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

DOINA DIMONIE[1]*, MIHAI DIMONIE[2] , GABRIEL VASILIEVICI[1]
[1] ICECHIM Bucharest, 202 Spl.Independentei, 060021, Bucharest, Romania
[2] "Politehnica"University, 149 Bucharest, Calea Victoriei, 010070, Bucharest, Romania

It was considered as contamination, the carbonyl growing in the primary and secondary polyolefins blends and as effects of contamination, the degradation rate increasing, the induction period and the service life diminishing of the products molded from these blends. Using the carbonyl time variation during the first life, it is possible to estimate, for a given contamination, the degradation rate, the induction period and the product service life molded from polyolefins post consumers goods and so the optimal solution for the polyolefins mechanical recycling.

Keywords: Mechanical recycling, secondary polyolefins, mathematical model, contamination

It is well known that the polymer degradation is a natural or/and an accelerated process, that in the most case, takes place in oxygen atmosphere during synthesis, processing and / or service life, under the action of the ageing factors (temperature, UV radiations, γ-irradiation, atmospheric pollutants, stress or strain, transitional metals and so) [1-38].

Because of degradation, the polymer chemical and morphological structure and so its physical and mechanical properties are changed [3, 4, 6, 8, 11, 12, 17, 18, 30, 37]. For this reason, the degradation can be also used for tailoring the polymer chemical structure, and so the obtaining of goods with desired utilization properties.

The degradation occurs by free radicals and implies a chemical reaction sequences with initiation, propagation, and interruption stages [11 – 15].

Considering the process rate, the polyolefins degradation has the following steps [1, 2, 5, 11, 12]: the induction, the auto – acceleration with an increasing rate, the stage with a constant rate and the stage with decreasing or constant rate. It is well known also the polyolefins degradation without induction (fig.1).

The time evaluation of the polyolefins degradation can be based on the analysis of the carbonyl index time variation. In the auto-accelerated stage, the carbonyl has an auto – catalytic effect [5, 15, 16, 18-27]. A new mathematical model for polyolefins degradation, with practical importance for polyolefins mechanical recycling, is proposed.

<u>Poliolefins Degradation</u>

Mathematical expression of the carbonyl variation during degradation

The polymer degradations mechanism occurs based on the following reaction sequence:

$$PH + \text{energy} \rightarrow P^{\cdot} + H^{\cdot} \tag{1}$$

$$P^{\cdot} + O_2 \rightarrow POO^{\cdot} \tag{2}$$

$$POO^{\cdot} + PH \rightarrow POOH + P^{\cdot} \tag{3}$$

$$POOH \rightarrow PO^{\cdot} + {}^{\cdot}OH \tag{4}$$

where:

PH is the macromolecule;
$P^{\cdot}$ is a macroalkyl radical;
$POO^{\cdot}$ correspond to a macroperoxyl radical;
$PO^{\cdot}$ is a macroalcoxy radical;

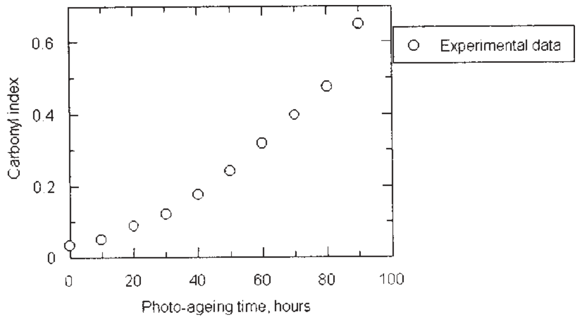
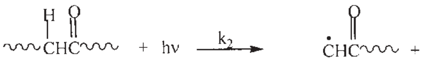


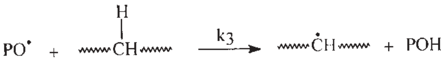
Fig. 1. Typical curve for degradation without induction (unstabilized polypropylene) [1]

${}^{\cdot}OH$ signify a hydroxyl radical and $H^{\cdot}$ stand for hydrogen radical.

