

Thermal and Fire Degradation of Recycled and Polluted Polypropylene-Based Materials

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ABSTRACT: In this study, the effect of processing cycles and two pollutants (engine oil (HM) and ethylene glycol (EG)) on the thermal and rheological properties of polypropylene-based materials (108MF97 and 7510) has been studied. It was investigated if polymers coming from bumper face bar could keep their properties and can be reused after recycling. The different results demonstrate that the two polymers that were polluted and recycled do not show any

decrease of their intrinsic properties. Moreover, for one of the two polymers (108MF97), the presence of engine oil enables to increase the thermal stability and reaction to fire. Finally, it appears that the reuse of such polymers is possible. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2270–2279, 2009

Key words: polyolefins; recycling; flame retardance; thermal degradation; kinetic analysis

INTRODUCTION

Automotive industry uses numerous types of materials, from metals to polymers. Nowadays, the main objective is to make a vehicle with improved esthetic and comfort characteristics. There are also general requirements such as weight and material consumption, besides ecological requisites. That is why the European directive 2000/53/EC¹ imposes waste reduction by reusing the plastics coming from the end-of-life cars. In 1999, in France, the end-of-life cars generated 160,000 tonnes of plastics wastes and before 2015, 1.3 million tonnes are expected. It is planned to reuse most of them in vehicles. Automotive industry is then facing the challenging problem of devising economically viable routes for recycling the plastic components of end-of-life cars.^{2–5}

Accordingly, the mechanical recycling of polyolefins containing polypropylene (PP) seems possible. Indeed, polypropylene blends used for bumper face bar have relatively simple material compositions and because of their large size, they have been targeted for recycling. There is a tendency to increase the PP proportion in the molding compositions for the automotive industry; so, it becomes necessary to identify and

to solve the problem of pollution, which can soil these materials (such as for example traces of oils and various organic liquids).

In this article, we focus on the characterization and thermal degradation of two polypropylenes, which are used by automotive industry: a copolymer PP/ethylene-propylene-rubber (EPR) utilized for front part bumper face bar, taken as a model material and hereafter called 108MF97, and a polymer blend used for back bumper face bar PP/EPDM/talc (polypropylene/ethylene-propylene–diene monomer/talc) hereafter called 7510. Those polymers underwent two types of pollution often mentioned in the field of polluted thermoplastics (engine oil (HM), ethylene glycol (EG)) and also several extrusion runs simulating the thermomechanical effect of the recycling process.

MATERIALS AND METHODS

Materials

Resin 108MF97 supplied by SABIC is a high impact polypropylene obtained by direct synthesis similar to spheripol process.⁶ The reinforcing phase consists of spherical copolymer EPR nodules. These EPR nodules are linked to the principal PP matrix, thanks to the synthesis. Resin 7510 also supplied by SABIC is a mechanical mixture obtained by extrusion of PP loaded with talc and EPDM.

To determine the amount of elastomers in polymers, the two PP-based materials are first dissolved in stabilized Irganox 1010 trichlorobenzene at 210°C.

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Cooling down the mixture, the PP phase crystallizes while the elastomer is kept in solution. PP is filtered, and the elastomer is recovered, dried up, and weighed. The amounts of elastomer are, respectively, 22 and 20% for 108MF97 and 7510.

Pyrolysis at 650°C leads to the amount of talc present in PP108MF97 and PP 7510 : 0.5 and 12%, respectively.

Regarding the pollutants, synthetic engine oil (HM) supplied by Total Activa 7000 10W40 and ethylene glycol (EG) supplied by Prolabo were selected. About 2 wt % of each pollutant was incorporated in mass during extrusion of the PP-based materials.

Sample preparation

The successive extrusion runs were carried out on a corotating twin screw extruder clextral BC 21. The temperature profile is 180-200-230-230-230°C. The average residence time is about 52 s at a flow rate of 10 kg/h (see screw profile in Table I).

Granulates are then molded at 230°C using an injection molding machine Billion Visumat 1000 for manufacturing 300 × 100 × 3 mm³ plates.

Sample characterization

Rheological behavior

Molar masses and their distributions are determined by steric exclusion chromatography. Experiments are performed on a Waters Alliance 2000 device equipped with refractometric and viscometric detectors. PP is dissolved at 150°C in trichlorobenzene with 1% of Irganox 1010 for 2 h. The chromatogram is fixed at 135°C. Because of the high amount of talc in 7510, those materials were not analyzed.

Flow experiments are carried out on a capillary rheometer Haake Rheoflizer, and the flow curves are corrected according to the Rabinowitch procedure.

TABLE I
Screw Profile

Nature	Screw pitch (mm)	Length (mm)
f	33.33	100
f	33.33	50
f	25	50
f	25	50
f	16.66	50
Ma-56°	6.25	75
cf	25	25
f	16.66	100
f	33.33	100
f	25	100
Ma-56°	6.25	75
cf	25	25
f	16.66	100

f, direct flight; cf, reverse flight; Ma, kneader block.

Melting and crystallization temperatures

Differential scanning calorimetry (DSC) measurements were performed in nitrogen flow (50 mL/min) at a heating rate of 10°C/min on a DSC Q100, TA Instruments. Melting temperature, T_m , and crystallization temperature, T_c , were evaluated from the second heating runs for each sample (temperature plateau for 30 min at 200°C at the end of the first heating run to remove completely the thermal history of the sample), on 7.5 mg (± 0.1 mg) in alumina pans.

