscosity and additives. The industrially recycled HDPE could not be studied due to too high viscosity. An explanation could be that the molecular weight of the recycled blend was too high, but no problems during processing were observed. Another explanation could be that the MFR was lower than 1, which is according to typical values for HDPE used in packaging applications, making it difficult to examine with the available equipment.

The results from surface analysis of both PP and HDPE by SEM clearly demonstrate considerable changes in surface morphology. The micrographs in Figure 3 show that the surface becomes damaged with small cracks and scrapes after both submission to reprocessing and ageing. The orientation of the material can be seen after both multiple processing and the thermal treatment of polymers, Figure 3(b,c). The change is obvious already after the fourth reprocessing cycle. An interesting observation was made for the surface of the polymer after 5 days of thermal treatments; it smoothens, which indicates a rapid change in the polymer morphology when exposed to heat. After 15 days in 120°C, the surface of the material appears scraped. Aurrekoetxea et al. have suggested that the reprocessing of PP reduces the spherulite size since contaminants are introduced into the matrix, enhancing the amount of nuclei sites. It was stated that crazing is the main mechanism of deformation in PP. This in term can explain the morphological changes observed in this study.[25]

It is interesting to note that the surface images of both the six times reprocessed and 15 days aged materials are quit similar to the industrially recycled sample, Figure 3(d), implying that the real recycling

	PP		HDPE	
	T_m (°C)	X (%)	T_m (°C)	X (%)
Processing cycles				
0	166.2	61	131.8	74
1	160.1	51	132.3	75
2	160.0	52	131.7	77
3	159.8	51	134.3	78
4	158.9	51	132.2	79
5	159.0	51	132.7	78
6	160.7	53	131.9	81
Accelerated thermal degradation				
5 days	160.8	52	131.7	69
10 days	159.1	48	131.8	74
15 days	159.3	51	132.0	71
Industrially recycled				
	160.9	29	131.5	56

gives rise to the same set of degradation mechanisms as the modeled recycling.

When the PP material is processed for the first time the melt temperature decreases, as the crystallinity decreases by 10%, thereafter both the temperature and crystallinity remain stable throughout reprocessing, Table III. The initial decrease is probably due to the storage effect of the virgin material and orientation effects during processing, reheating, and cooling. The later reprocessing cycles do not indicate changes in either melt temperature or crystallinity although degradation by chain scission proceeds. The amount and the thickness of the crystals remain unchanged.

The almost consistent melt temperature throughout the reprocessing and thermal oxidation of HDPE show that no substantial changes in the mechanical properties should be expected which agrees well with the results from both the tensile test and the

melt mass-flow rate measurements, similar to conclusions by Boldizar et al.[26] It is plausible that during the reprocessing the free chain ends may rearrange giving a gradual increase in crystallinity.

Figure 4 presents the melt temperature of the industrially recycled PP which was similar to the melt temperature of a one time processed PP. The DSC curve, however, showed a small melt peak at ∼ 130°C, which can derive from PE that is difficult to separate from PP during recycling. The melt temperature of the industrially recycled PE was similar to the melt temperature of a one time processed HDPE. The crystallinity of the recycled materials was, however, ∼ 20% lower. The crystallinity can be affected by the variations in molecular weight or by additives, both probable causes since the recycled specimen consists of materials blends and have probable variations in the material grade within the blends.

