Polyolefines Mechanical Recycling Considering the Carbonyl Variation During the First Life (II)

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A degradation mathematical model based on the dependence of the carbonyl index by the degradation time to measure the polyolefins degradability was proposed. The mathematical model was verified with good results with own and literature degradation data. It was demonstrated that the three aging parameters of the mathematical model that can be calculated by fitted method, reflect the degradation behaviour of primary and secondary polyolefins and can be used for quantitative estimation of the polyolefins degradability. The possibility of using the mathematical model for estimation the opportunity of using the mechanical recycling as recycling method is the practical importance of the obtained results. There is also, a mathematical demonstration of the reason for which the polymers can not be infinitely recycled as other materials like metals, glass e.g.

Keywords: mechanical recycling, ageing parameters, contamination

The renewable resources usage, the bio-degradability and the recyclability are the criteria which are the base of the development of the new plastic materials generation and of the plastic products manufacture designing. During the entire mechanical recycling experience it was observed that, even after the blending of degradated polymers with primary ones , the physical and mechanical properties of the obtained blends are acceptable and sometimes comparable with the properties of the neat polymers, the degradation induction time is smaller than that of primary polyolefins.

In [1] it was demonstrated that for a given "contamination" it is possible to estimate,, the degradation rate, the induction period and the product service life considering the carbonyl growing in the primary and secondary polyolefins blends using the mathematical expressions of the "contamination" (formula 1). According to [1], the "contamination " means the carbonyl growing of the primary with the secondary polyolefins blends durind the new material life.

$$[C] = \frac{\frac{[P][C_0]}{[P-C_0]} \cdot \exp(K \cdot [P] \cdot t)}{1 + \frac{[C_0]}{[P-C_0]} \cdot \exp(K \cdot [P] \cdot t)} \qquad (1)$$

where:

[P], [C_0] and K are the ageing parameters and are related with the model parameters *m*, *n* and *p* by the following mathematical expresions:

$$m = \frac{[P][C_0]}{[P-C_0]} \quad (2); \qquad n = \frac{[C_0]}{[P-C_0]} \quad (3); \qquad p = K \cdot [P] \quad (4)$$

Taking into consideration the equation (1) it can be observed that by blending the primary with secondary polyolefins, the carbonyl concentration of the blend ([C_0]) will be inevitable greater than the carbonyl content of the primary polymer.

Regarding the things in this way, it can be understood why the mechanical recycling, which present at a first sight, a great advantage as a new raw material source, is used only in a very few ratio, as a method for polyolefins mechanical recycling [1].

The proposed "contamination" mathematical expression was verified with good results, based on the fitting method, using literature and own degradation data [1].

The paper aim is to demonstrate the measure in which the aging parameters calculated according to the new proposed mathematical model for polyolefins degradation [1] reflects the polyolefins degradation susceptibility and the possibility of use of the ageing parameters for analysing the opprotunity of the post usage polyolefins mechanical recycling .

Experimental part

For polyolefins ageing studies 0.1 mm thin films obtained by the pressing techniques that were naturally and artificially degradated were used. Periodicaly, the carbonyl index and physical and mechanical properties it were determinated.

The mechanical recycling studies were made on the natural and artificial degradated films .

Materials

- neat polyolefins: A12FMA /005 low density polyethylene (LD – PE), Moplene A 30 G and F 401 polypropylene;
- secondary polyolefins from agriculture used films and used accumulators, decontaminated through shredding, whashing and drying.

Characterization

The degradation degree: carbonyl index (IR measurements), molecular weight (viscozimetric measurements) and physical and mechanical properties.

Results and discussions

For polyolefins degradation susceptibility characterization, it was comparatively analyzed the degradation behavior of primary and secondary polyolefins using the ageing parameters, [P], [C_0] and K calculated based on the 2 - 4 equations.