The degree of mass crystallinity, X_m , is calculated using:

$$X_m = \frac{\Delta H_{PP}}{\Delta H_{100\%}} = \frac{\Delta H_{\text{sample}}}{\Delta H_{100\%}} \times \frac{w_{\text{sample}}}{w_{PP}} = \frac{\Delta H_{\text{sample}}}{\Delta H_{100\%}} \times \frac{1}{\text{rate}_{PP}} \quad (1)$$

where $\Delta H_{100\%}$ is the enthalpy of pure PP (149 J/g); w_{sample} and w_{PP} are the weights of sample and pure PP, respectively; rate_{PP} is the quantity of PP in the sample (78 for 108MF97 and 68 for 7510).

Thermal degradation

Thermogravimetric analysis (TGA) was carried out using a TA Instruments SDT Q600 in air flow (100 cm³/min) at 10°C/min from room temperature up to 800°C. Samples of 10.5 mg (± 0.1 mg) were put in open alumina pans.

Kinetics of degradation

The kinetic parameters of thermal decomposition can be calculated using methods developed by Kissinger,⁷ Ozawa,⁸ and Friedman.⁹ Our kinetic approach is based on the one proposed by Opfermann¹⁰ where the reaction is expressed by the stoichiometric equation:



The rate of reaction can be described in terms of two functions: $k(T)$ and $f(\alpha)$. Thus,

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (3)$$

where k is the kinetic constant, $k(T) = Ae^{-E_a/RT}$. According to the Arrhenius law, A is the frequency factor, E_a is the activation energy, α is the degree of conversion and $f(\alpha)$ is the so-called "reaction equation" or in the case of TGA, the "degradation function."

All reactions are assumed to be irreversible. In the case of degradation and as the evolved gases are continuously removed by the fluid flow in the TGA chamber, this is a reasonable assumption. It is also assumed that the overall reaction [eq. (2)] is the sum of individual reaction steps with constant activation

TABLE II
Molar Masses and Degree of Polydispersity Index of Recycled 108MF97

Reference	Mn	Mw	IP
0P	39,900	160,300	4
1P	34,000	132,600	3.9
3P	31,000	129,800	4.2
6P	32,600	124,600	3.8
9P	31,300	118,200	3.8
12P	30,500	117,300	3.85

energy. The model can then include competitive, independent, and successive reactions. The equations are solved with multivariate kinetic analysis (determination of the parameter via a hybrid regularized Gauss-Newton method or Marquardt method).¹¹

Nonisothermal curves of a thermal reaction can satisfy the kinetic equations developed for the kinetic analysis of "nth order reactions" even if they follow a quite different mechanism.¹²

Kinetic analysis and modeling of the degradation of the samples were made using an advanced thermokinetic software package developed by Netzsch Company.

Mass loss calorimeter

Fire testing technology (FTT) mass loss calorimeter was used to carry out measurements on samples following the procedure defined in ASTM E 906. The equipment is identical to that used in oxygen consumption cone calorimetry (ASTM E-1354-90), except that a thermopile in the chimney is used to obtain the rate of heat release (RHR) rather than employing the oxygen consumption principle. Our procedure involved exposing specimens measuring 100 mm × 100 mm × 3 mm in horizontal orientation. External heat flux of 35 kW/m² was used for running the experiments. This flux corresponds to common heat

flux in mild fire scenario. When measured at 35 kW/m², RHR is reproducible to within ± 10%. The data reported in this article are the average of three replicated experiments.

RESULTS AND DISCUSSION

Molar weight distributions and rheological behavior

The intrinsic properties of materials in terms of molar mass and viscosity are first examined to investigate the recycling and the pollution effects.

Concerning the SEC, all chromatograms of 108MF97 are described by nearly Gaussian curves. 7510 can not be studied by SEC because of the presence of talc, what justifies the additional flow behavior investigation.

The first step of the study consists of evaluating the effect of the recycling steps.

Table II shows that molecular weight (Mw and Mn) decreases with the number of extrusion runs, whereas the polydispersity index remains practically constant. It can be explained by the beta scission of polymeric PP chains.

Flow curves show significant differences particularly at low shear rate (Fig. 1). Those results are consistent with the evolution of molar masses. However, the degradation of 7510 is less. Talc seems to provide a stabilizing effect to 7510 (Fig. 1).

For the rest of our study, we shall be interested only in six-time recycled polymer because it is the one that presents a good compromise between industrial and scientist interests.

To study the influence of pollutants in polymers, the pollutants (motor oil (HM) and ethylene glycol (EG)) were incorporated in pure materials during the first extrusion run. The resulting samples are referenced as follows (Table III).