No evident alteration of the oxidation temperature (T_{ox}) could be observed after reprocessing and thermal aging of both PP and HDPE (Table IV). Taking into account that T_{ox} is analyzed as a bulk property, this is an indication that the stabilization system was not depleted, even after several reprocessing cycles, and thereby the amount of hydroperoxides that degrade and form radicals may still be neutralized. To even closer investigate the oxidative stability of the materials, OIT was determined. The results, presented in Table V, pointed out that the PP stabilization system was indeed affected by both reprocessing and even at a higher degree by ageing, due to consumption of antioxidants. Both PP and HDPE were highly affected after two processing cycles, but HDPE remained quit stable during thermal ageing. As expected OIT measurements showed more detailed results than T_{ox} due to the higher
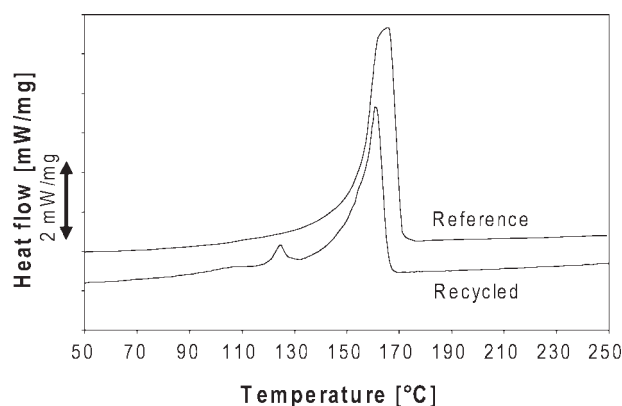
Figure 4 Comparison of melt temperature thermograms of virgin and industrially recycled PP.

	PP	HDPE
	T_{ox} (°C)	T_{ox} (°C)
Processing cycles		
0	205.2	226.4
1	206.9	225.6
2	206.5	224.2
3	207.6	224.1
4	207.2	227.2
5	207.5	225.2
6	205.4	225.6
Accelerated thermal degradation		
5 days	203.2	228.9
10 days	205.5	224.4
15 days	205.2	228.3
Industrially recycled		
	209.7	210.7

TABLE V
OIT Results for Multiple Processed and Aged PP and HDPE

	PP	HDPE
	OIT (min)	OIT (min)
Processing cycles		
0	11.99	11.03
1	10.19	10.72
2	7.41	8.58
3	5.89	8.57
4	6.79	7.29
5	6.79	7.33
6	6.60	6.31
Accelerated thermal degradation		
5 days	6.46	10.98
10 days	7.03	10.93
15 days	4.31	10.76

sensibility of the technique. The industrially recycled PP and HDPE showed a slightly higher and lower T_{ox} respectively, which was to be expected due to probable larger extent of degradation of the materials during the service life.

ATR-FTIR analysis showed extensive surface oxidation that occurred during the multiple processing of PP, Figure 5(a), showing that the oxidative thermal degradation increases during injection molding. The results clearly showed changes in the chemical structure of PP due to oxidative mechanisms.

The studied area of wavelengths displaying the occurrence of a series of functional groups, here also denoted as oxidation indicators, consists of ketones, aldehydes, and carboxylic acids between 1550 and 1800 cm^{-1}. This is the region where the carbonyl groups (i.e., oxidation indicators) have strong absorption bands. For PP, a shift to a lower wavelength within the area took place after the fourth reprocessing cycle, where the peak at 1648 cm^{-1} cor-

responding to the α,β-keto aldehydes formation decreased, while the peak at 1592 cm^{-1} corresponding to the carboxylic acid salt groups increased. However, the peak at 1592 cm^{-1} represents carboxylate species which may arise both from degradation of the polyolefins and the presence of stearate in the PP.

The carbonyl area for HDPE remained almost unaffected after six reprocessing cycles. These results correspond to the results obtained from physical- and mechanical-property analyses performed in this study. Accordingly, HDPE appears to withstand the thermo-oxidative and mechano-oxidative degradation to a higher extent than PP. The high oxidation stability of HDPE is in accordance with other studies.[26]

The industrially recycled polymers seem to contain lower amount of oxidation indicators, earlier defined. This could be the result of a loss of low molar mass products from the matrix during use and reprocessing of the polymers but in general it is very difficult to draw a conclusion that the real recycled polymers are less affected by the oxidation since the other results show a higher overall degradation.

Figure 6 shows that during the accelerated thermal oxidation the carbonyl index, for PP and HDPE, increased continuously as a result of the degradation of the material surface and the antioxidant consumption. This was expected due to the possibility of increased oxidation over time and in accordance with the OIT results.