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Table 1
THE INFLUENCE OF THE DEGRADATION FROM UTILIZATION ON THE VALUES OF THE AGEING PARAMETERS FOR MECHANICAL RECYCLED LD-PE (AS FOR FIG.1)

Polymer	[P]	K	$[C_0]$
Primary LD-PE	18.22	0.0003	0.567
Mechanical recycled LD-PE	26.17	0.0002	1.688

The degradation susceptibility of mechanical recycled photo-degradated low density polyethylene

It is compared the photo – oxidative resistance of the films molded from mechanical recycled photo-degradated low density polyethylene (LD – PE) [2] with that of a film molded from primary LD – PE. The quantitative differences between the degradabitility of secondary and primary polymers is relevantly illustrated in figure 1 and by the ageing parameters values presented in table 1.

Considering the physical meaning of the *ageing parameters*, it can be noticed that, the [P] value for mechanical recycled LD – PE is greater with 43 % than [P] value for primary LD – PE, the quantity of polymer that can be oxidized during the second life is almost 40 % greater than in case of first life. Also the initial structural defects concentration of secondary polyethylene, expressed like initial carbonyl concentration $[C_0]$ is three times greater than that of primary LD-PE. For this reasons the secondary polymer will be more degradable during the service life. These results show that, a very well known situation, respectively the greater degradability of secondary polymer as compared with the primary ones , is very well illustrated by the ageing parameters.

The degradation susceptibility of mechanical recycled polypropylene from used accumulators

The quantitative differences between the photo - degradability of primary polypropylene and mechanical recycled polypropylene obtained from used accumulators, were analysed [3]. The degradation was surveyed based on the time variation of carbonyl index. The differences between the degradability of the two polypropylenes are very well reflected by the experimental [3] and calculated data obtained based on the new mathematical model (fig. 2). If we try to characterize the degradability based on the ageing parameters we obtain the values presented in table 2.

These results illustrate that the different degradability between the primary and secondary polypropylene can be quantitatively expressed by the ageing parameters, $[C_0]$, K and [P]. The secondary polypropylene from used accumulators has a greater polymeric content that can be degredate (more than 70 %) and greater initial structural defects (more than 30 %).

The degradation susceptibility of reprocessed polypropylene

Another situation in which the degradability of secondary PP was compared with of primary

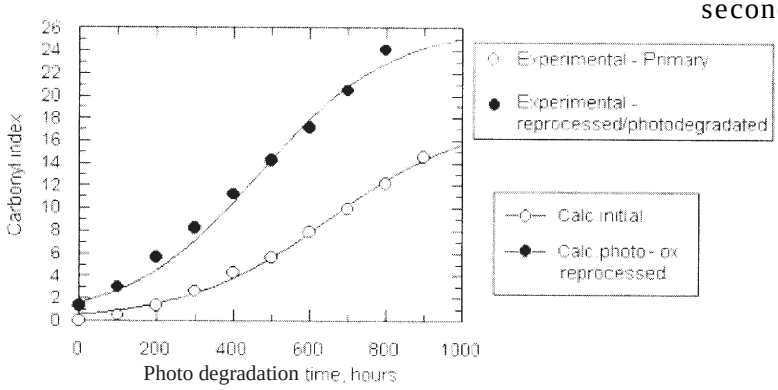

Fig.1. Experimental [1] and calculated data regarding the influence of the first life degradation of LD – PE on the degradation behaviour during the second life (Calculus parameters: First life m=0.5851; n=0.0321; p=0.0053; Second life m=1.6957; n=0.0648; p=0.0058)

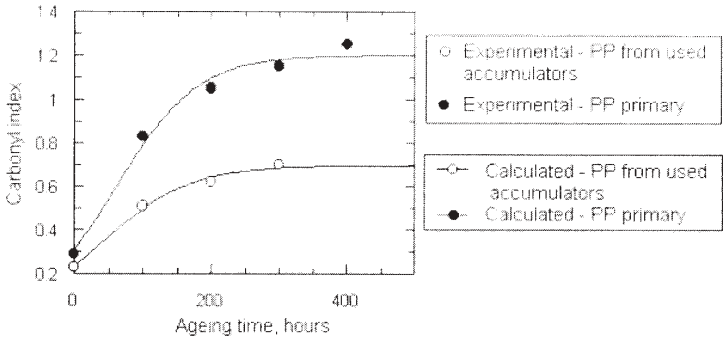

Fig.2. The experimental [3] and calculated data concerning the degradation susceptibility of mechanical recycled polypropylene from used accumulators (Calculus parameters: Primary PP *m*=0.42061; n=0.35071; *p*=0.01715; Secondary polypropylene from used accumulators *m*=0.35535, *n*=0.51010, *p*=0.01586)