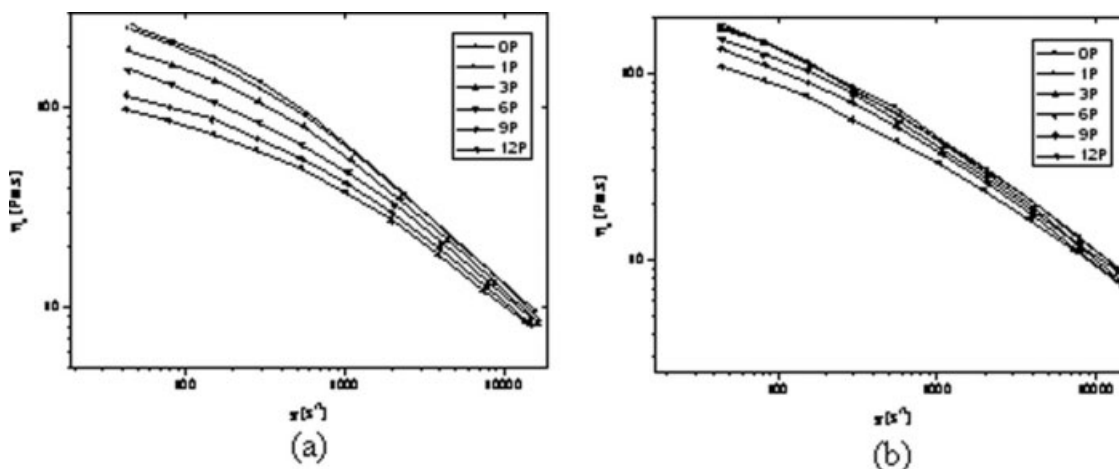


Figure 1 Influence of recycling on flow curves for (a) 108MF97 at 230°C and (b) 7510 at 230°C.

TABLE III
Molar Masses and Polydispersity Index
of Polluted 108MF97

Reference	Mn	Mw	IP
1P	34,000	132,600	3.94
1P 2HM	34,300	139,000	4.05
1P 2EG	37,000	149,600	4.05
1P 2EG 2HM	38,600	163,500	4.2

Considering an acceptable standard deviation of more or less 15%, polydispersity index remains similar. Mw seems to be affected by the presence of pollutants during the extrusion process. Surprisingly, the weight molar mass is recovered at the virgin material level when both pollutants are present.

To confirm these results, viscosity measurements have been performed. It is observed that pollutants do not modify the flow curves for 108MF97 and for 7510 (Fig. 2). So, it can be concluded that pollutants do not significantly modify the molar weight distribution of both materials.

Now, concerning the materials that are both polluted and recycled, Table IV shows that the presence of pollutants limits the degradation of polymers. Furthermore, when both pollutants (EG and HM) are associated, Mn and Mw values are recovered at the virgin material level.

Moreover, Figure 3 shows that polluted recycled materials keep close to references. Thereby, the stabilizing effect of the combined pollutants (engine oil (HM) and ethylene glycol (EG)) is undeniable. In addition, the stabilizing effect of talc is confirmed because the difference between reference 7510 and polluted recycled 7510 is negligible.

Finally, the SEC and flow studies show that recycling decreases the intrinsic properties of products, whereas pollutants do not have a deleterious effect.

Furthermore, we notice that for both recycled and polluted products, the properties do not change, and the negative effect of recycling is counterbalanced by the presence of pollutants during the extrusion runs. It is not the purpose here to investigate this point, but further work is in progress to explain it.

Differential scanning calorimeter

Differential scanning calorimetry (DSC) allows to determine other intrinsic properties including crystallinity and melting enthalpy.

Figure 4 shows typical DSC curves.

Thermograms (Fig. 4) show the melting point of polypropylene (α phase) at 166°C. A second melting point, which corresponds to polyethylene (polyethylene is contained in the elastomeric phase), is observed at 113°C.^{13,14} In fact, to make co or ter-polymers of ethylene-propylene, ethylene is usually introduced in excess and lead up to polymerization of polyethylene.¹⁵

Table V gathers melting (T_m) and crystallization (T_c) temperatures, and the crystallinity rate, X_m , calculated from DSC curves similar to those of Figure 4.

108MF97 and 7510 materials exhibit melting and crystallization temperatures higher than pure polypropylene.^{13,16} The difference is larger for the crystallization. According to Alonso et al.,¹⁷ as soon as talc is present in the polymer, the crystallization temperature raises. They also concluded that this effect does not increase linearly with the talc content. It is consistent with our measurements.

For 108MF97, melting temperature is the same for pure and polluted materials (166°C). However, there are significant differences between crystallization temperatures. The addition of ethylene glycol (EG) decreases this temperature from 131°C for pure PP and PP polluted with engine oil (HM) to 127°C, that is to say crystallization phenomenon is delayed.