$$\sim\sim\overset{H}{\overset{|}{C}}H\sim\sim + h\nu \xrightarrow{k_1} \sim\sim\dot{C}H\sim\sim + H^{\bullet} \tag{5}$$



$$\sim\sim\overset{H}{\overset{|}{C}}H\overset{O}{\overset{\|}{C}}\sim\sim + h\nu \xrightarrow{k_2} \dot{C}H\overset{O}{\overset{\|}{C}}\sim\sim + H^{\bullet} \tag{6}$$



$$PO^{\bullet} + \sim\sim\overset{H}{\overset{|}{C}}H\sim\sim \xrightarrow{k_3} \sim\sim\dot{C}H\sim\sim + POH \tag{7}$$

$$PO^{\bullet} + \sim\sim\overset{H}{\overset{|}{C}}H\ \overset{O}{\overset{\|}{C}}\sim\sim \xrightarrow{k_4} \sim\sim\dot{C}H\ \overset{O}{\overset{\|}{C}}\sim\sim + POH \tag{8}$$

Considering the auto-catalytic effect of the carbonyl, based on the following prerequisites, a mathematical model for polyolefins degradation is proposed:

-the rate of the carbonyl functions content formation, at a given moment, is in proportion with the un – degradated polymer concentration:

$$d[C] / dt = k [P - C] \tag{9}$$

-The constant of the degradation has a breeder value. As we have already shown, the constant rate of the macromolecular radical formation, in the neighborhood of a carbonyl function (k_2), is much greater than in the absence of a such vicinity (k_1):

$$k_2 >> k_1 \tag{10}$$

---

* *email: ddimonie@rdslink.ro*

For this reason the process is auto-accelerated and the k constant has a continuous growing:

$$k=K*[C]^{\alpha} \tag{11}$$

where:

K is the degradation rate of the polymer without carbonyl content and α is a constant, which can be > 0 or, for the most simple case, equal with 1.

Because of the polymer solid state, for describing the whole degradation process, it was considered that, only a restricted quantity of polymer can be degraded. If [P] is the maximum concentration of the polymer that can be oxidized, the carbonyl formation rate can be expressed by the following formulas:

$$\frac{dC}{dt} = K[C][P-C] \tag{12}$$

After integration it was obtained:

$$\ln\frac{[C]}{[P-C]}*\frac{[P-C_0]}{[C_0]} = K[P]t \tag{13}$$

And after some simple transformations:

$$[C] = \frac{\frac{[P][C_0]}{[P-C_0]}*\exp(K*[P]*t)}{1+\frac{[C_0]}{[P-C_0]}*\exp(K*[P]*t)} \tag{14}$$

Where:

[C] is the carbonyl concentration, at a given time;

$[C_0]$ is the carbonyl concentration before the auto–acceleration stage;

[P] is the maximum quantity of the polymer that can be oxidized;

K is the global constant reaction rate that depends on factors like chemical structural defects that promote the degradation (carbonyl groups, double bonds and so.), concentration and the nature of the non-polymeric impurities that catalyzed the degradation, physical factors (the crystalline content so.).

For these reasons, for the same polyolefin, in different degradation conditions, the K values can oscillate in huge limits.

$$\ln\frac{[C]}{[P-C]}*\frac{[P-C_0]}{[C_0]} = K[P]t \tag{15}$$

After constants group it can be obtained:

$$[C] = \frac{m*\exp(p*t)}{1+n*\exp(p*t)} \tag{16}$$

Where:

$$m=\frac{[P][C_0]}{[P-C_0]}\ (17); \qquad n=\frac{[C_0]}{[P-C_0]}\ (18); \quad p=K*[P]\ (19)$$

where m, n and p represent the mathematical model parameters and have no physical meaning.

The verification of the mathematical model was made based on the fitting method. For fitting with experimental data it was used the carbonyl index, as an expression of the intensity of the carbonyl formation during degradation. It was considered that the dimensionless carbonyl index is in proportion to carbonyl functions concentration (expressed in concentration unities). The carbonyl index can be relatively easy measured [13, 30, 32 - 37].

The equation number (16) describes the auto-acceleration stage of the degradation. It can be fitted with experimental data.

Is case of a degradation with induction period the calculated data based on the equation 16 can be obtained only after the elimination of the induction period.

As consequence, in this situation, the time origin, on the time scale is the moment when the degradation becomes autoaccelerated.

The mathematical model was verified with literature and own degradation data. As it can be seen from figure 2, that represent the data from figure 1 worked out with the mathematical model, the equation 16 very well verifies the experimental data. In figure 3 it is presented a typical rate curve (d (I.C)/dt) for polyolefins degradation.