Table 2
THE AGEING PARAMETERS FOR THE DEGRADATION OF THE PRIMARY AND MECHANICAL RECYCLED POLYPROPYLENE (AS FOR FIG.2)

Polypropylene	[P]	K	[Co]
Primary	0.690	0.020	0.23
From used accumulators	1.199	0.021	0.31

Table 3

THE AGEING PARAMETERS FOR THE REPROCESSED POLYPROPYLENE DEGRADATION (AS FOR FIG.3)

The reprocessing number	[P]	K	[Co]
Martor	0.2515	0	1.428
1	0.2500	0.26277	2.71102
2	0.2700	0.25475	2.40705
3	0.2700	0.19686	8.64677
4	0.4070	0.17279	3.00048

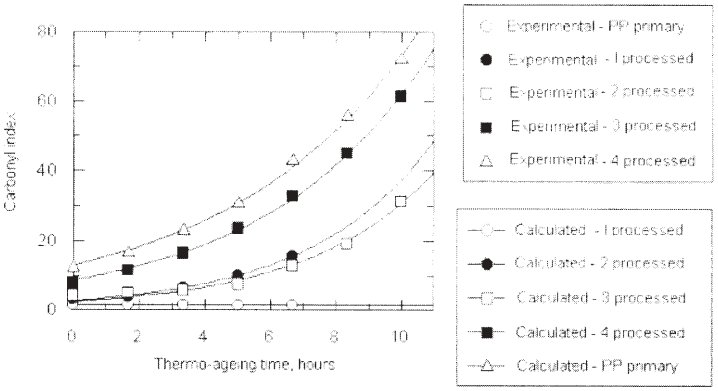

Fig. 3. The experimental [20] and calculated data concerning the degradation susceptibility of reprocessed polypropylene (calculus parameters: Martor m=1.01307; n=0.05187; p=0.00552; Once reprocessed m=1.41729; n=0.05779; p=0.00552; Twice reprocessed m=1.76256; n=0.06483; p=0.00576; Three times reprocessed m=2,08175; n=0.008718; p=0.00862; Four time reprocessed m=2.48114; n=0.008258; p=0.00833

polypropylene concerns the thermo oxidative behaviour (T = 110^{0}C) of reprocessed polypropylene [4]. The experimental and calculated data for the dependence of the carbonyl index on the degradation time and on the reprocessing number is presented in figure 3.

The quantitative estimation of the degradability of the reprocessed polypropylene based on the P, K and C_0 *ageing parameters* gives the results presented in table 3. It can be noticed that the increasing of the PP degradability with the reprocessing number is determined by the increasing, with the reprocessing number, of the polymer quantity that can be degraded, as well as of the initial concentration of structural defects and of the degradation rate constants.

The degradation susceptibility of the primary and secondary polypropylene blends

The polyolefins degradation susceptibility was also characterized based on *the ageing parameters* in case of the blends of primary with secondary polypropylene (blending ration as in figure 4 legend)[5]. It can be observed the very well correlation between the experimental and calculated data. The ageing parameters for the studied blends (table 4) demonstrate that the constant rate of the degradation and the initial structural defect concentration of the studied blends are twice greater than that of primary polymer, even if the blend contain only 5 % secondary polymer. Also the degradation rate increases with the increasing of the secondary polymers quantity from the blends.

All the above results confirm the possibility of quantitative estimation of the secondary polymer degradability based on the ageing parameters. Summarizing and analyzing the above results, it can be concluded that polyolefins degradability is very well quantitatively expressed by the ageing parameters (table 5, 6).