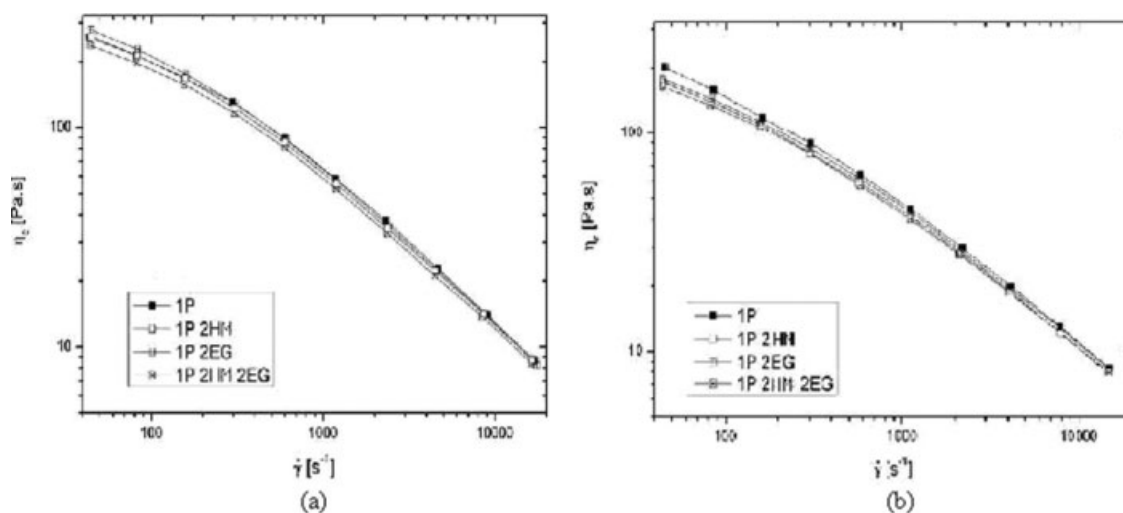


Figure 2 Influence of pollutants on flow curves for (a) 108MF97 at 230°C and (b) 7510 at 230°C.

TABLE IV
Molar Masses and Degree of Polydispersity Index of
Polluted and Recycled 108MF97

Reference	Mn	Mw	IP
108MF97 0P	39,900	160,300	4.1
108MF97 6P	29,000	116,000	4
108MF97 6P 2HM	23,300	129,000	5.5
108MF97 6P 2EG	33,100	129,000	3.9
108MF97 6P 2EG 2HM	37,700	151,000	4

Furthermore, this phenomenon is more pronounced when ethylene glycol (EG) and engine oil (HM) are simultaneously added to the copolymer (123°C). It seems that pollutants modify the crystals size of PP but not enough to change the melting temperature because of the low amount of pollutants and they play the role of antinucleating agent.

Regarding polymer 7510, there is no difference between polluted and pure materials for the melting temperature as well as for the crystallization temperature. These results are similar to those obtained during the studies of viscosity. So, the stabilizing effect of talc is still confirmed.

Thermo gravimetric analysis

There is much literature on mechanisms of oxidative degradation of polypropylene.^{18–23} Many researchers agree fundamentally with the following mechanistic scheme:

Initiation:



Propagation:



Chain branching (including chain scission):



Figure 5 shows that polluted and pure 108MF97 begin to degrade at a similar temperature (about 220°C). Two apparent degradation steps are observed: the first (220–410°C) is the early stage of thermal oxidative degradation called “induction period”²¹ and corresponds to reactions (I) (II) (III), and the second (420–500°C) corresponds to reactions (IV) and (V) and represents a hydroperoxide decomposition.²³

Moreover, at 800°C, a residue (0.4%) is observed; this residue can be assigned to talc, which is used as a mold lubricant.

Similar conclusions may be given for 7510, [Fig. 5(b)] except the residue of 12 wt % at 600°C due to the high amount of talc incorporated in the material.

Engine oil (HM) begins to degrade at 150°C, and a “discontinuity” due to the ignition of engine oil is visible at 325°C. It should be noticed that pollutants do not modify the apparent thermal degradation of polymers (108MF97 and 7510). Even if engine oil degrades at lower temperatures than polymers, no destabilizing effect is observed in the materials containing oil.

Kinetics of degradation

The degradation of 108MF97 and 7510 in oxidative conditions and as a function of heating rate is presented in Figure 6. About 0 and 12% residues are obtained for 108MF97 and 7510, respectively, whatever the heating rate. The shape of the curves suggest an oxidative degradation of 108MF97 and 7510 involving competitive reactions because the transient residue (between 350 and 450°C) is more important when the heating rate decreases.

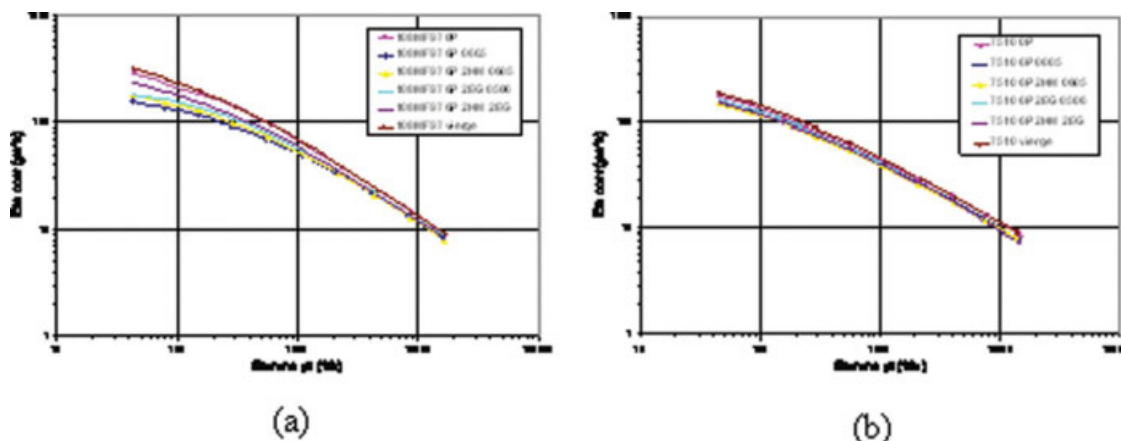


Figure 3 Influence of pollutants and recycling on flow curves for (a) 108MF97 and (b) 7510. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