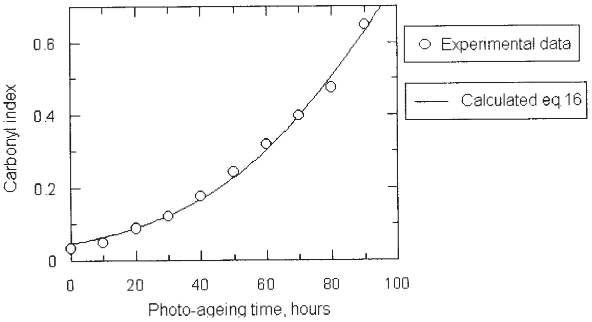


Fig.2. Typical curve for a degradation process without induction period, processed with the mathematical model (Calculus parameters: m=0.0303; n=0.047; p=0.0344

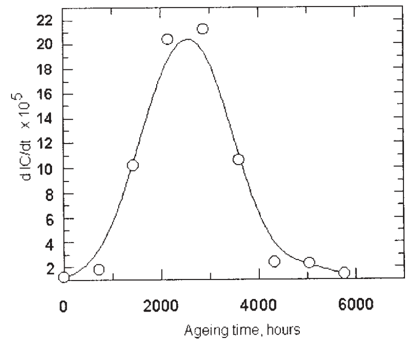


Fig.3 Typical rate curve (d (I.C)/DT) for polyolefins degradation obtained with the mathematical model

Verification of the proposed mathematical model

Natural photo-agening of low density polyetilene

In figure 4 is presented the dependence of the carbonyl index by the degradation time for low-density polyethylene photo–aged in natural maritime condition, at the Black Sea Shore (Constanta platform - Romania). It can be observed the very well concordance between the experimental and calculated data that was obtained based on the mathematical working out of the experimental data with the equation 16.

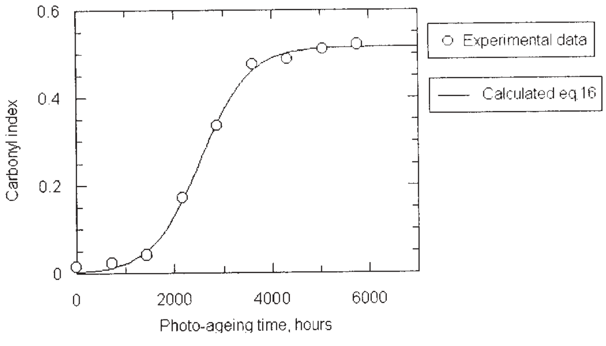


Fig.4. Experimental and calculated data for carbonyl index variation of un-stabilized low-density polyethylene by the photo - aging time in a typical degradation process with induction period (Calculus parameters: m = 0.0031; n=0.006; p=0.002)

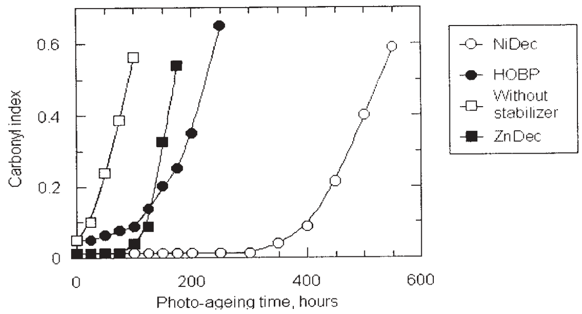


Fig.5. The photo-resistance of the polypropylene stabilized with different stabilizers [39]

Stabilizers influence on the polypropylene photo-oxidative resistance

In [33] it was studied the photo – resistance of polypropylene stabilized with 3 . 10^{-4}mol/100g 2 hydroxi 4 octilbenzofenona (HOBP), Irganox 1076, dietilditiocarbamat de zinc (ZnDec) and dietilditiocarbamat de nickel (NiDec). The dependence of the carbonyl index by the photo-degradation time are presented in figure 5.

In this case, the degradation has a very well defined induction period as comparing with the situation 2.2.1. For the beginning, it was eliminated the induction period and the time origin was considered the moment when the degradation became auto-accelerated.Then the experimental data were mathematical processed using the equation 16. The experimental and calculated data are presented in figure 6 It can be observed the very well concordance between the experimental and calculated data.