The mathematical expression of poliolefins degradability, expressed through the ageing parameters presented in table 5 are the measure of:

Table 4

THE VALUES OF THE AGEING PARAMETERS FOR DEGRADATION OF PRIMARY AND SECONDARY POLYPROPYLENE BLENDS (AS FOR FIG..4)

Blends composition	[C_0]	K
100 PP	0.03158	0.03722
95 PP/5 PPR	0.0510	0.0664
90 PP/10 PPR	0.0656	0.0799
75 PP/25 PPR	0.0881	0.0797
50 PP/50 PPR	0.1485	0.0684
25 PP/75 PPR	0.1971	0.0736

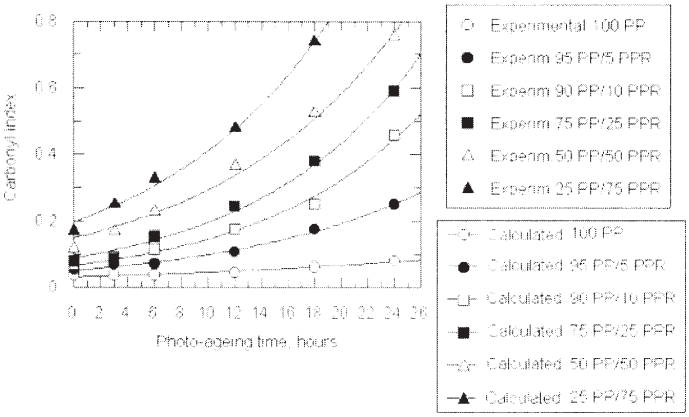

Fig.4. The experimental [23] and calculated data concerning the degradation susceptibility of the primary and secondary polypropylene blends (calculus parameters **100 PP** m=0,005; n=0.050; p=0.01; 95 PP/5 PPR m=0,0063; n=0.0031; p=0.012; 90 PP/10 PPR m=0,0059; n=0.045; p=0.02; 75 PP/25PPR m=0,0065; n=0.047; p=0.02; 50 PP/50PPR m=0,007; n=0.047; p=0.03; 25 PP/75 PPR m=0,073; n=0.05; p=0.05)

Table 5

THE AGING PARAMETERS FOR THE DEGRADATION OF SOME PRIMARY POLYOLEFINS

Polyolefin	The ageing parameters		
	[P]	K	$[C_0]$
Photo–degradated, unstabilized polypropylene [6]	0.644	0.64400	0.02060
Unstabilized photo – degradated low density polyethylene [7]	0.516	0.00397	0.00308
Photo–degradate drawn low density polyethylene, as for fig.no.4 [1]			
-Undrawn	0.40727	0.09900	0.01090
-Drawing ration: 6	1.03200	0.00387	0.04280
-Drawing ration: 12	1.08670	0.00349	0.02089
Photo – ageing stabilized polypropylene [8]			
-Stabilizers incorporation in closed blend	0.5050	0.04490	0.00980
-Stabilizers incorporation in opend blend	1.5079	0.00305	0.01876
Photoaged ethylene copolymers [9]			
-Ethylene –butene copolymers	1.27419	0.0109	0.06730
-Ethylene –hexene copolymers	1.0560	0.0153	0.03974
Photo – aged stabilized low density polyethylene [10]			
-Formulation P_1*			
-Formulation P_3*	0.515	0.0037	0.005
-Formulation P_4*	0.296	0.0038	0.0009
-Formulation P_6*	0.300	0.0050	0.0003
Photo–aged stabilized polypropylene , as for fig.no.5 [1]			
-Without stabilizer;	0.7825	0.0460	0.0480
-With HOBP[2]*	3.0200	1.0200	0.0040
-With NiDec[2]*	0.7900	0.0520	0.0130
-With ZnDec[2]*	0.7800	0.0630	0.0120
Stabilized polypropylene degradated in H_2SO_4 [3]:			
- Flowing direction;	0.1200	0,0163	0,0007
- Perpendicular on flowing direction	0.1327	0,0009	0,0004