CONCLUSIONS

The extent of the degradation processes occurring during the service life and the recycling of polymeric materials are partly unknown. It is now
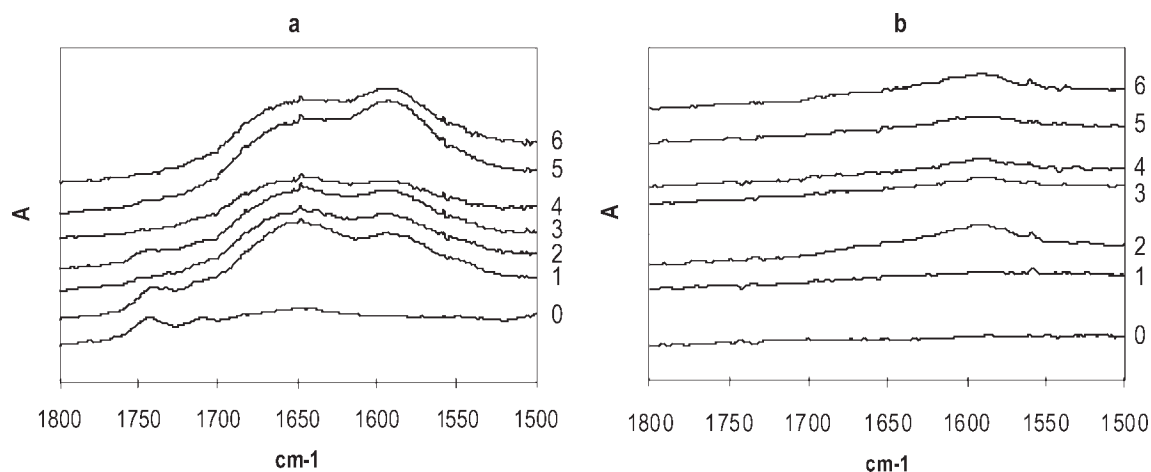
Figure 5 Carbonyl regions of multiprocessed (a) PP and (b) HDPE. Numbers 0–6 correspond to the number of the reprocessing cycles.
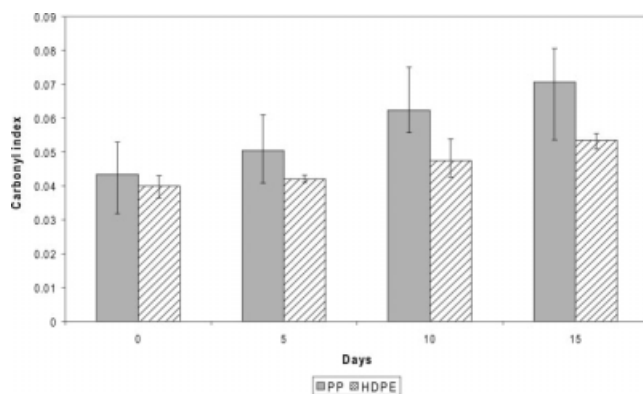
Figure 6 Carbonyl indexes of thermally aged PP and HDPE.

demonstrated that it is possible to model these processes by reprocessing and adding an ageing step. This work presents correlation between macroscopic/bulk (mechanical) and microscopic/molecular properties (molecular weights, chemical composition, thermal, and morphological). The thermal and tensile properties of PP and HDPE do not deteriorate significantly during the multiple processing even though the degradation of the materials occurred. However, a large increase is observed in the melt flow index of PP because of the chain scission due to thermomechanical ageing. On the other hand, the melt flow index of HDPE remains almost unchanged. The industrially recycled polymers show somewhat poorer mechanical properties than the materials used in modeled recycling, nevertheless, the polyolefins are well-suited materials for several recycling cycles.

This study proved that the test protocol allowed the prediction of properties of recycled polymeric materials during reprocessing and thermal degradation and is a good tool to model the service life and repetitive processing of plastics subject to recycling.

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