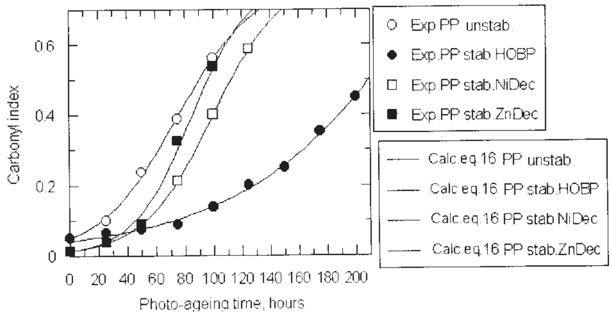


Fig.6. Experimental and calculated data for photo-stabilized polypropylene stabilized with different stabilizers (Calculus parameters: PP un-stabilized m=0.0511; n=0.0653; p=0.0366; PP stabilized with HOBP m=0.0409; n=0.0135; p=0.0128; PP stabilized with NiDec m=0.0129;n=0.0163,p=0.0414; PP stabilized with ZnDec m=0.0123;n=0.0157;p=0.0491)

Photo-degradation of the cold drawn polyethylene

In [34] it was followed the influence of the cold draw ration on the photo-degradation behaviour of low-density polyethylene. The dependence of the carbonyl index by the photo-aging time is presented in figure 7 and the relation between the experimental data and the calculated those obtained by using the mathematical model (the equation 16) is presented in figure 8.

It can be observed the very well concordance between the experimental and calculated data.

Photo degradation of polyethylene - polypropylene blends

In [35] was studied the influence of the polypropylene content on the photo-degradation behaviour of the polypropylene-polyethylene blends (fig.9). Because of the high polypropylene degradability, the blend degradation depends by its composition.

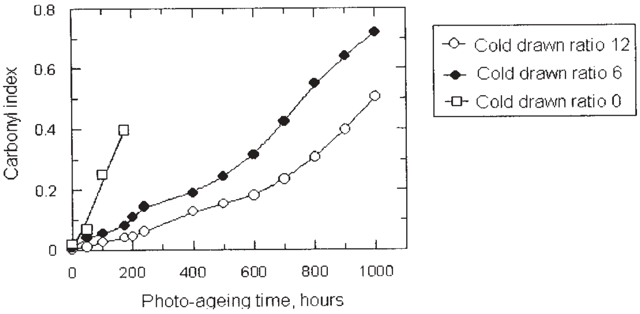


Fig.7. The dependence of the carbonyl index of the low density polyethylene by the photo-ageing time and the cold drawn ratio [40]

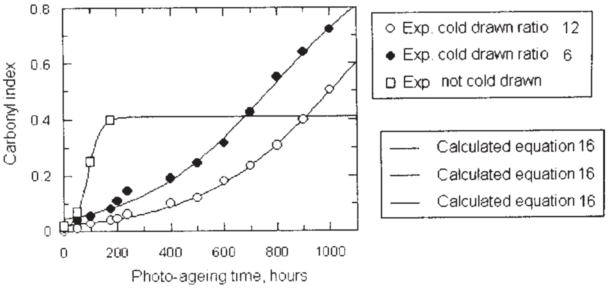


Fig.8. Experimental and calculated data for de dependence of the carbonyl index of low- density polyethylene by the photo-aging time and cold drawn (Calculus parameters: un-drawn m=0,0112; n=0,0275; p=0,0404; 6 cold draw ratio m=0,0447; n=0,0433; p=0,004; 12 cold draw ratio m=0,0213; n=0,0196,p=0,0038)

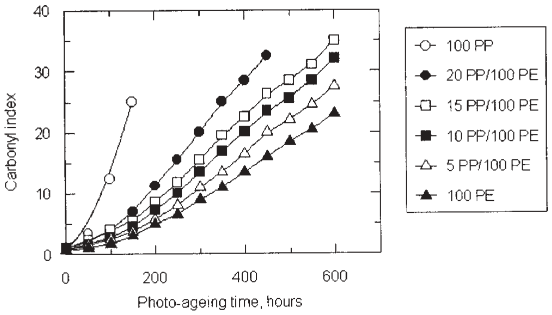


Fig.9. The polypropylene concentration influence on the dependence of the carbonyl index of the photo-aged PP/PE blends by the degradation time [35]