* Different stabilization formulae; [2]*HOBP – hydroxi-4-octylbenzofenona; NiDec - nickel diethyldithyocarbamate; ZnDec - zinc diethyldithyocarbamate

- the greater degradation susceptibility of polypropylene as compared with polyethylene because of the greater number of tertiary carbons;
- the decreasing of the degradation susceptibility of drawn polyethylene with the drawn ration because of the increasing of the crystalline content with the drawn ration;
- the dependence of the polypropylene degradation susceptibility on the melting conditions. If the stabilizers had been incorporated in an open melt blend, the degradation susceptibility, as compared with the case when the blend was closed, will be greater because of the greater oxygen quantity that acts as a degradation initiator;
- the smaller degradation susceptibility for the ethylene copolymers with smaller number of ramifications because of the smaller content of tertiary carbon;
- the dependence of the degradation susceptibility of polyolefins on the stabilizers efficiency;
- the dependence of the polymer stability on the mold flowing orientation at molding. The susceptibility will be smaller on the melt flowing direction;
- the greater degradability during the accelerated ageing as compared with natural process because of the greater intensity of the degradation factors.

The mathematical expression of secondary poliolefins degradability for well known situation concerning the mechanical recycling situation, expressed through the ageing parameters, presented in table 6 is the measure of:

- the greater degradability of secondary polypropylene as compared with the primary ones because of the greater polymeric quantity that can be oxidized and the greater initial carbonyl concentration of the secondary polymers;
- the increasing of the degradation susceptibility of the mechanical reprocessed polyolefins because of the increasing with the number of reprocessing, of the polymeric quantity that can be oxidized and of the initial carbonyl concentration (fig. 5 a, b);
- the increasing of the degradability of the blends of primary with secondary polyolefins with the reprocessing number because of the increasing of the initial defect concentration $[C_0]$ (fig. 6) and of the polymeric quantity that can be degradated This means that the ageing parameters can have a great importance in quantitative estimation of the degradability of the polyolefins especially for mechanical recycled types as blends with neat polymer.

Considering all the degradation data it was possible to establish the dependence between the ageing parameters

and induction period (fig. 7 a- for polypropylene and fig.7 b for polyethylene).

It can be observed that for a convenable induction period (minimum 2000 h – Xenotest 1600) the initial carbonyl content (expressed as carbonyl index) must be not greater than 0.015, considering a stabilized polymer. So, the greater the initial carbonyl content [C_0], the greater the polyolefins degradability, the shorter the induction period and the service life (considering the service life approximate equal with induction period).

Table 6
THE AGEING PARAMETERS FOR DEGRADATION OF SOME SECONDARY POLYOLEFINS

Polyolefines	[P]	K	[C_0]
Low density polyethylene:			
- First life;	18.22	0.0003	0.567
- Second life	26.17	0.0002	1.688
Polypropylene (fig.no.2):			
-Primary;	0.690	0.020	0.230
-Mechanical recycled from used accumulators.	1.199	0.021	0.310
Reprocessed low density polyethylene [7]			
-Once;	0.501	0.0010	0.0145
-Twice;	0.908	0.0080	0.0148
-Three times;	1.285	0.0093	0.0207
-Four times.	0.950	0.0073	0.0470
Reprocessed polypropylene (as for fig.no.3) :			
-Once;	0.2515	0.00107	0.0398
-Twice;	0.2500	0.00120	0.0556
-Three times;	0.2730	0.00139	0.0797
-Four times;	0.2700	0.00158	0.1100
-Five times.	0.4070	0.00200	0.16
Neat (PP) and mechanical reprocessed polypropylene (R-PP) blends(as for fig.no.4):			
-100 PP;		0.03722	0.03158
-95 PP / 5 R – PP;		0.06640	0.05100
-90 PP / 10 R – PP;		0.06560	0.07990
-75 PP / 25 R – PP;		0.08810	0.07970
-50 PP / 50 R – PP;		0.14850	0.06840
-25 PP / 75 R – PP.		0.19710	0.07360