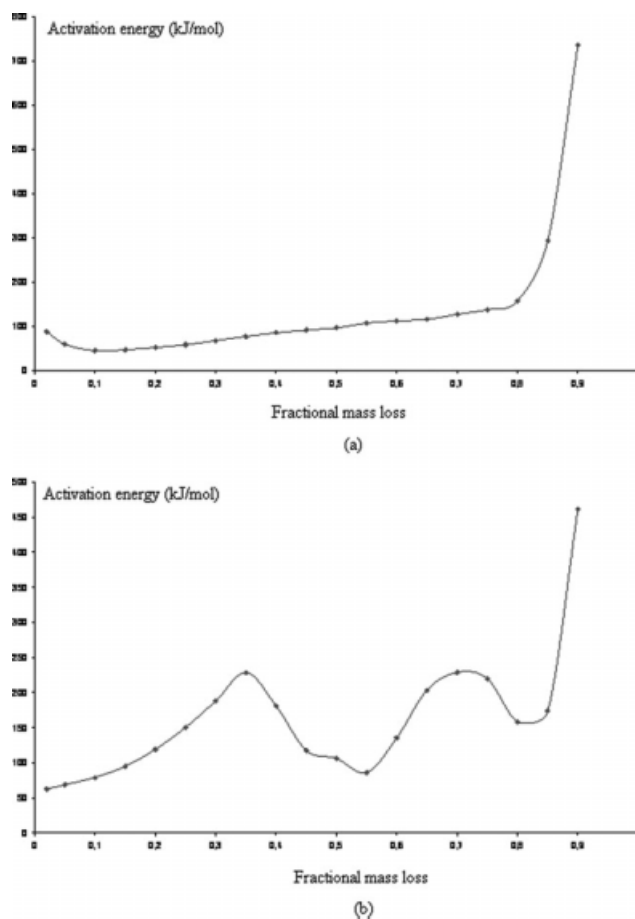


Figure 7 Activation energies of (a) 108MF97 and (b) 7510 versus fractional mass loss determined using the Friedman analysis.

rials are then degraded into C and E (final residues). Our model fits the experimental TGA curves very well (typical curves shown in Fig. 8), and the associated kinetic parameters are presented in Table VI for pure and polluted 108MF97 and 7510.

Oxidative degradation of polymers involves hydroperoxide radical in the propagation step of degradation.

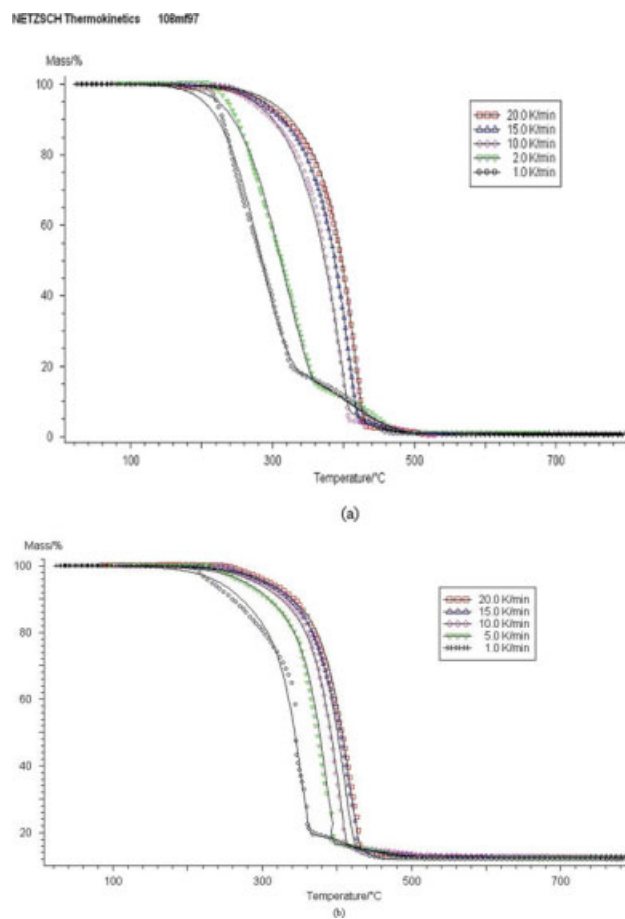


Figure 8 Simulation of (a) 108MF97 and (b) 7510. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Oxygen-initiated depolymerizations have activation energies in the 80–190 kJ/mol range.^{27,28} This supports the value calculated for reaction 1. Reaction 3 could be assigned to the molecular decomposition of hydroperoxides. The activation energy of this reaction is around 67–72 kJ/mol^{29–31} and is close to our values. Reactions 2 and 4 can be assigned to char oxidation

TABLE VI
Apparent Activation Energies of (a) Pure and Polluted 108MF97 and (b) Pure and Polluted 7510