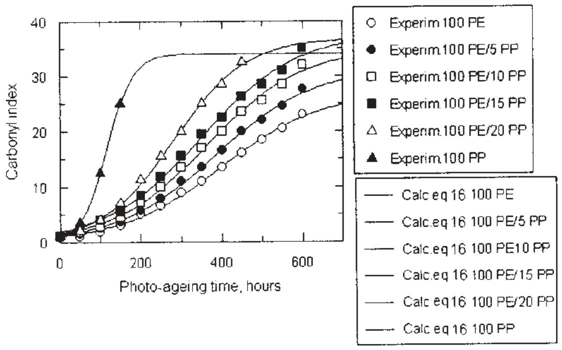


Fig.10.Experimental and calculated data for the PP concentration influence on the dependence of carbonyl index of photo-degradated PP/PE blends by the degradation time

The results of the mathematical processing of the experimental data with the equation 16 presented in figure 10 that shows once again the very good concordance between the experimental and calculated data.

Results and discussions

The very well concordance between the experimental and calculated data shows that the theoretical premises of the mathematical model are correct. Because of the carbonyl content and many another chemical defects, the secondary polymers will be much more susceptible to degradation.

The carbonyl content determines the ”contaminant” effect of the degradated polyolefins upon the primary polyolefins with which it is blended in view of mechanical recycling.

Even if after blending of the degradated polymer with primary those, the physique and mechanical properties of the obtained blends are acceptable and sometimes comparable with the properties of the primary polymers, the degradation induction time of the resulted blend (which, after blending and granulation, is named regenerated polymer) will be smaller than that of primary polyolefins. Also the degradation rate and the service life of the product molded from regenerated polyolefins will be smaller than that of the primary polyolefins.

The “contamination” effect of the degradated polymer on the degradation behavior of the regenerated polymers determines huge differences between the recycling of polymers and the recycling of other materials (glass, metals a.s.o). The glass and metals can be infinitely recycled without loosing their utilization properties.

Taking into consideration the equation 20 it can be observed that by blending the primary with secondary polymers, inevitable the carbonyl concentration of the blend ($[C_0]$) will be greater than the carbonyl content of the primary polymer. This equation is the mathematical expressions of the “contamination” effect of the degradated polymers up on the primary ones.

$$[C] = \frac{\frac{[P][C_0]}{[P - C_0]} * \exp(K * [P] * t)}{1 + \frac{[C_0]}{[P - C_0]} * \exp(K * [P] * t)} \qquad (20)$$

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 source of raw material is used only in a very small ratio as a method for polyolefins mechanical recycling [38].

Conclusions

The polymer degradation is a natural or an accelerated process, that generally takes place in oxygen atmosphere during synthesis, processing and / or service life, under the ageing factors action (temperature, UV radiations, γ-irradiation, atmospheric pollutants, stress or strain, transitional metals a.s.o;

The mathematical model gives the possibility of calculation of the “contamination” of the regenerated polyolefins and, for a given “contamination”, of the estimation of the degradated rate, degradation induction period and of the service life of the product molded from regenerated polyolefins;

The measurement of degradation rate increasing as a function of the carbonyl content, and the induction period diminishing as a function of the carbonyl content will be presented in a future paper in which the polyolefins mechanical recycling based on the carbonyl variation during the first life will be studied.