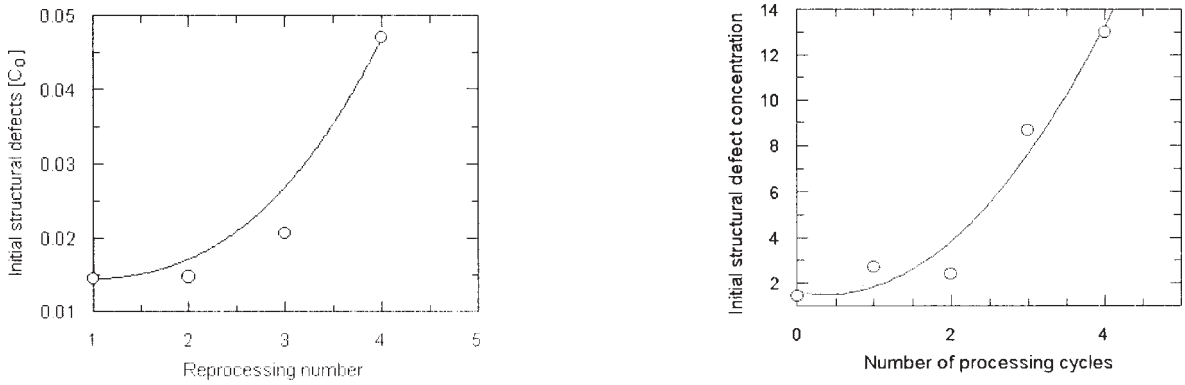

Fig.5. The increasing of the initial carbonyl content of the reprocessed polyolefins with the reprocessing number (low density polyethylene (a), polypropylene (b))

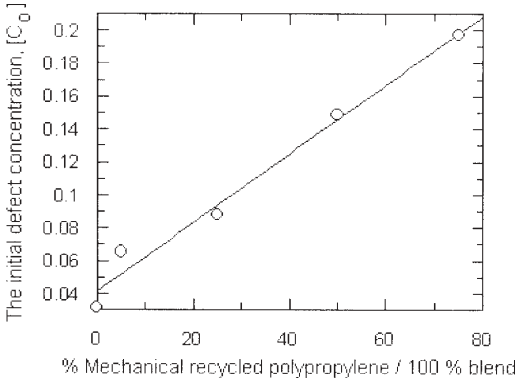

Fig.6. The increasing of the carbonyl content of the blends of neat and secondary polypropylene with the secondary polypropylene content

Practical importance of the mathematical expression of the polyolefines degradability

The very well concordance between the experimental and calculated data validata the premises of the mathematical model. The possibility of mathematical expression of the degradability has practical importance, especially for mechanical recycling. From the three ageing parameters, [C_0] has a special importance that will be demonstrated in the followings especially for the blends of secondary with primary polyolefins.

In case of the blends of primary with secondary polymers, because of secondary polymer presence, inevitable the initiate carbonyl content of the blend will be