	Log A_1 (s^{-1})	E_1 kJ/mol	Log A_2 (s^{-1})	E_2 kJ/mol	Log A_3 (s^{-1})	E_3 kJ/mol	Log A_4 (s^{-1})	E_4 kJ/mol
(a)								
108MF97	8.8	177.5	11.2	155.4	1.7	54.5	13.4	215.8
108MF97 6P	6.1	182.8	8.6	105.3	3.1	67.9	11.0	161.3
108MF97 6P 2HM	5.8	163.7	5.9	93.0	2.6	61.7	12.1	182.4
108MF97 6P 2EG	7.4	175.9	8.6	101.9	2.1	58.3	11.2	184.6
108MF97 6P 2EG 2HM	4.6	111.0	7.8	116.2	3.2	69.1	19.8	293.4
(b)								
7510	9.4	169.0	11.8	162.1	0.8	59.9	15.1	251.7
7510 6P 2EG	3.2	103.1	9.5	179.0	2.6	66.3	18.6	254.9
7510 6P 2HM	11.3	192.8	15.4	205.3	2.3	71.3	11.4	192.4
7510 6P 2EG 2HM	6.3	120.0	11.6	219.5	2.2	74.0	22.1	278.6

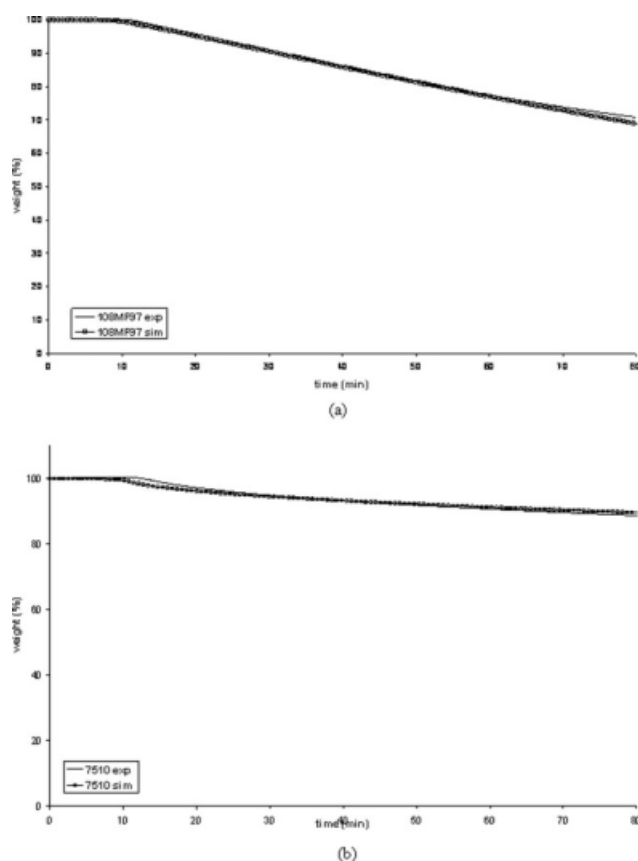


Figure 9 Comparison between experimental and simulated curves in isothermal conditions at 235°C during 80 min for (a) 108MF97.

reactions. The values of activation energies found for the reactions are similar to other studies.^{32,33}

To verify the accuracy of our modeling, we simulate the degradation of 108MF97 and 7510 in oxidative conditions as follows:

- Ramp from 25 to 235°C at 20°C/min
- Isothermal at 235°C for 80 min (235°C being the extrusion temperature of our products)

Figure 9 allows to compare the experimental and the simulated curves. It can be observed that our model can predict very well the oxidative degradation of our materials under isothermal conditions.

This approach was also applied for recycled and polluted polymers, but only the values of apparent activation energy and of the pre-exponential factor are given in Table VI.

Figure 10 compares the simulated curves of pure, polluted, and recycled polymers for an isothermal at 235°C for 250 min.

In such conditions, in the case of 108MF97, the degradation of pure polymer appears earlier than for any polluted polymer. Moreover, the presence of engine oil (HM) alone improves markedly the ther-

mal stability of pure 108MF97. Skachkova et al.³⁴ have already worked on PP/EPD (ethylene-propylene-diene elastomer)/oil system. Thanks to atomic force microscopy, they have shown that on heat treatment a multilayer structure is formed near the polymer surface. According to Skachkova et al., this structure can hinder oxygen diffusion into the polymer bulk and thus can prevent the major part of the thermoplastic elastomer from thermooxidative degradation. This phenomenon could explain the stabilizing effect obtained with engine oil on 108MF97.

On the contrary, the addition of pollutants destabilizes the 7510-based material. Indeed, Figure 10(b) shows that the presence of ethylene glycol (EG) leads to a strong thermal destabilization of 7510. This destabilization is less for products polluted with engine oil and with both pollutants simultaneously even if these products remain less stable than the reference. This effect is not clear to us, and further studies are in progress to explain the phenomenon.