Bibliography

1. RAAB, M., J. Appl. Pol. Sci., **27**, 1982, p. 2457
2. ALLEN, N., Polyolefins Degradations, Elsevier Publishing Company, London, 1988
3. QURESHI, F.S., Polym.-Plast. Technolog. Eng., **28**, nr. 7&8, 1989, p. 649
4. PABIOT, J., Polym. Eng. Sci., **21**, nr.1, 1981, p. 32
5. B.RANBY, Photodegradation, Photo-oxidation and Photostabilization of Polymers, John Wiley &Sons, New York, 1975
6. BRAUN, B., Polym. Eng. Sci., **14**, nr.3, 1974, p.206
7. SEVERINI, F., Environmental Degradation of Polyolefins, AJSE, **4**, 1982, p.533
8. AKAY, G., TINCER, T., ERGOZ, H.E., Eur. Polym. J., **16**, 1980, p.601
9. CARLSSON, D.J., Macromolecules, **23**, nr.23, 1990, p.4934
10. WHITE, J., Surface Degradation of Polymeric Materials, NPL Report DMM(A), **75**, 1992
11. SCOTT, G., Developments in Polymer Stabilization, ap-plied science publishers, 1982, London
12. JELLINEK, H.G., Some Aspects of Degradation and Stabilization of Polymers, Ind. Polym. Rad., Proceedings of Symp., 1970, Sardar Pater Univ.India
13. GUGUMUS, F., Contribution to the Photolysis of Hydroperoxides in Polyethylenes, Polym. Degrad. Stab., **27** , 1990, p.9
14. CARLSSON, D.J., J. Appl. Polym. Sci., **21**, 1977, p.2963
15. CONLEY, T., Thermal Stability of Polymers, Department of Chemistry Wright State University Dayton, Ohio, Marcel Dekker Inc., New York, 1977
16. BILLINGHAM, N.C., Some Notes on Oxidative Degradation of Polymers, course on Degradation and Stabilisation of Polymeric Materials, 1992, Oct. 26 – 30, Turin, Italy
17. GRASSIE, N., SCOTT, G., Polymer Degradation & Stabilization, Cambridge University Press, Cambridge, 1988
18. CARLSSON, D.J., The photo-oxidative Degradation of Polypropylene, J.Macromol.Sci.-Rev. Macromol. Chem., Part.I, **C14** , 1, 1976, p.65
19. CARLSSON, D.J, J.Macromol.Sci.-Rev.Macromol.Chem., The photo-oxidative Degradation of Polypropylene , Part.II, **C14,** 2, 1976, p.155
20. FERARU E., Mat. Plast., **42**, nr. 3, 2005, p.163
21. ARMSTRONG, C., PLANT, M.A., SCOTT, G., Mechanism of Antioxidant Action:the Nature of the Redox Behavior of Thiodipropionate Esters in Polypropylene, Eur. Polym. J., **11**, 1983, p.161
22. ALBERTSSON, A.C., The Three Stages in Degradation of Polymers-Polyethylene as a Model Substance, J. Appl. Polym. Sci., **35**, 1988, p.289
23. GARTON, A., CARLSSON, D.J., WILES, D.M., Macromolecules, **12**, 6, 1979, p.179
24. HENRY, J., GARTON, A., J. Polym. Sci.:Part A:Polym. Chem., **30**, 1992, p.1693
25. SCOTT, G., Polym. Eng. Sci., **24**, 1984, p.1007
26. JIPA T., Mat. Plast., **42**, nr. 1. , p.5
27. Zaharescu T.,Mat. Plast**.**, **43**, nr.1, p.59 – 61, 2006
28. KIRYUSHKIN, S.C., SHLYAPNIKOV, YU.A., Polym. Degrad. Stab., **23**, 1989, p.185
29. NENITESCU, C.D., Organique Chemistry, Vol.1, Ed.Didactica si Pedagogica, Bucuresti, 1980
30. LACOSTE, J., J. Polym. Sci.:Part A: Polym. Chem., 1993, **31**, p.715
31. LAZAR, M., Adv. Polym. Sci., **102**, 1992, Springer –Verlag Berlin Heilderberg
32. SADRMOHAGHEGH, C., SCOTT, G., Polym. Degrad. Stab., **3**, 1980-81, p.333
33. CHAKRABORTY, K. B., SCOTT, G., Polym. Degrad. Stab., **1**, 1979, p.37
34. HAMID, S.H., The Arabian J. Sci. Eng., **13**, 14, 1988, p.503
35. SADROMOHAGHEHG, C., Polym. Degrad. Stab., **3**, 1983, p.469
36. KIRUD, B., Polym. Degrad. Stab., **1**, 1979, p.37
37. TIDJANI, A., Nat. J. Appl. Polym. Sci., **47**, 1993, p.211
38. * * * , Plastics – A Material of Choice for the 21 st Century – Insight into plastics consumption and Recovery in Western Europe, 1997, Association of Plastics Manufacturers in Europe, Brussel

---

Manuscript received: 18.10.2007