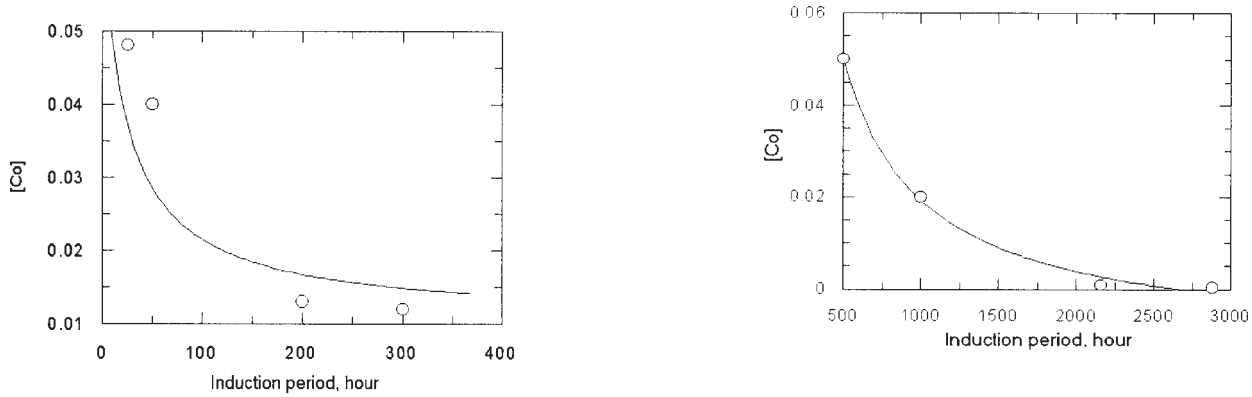

Fig.7. The dependence of the induction degradation period for different polyolefins (polypropylene (a) and polyethylene (b))

greater. It can be said that the secondary polymer act as a real "contaminant" for primary polymer. Because of contamination (with equation 1 as mathematical expression) the degradability of the blends of primary with secondary polymers will be greater. The greater degradability will determine the diminishing of the induction period, the faster losing of the utilization properties and the faster reduction of the service life. The greater the number of the reprocessing the smaller the utilization properties and finely the number of service life.

These results demonstrate the reason for which, even after blending, the physical and mechanical properties of the blends are comparable with those of primary polymers, the polymers can not be infinitely recycled as other materials like metals, glass e.g. Practically the number of the polymer recycling is limited especially by the initial "contaminant" content.

The determination of the carbonyl concentration, of the secondary polyolefins, before the mechanical recycling, is very important for the estimation of this recycling type considering the life time / cost ration . In case of a new primary with secondary polyolefins blend, for a good service life, the $[C_0]$ parameter must be included into the 0.0003 – 0.01 interval.

From the upper demonstration results that, for a convenable usage life, the blends of primary and secondary polymers can contain only certain secondary polymers quantity. If this condition is not respected then the final blend will be much more degredable in usage.

The existence of a certain carbonyl concentration, always the same, at which began the accelerated degradation, can be used as criteria for the maximum quantity of secondary polymer (limited quantity) that can be used for blending with primary polymers. The physical meaning of this limited quantity is the maximum carbonyl content at which the accelerated degradation does not begin.

Basically, the polymers mechanically recycling consist in finding an optimum between the advantages got by recycling and the reduction of the degradation induction period, namely of the service life.

Through the possibility of calculation of [P], K, and $[C_0]$ parameters the mathematical model is a practical instrument for quantitatively evaluate of the polyollefins degradation behavior.

The most important conclusion of this study is that it can quantitatively study evaluation of the structural defect (carbonyl concentration, ($[C_0]$)) that promotes the oxidative degradation for every concrete case.

Conclusions

A degradation mathematical model based on the variation of the carbonyl index during degradation to measure the polyolefines degradability was proposed. The mathematical model was verified with good results with own and literature degradation data.

The mathematical model comprise three aging parameters, [P], K, $[C_0]$, that can be calculated using specific equations. It was demonstrated that the aging parameters reflect the degradation behaviour of primary and secondary polyolefins. This fact has practical importance for polyolefins mechanical recycling because it is possible to know, for a given "contamination", the degradation rate, the degradation induction period and the service life of the product molded from regenerated polyolefins.

Considering all the processed degradation data it was possible to establish the dependence between the carbonyl index and induction period. For a reasonable service life, the initial carbonyl index must be not greater than 0.015, that means that the blend of primary with secondary polymer can contain only certain quantity of secondary polymers. If this condition is not respect, the final blend will degrade in usage much more.

The obtained results demonstrate that the polymers mechanically recycling consist in finding an optimum between the advantages obtain by mechanical recycling and the reduction of the degradation induction period.

These results constitute a mathematical demonstration of the reason for which, even after blending, the physical and mechanical properties of the blends are comparable with those of primary polymers, the polymers can not be infinitely recycled as other materials like metals, glass e.g. Practically the number of the polymer mechanical recycling is limited by the initial "contamination" (that increased with the reprocessing number) that diminishes the utilization properties and the service life.

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