Mass loss calorimeter

According to the results obtained by TGA and kinetics of degradation, it is interesting to evaluate the reaction to fire of the materials by mass loss

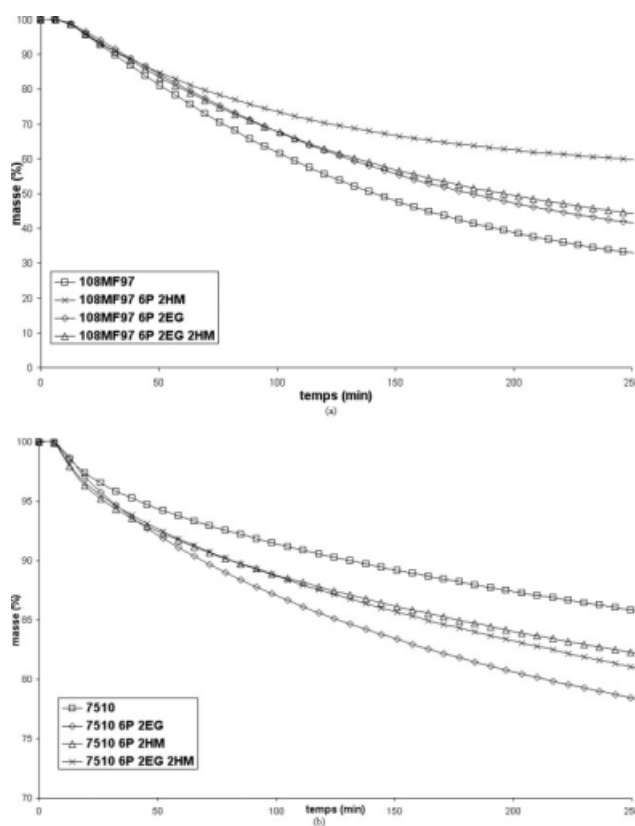


Figure 10 Degradation of (a) 108MF97 and (b) 7510 for an isotherm at 235°C during 250 min.

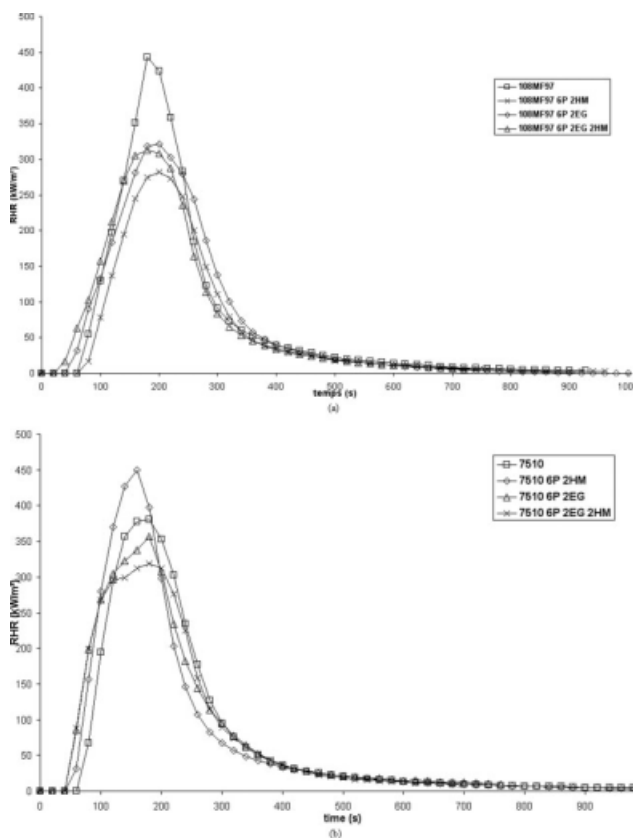


Figure 11 Comparison between experimental and simulated curves in isothermal conditions at 235°C during 80 min for (b) 7510. RHR curves of (a) 108MF97 and (b) 7510.

calorimeter recognizing that better heat stability might lead to better flame retardancy.

Figure 11 allows to study the influence of pollutants, alone or in combination, on the RHR curves of 108MF97 and 7510. For 108MF97, it can be observed that the ignition time decreases when ethylene glycol (EG) is incorporated to the polymer. The presence of ethylene glycol or both pollutants also leads to a decrease of the RHR peak by 28% with regard to the pure 108MF97. Moreover, the presence of engine oil (HM) alone increases the time of ignition and enables to decrease the RHR peak by 38% compared to pure 108MF97 (RHR peak of 108MF97 = 450 kW/m²; RHR peak of 108MF97 6P 2%HM = 280 kW/m²). It can be explained at least partially, by the higher thermal stability of materials containing engine oil as shown by kinetic analysis. This phenomenon can result from the presence of loads in the engine oil. Indeed, according to several studies already realized on engine oil,^{35,36} the minerals generally present are: phosphor, zinc, magnesium and calcium. Now, the presence of minerals, as phosphor, allows to stabilize the matrix polymer as would make it a fireproof classic agent.

Concerning 7510, all curves are similar, and the slight decrease in terms of RHR peak is not signifi-

cant. It suggests that the effect of oil is wiped out by the presence of talc.

CONCLUSIONS

The investigation of the effect of pollutants and recycling on thermal properties of polypropylene-based materials has shown that even if recycling has a negative effect on the intrinsic properties of PP, the addition of pollutants permitted to keep the polymer its initial properties. Recycling, engine oil (HM) and ethylene glycol (EG) do not modify degradation of polymers in dynamic conditions. However, in the case of a high impact polypropylene, presence of ethylene glycol reduces the crystallization rate. Using thermal degradation kinetics, we observe that engine oil provides a better thermal stability for 108MF97; this conclusion is corroborated by mass loss calorimetry suggesting that engine oil might act as a flame retardant in this particular case. No beneficial effect of pollutants is observed in the case of 7510 probably because of the high amount of talc in the material.

So, our study shows that the reuse of virgin or polluted polypropylene blends used for bumper face bar seems to be possible after a process of recycling. Results offer news perspectives to automotive industry to meet the expectations partially of the European Directive.

References

1. Directive 2000/53/EC of the European Parliament and of the Council of 18 September 2000 on end-of life vehicles. Off J L 2000, 269, 34.
2. Luda, M. P.; Ragosta, G.; Musto, P.; Acierna, D.; Di Maio, L.; Camino, G.; Nepote, V. *Macromol Mater Eng* 2003, 288, 613.
3. Pospíšil, J.; Nespurek, S.; Pfaendner, R.; Zweifel, H. *Trends Polym Sci* 1997, 5, 294.
4. Tsenoglou, C. J.; Kartalis, C. N.; Papaspyrides, C. D.; Pfaendner, R. *Adv Polym Technol* 2002, 21, 260.
5. Pfaendner, R.; Herbst, H.; Hoffmann, K. *Macromol Symp* 1998, 135, 97.
6. Urdampilleta, I.; Gonzalez, A.; Iruin, J. J.; de la Cal, J. C.; Asua, J. M. *Ind Eng Chem Res* 2006, 45, 12.
7. Kissinger, H. E. *Anal Chem* 1957, 29, 1702.
8. Ozawa, T. *Bull Chem Soc Jpn* 1965, 38, 1881.
9. Friedman, H. L. *J Polym Sci* 1965, C6, 175.
10. Opfermann, J. *J Therm Anal Calorim* 2000, 60, 641.
11. Kaisersberger, E.; Opfermann, J. *Thermochim Acta* 1991, 187, 151.
12. Opfermann, J.; Kaisersberger, E. *Thermochim Acta* 1992, 203, 167.
13. Grein, C.; Plummer, C. J. *Polymer* 2002, 43, 3279.
14. Nihlstrand, A.; Hjertberg, T.; Johansson, K. *Polymer* 1997, 38, 3581.
15. Kim, G. M.; Michler, G. H. *Polymer* 1998, 39, 5689.
16. Vleeshouwers, S. *Polymer* 1997, 38, 3213.
17. Alonso, M.; Velasco, J. I.; de Saja, J. A. *Eur Polym J* 1997, 33, 255.
18. Kato, Y.; Carlsson, D. J.; Wiles, D. M. *J Appl Polym Sci* 1969, 13, 1447.
19. Carlsson, D. J.; Wiles, D. M. *Macromolecules* 1969, 6, 597.

20. Billingham, N. C. *Makromol Chem Macromol Symp* 1989, 28, 145.
21. Audouin, L.; Gueguen, V.; Tcharkhtchi, A.; Verdu, J. *J Polym Sci Part A: Polym Chem* 1995, 33, 921.
22. Alam, M. S.; Nakatani, H.; Ichiki, T.; Goss Ben, G. S.; Liu, B.; Terano, M. *J Appl Polym Sci* 2002, 86, 1863.
23. Achimsky, L.; Audouin, L.; Verdu, J.; Rychly, J.; Matisova-Rychla, L. *Polym Degrad Stab* 1997, 58, 283.
24. Opfermann, J.; Kaisersberger, E.; Flammersheim, H. J. *Thermochim Acta* 2002, 391, 119.
25. Sewry, J. D.; Brown, M. E. *Thermochim Acta* 2002, 390, 217.
26. Friedmann, H. L. *J Polym Sci C* 1964, 6, 183.
27. Peterson, J. D.; Vyazovkin, S.; Wight, C. A. *Macromol Chem Phys* 2001, 202, 775.
28. Dickens, B. *J Polym Sci Polym Chem* 1982, 20, 1169.
29. Chien, J. C. W.; Kiang, J. K. Y. *Macromolecules* 1980, 13, 280.
30. Chien, J. C. W.; Kiang, J. K. Y. *Makromol Chem* 1980, 181, 47.
31. Rychly, J.; Matisova-Rychla, L.; Csmorova, K.; Achimsky, L.; Audouin, L.; Tcharkhtchi, A.; Verdu, J. *Polym Degrad Stab* 1997, 58, 269.
32. Vyazovkin, S. V.; Bogdanova, V. V.; Klimovtsova, I. A.; Lesnikov, A. I. *J Appl Polym Sci* 1991, 42, 2095.
33. Day, M.; Cooney, J. D.; MacKinnon, M. *Polym Degrad Stab* 1995, 48, 341.
34. Skachkova, V. K.; Erina, N. A.; Chepel, L. M.; Prut, E. V. *Vysoko Mol* 2003, 45, 2040.
35. Zieba-Palus, J.; Koscielniak, P. *Forensic Sci Int* 2000, 112, 81.
36. Zieba-Palus, J.; Koscielniak, P. *J Mol Struct* 1999, 482, 533.