ZBIGNIEW DOBKOWSKI

Industrial Chemistry Research Institute
ul. Rydygiera 8, 01-793 Warszawa
e-mail: zbigniew.dobkowski@ichp.pl

Lifetime prediction for polymer materials using OIT measurements by the DSC method

RAPID COMMUNICATION

Summary — The standard procedure of OIT measurements by DSC method was applied for prediction of lifetime of polymer materials. Investigations of unmodified and modified, *i.e.* grafted and filled PE-LLD have been described, as an example. OIT values were measured in the temperature range (in general) from 180 to 240 °C, then the activation energy and the lifetime values were calculated. The following sequence of increasing thermal stability and increasing lifetime values has been found PE-LLD grafted < PE-LLD unmodified < PE-LLD filled compositions. The described approach can be recommended for the lifetime prediction of other polymer materials, in particular those susceptible to the thermooxidative degradation.

Key words: oxidation induction time OIT, activation energy from OIT, lifetime values of polymer materials, modified PE.

The oxidation induction time (*OIT*) is commonly used for assessment of the thermooxidative stability of polymeric materials. Usually, the differential scanning calorimetry (DSC) method is applied for *OIT* determinations, as it is currently recommended by standards [1—2] and described elsewhere [3—6]. Moreover, *OIT* measurements can also be used for calculation of the activation energy of thermooxidative degradation process [4, 7, 8], and then the lifetime of polymer materials can be predicted.

Lifetime (or service life, or long term performance) of a polymer material, as well as of a polymer end-use product, at ambient temperature or at elevated temperature is a crucial property, which determines the scope of application of polymer materials. Reasonable lifetime predictions can be obtained from accelerated ageing tests when results of such tests are extrapolated to service conditions, using an appropriate time-temperature model [9]. Various degradation tests, usually based on determination of time-dependent mechanical properties, *e.g.* tensile strength [10] or ultimate elongation [11], as well as based on weight loss [10—13], can be applied. Then, the Arrhenius model is used to evaluate accelerated test results involving the effect of temperature. Therefore, kinetics of the thermooxidative degradation process can be described by the Arrhenius equation

$$k(T) = A \exp(-E_{ad}/\mathrm{R}T) \qquad (1)$$

or in the logarithmic form

$$\ln k(T) = -E_{ad}/\mathrm{R}T + C_A \qquad (2)$$

where: *k(T) — degradation process rate constant,* E_{ad} *— activation energy, T — absolute temperature in K, R — gas constant, A and* C_A *— constants.*

The plot of ln $k(T)$ *vs.* $1/T$ is a straight line with the slope equal to $-E_{ad}/\mathrm{R}$.

Time-to-failure $t_{f(P)}$ can be calculated from the following equation [11, 12, 14, 15]:

$$t_{f(P)} = \{f(P)/A \exp(E_{ad}/\mathrm{R}T)\} \qquad (3)$$

where: *f(P) — function dependent on the considered polymer property but independent on temperature.*

Then the lifetime at specific temperature, or permissible temperature of service during a specified time range, can be estimated from the plot of ln t_f *vs.* $1/T$ [12].

OIT value corresponds to the initial time-point of the oxidation curve, *i.e.* to the time-to-failure and thermal stability of a given material [$t_{f(OIT)}$ = *OIT*] [4, 6, 8, 15]. It means that *OIT* is a given property *P* in eq. (3). Therefore, time-to-failure is given by

$$t_{f(OIT)} = C_{ox} \exp(E_{ad}/\mathrm{R}T) \qquad (4)$$

where: C_{ox} *— constant corresponding to the preexponential term in eq. (3).*

The lifetime measured as the time-to-failure can be estimated from the plot of ln $t_{f(OIT)}$ *vs.* $1/T$ [4, 8, 15, 16].

In this paper, the comparative thermal stability assessment and the lifetime prediction for unmodified and chemically modified PE and its compositions is described.

EXPERIMENTAL

Materials

The following polymer materials (some of them prepared in the laboratory of polymer compositions in our Institute [16]) were used in this work:

— commercially available linear low density polyethylene (PE-LLD), Stamylex PE-LLD, DSM;

— chemically modified (grafted) PE-LLD;

— physically modified (filled) PE-LLD, *i.e.* composites of grafted PE-LLD with a flame retardant filler (aluminum hydroxide).

Method

A differential scanning calorimeter DSC 7 Perkin-Elmer with GSA 7 Perkin-Elmer automatic gas flow switch was used for *OIT* measurements. The standard procedure [5] was used both for the instrument calibration and for *OIT* measurements, however appropriate measurement temperatures were selected to make the subsequent calculations of activation energy possible.

RESULTS AND DISCUSSION

OIT values were measured for unmodified and modified PE-LLD samples at various temperatures: 190—220 °C, 180—210 °C and 210—240 °C in the case of unmodified, grafted and filled PE-LLD, respectively (Table 1). The temperature range was selected according to the reasonable time of measurement. As can be seen from Fig. 1 the thermal stability of tested materials can be compared according to the temperature range, and the following sequence of increasing thermal stability was found:

PE-LLD grafted < PE-LLD unmodified (matrix) <
< PE-LLD filled composites.

Table 1. ***OIT*** **experimental values for unmodified, grafted and filled PE-LLD**

PE-LLD	Number of lot	*OIT* values at given temperature, min						
		180 °C	190 °C	200 °C	210 °C	220 °C	230 °C	240 °C
unmodified	1	—	50	28	13	7.6	—	—
	2	—	83	24	12	4.7	—	—
	3	—	30	11	5.1	2.8	—	—
grafted	1	55	14	11	2.9	—	—	—
	2	43	14	8.2	4.9	—	—	—
	3	60	31	7.0	5.2	—	—	—
filled	1	—	—	—	79	32	12	5.7
	2	—	—	—	70	32	14	5.9
	3	—	—	—	70	30	13	4.4

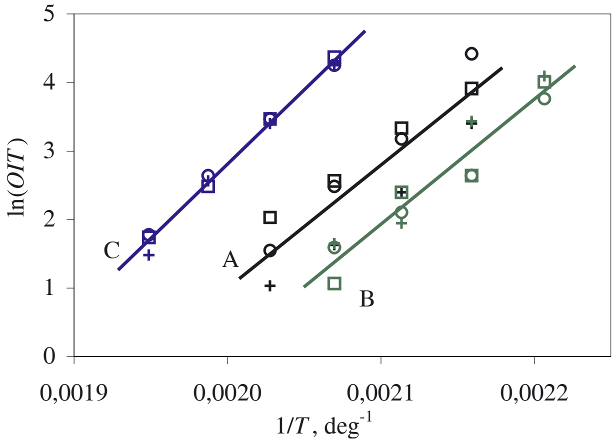

Fig. 1. Plot of ln (OIT) vs. 1/T for: A — PE-LLD unmodified, B — PE-LLD grafted, C — PE-LLD filled (in all cases three series of measurements of OIT were done-denoted by □, o *and* +*)*

Table 2. Activation energy of thermooxidative degradation (E_{ad}) determinated by correlation and calculated lifetime ($t_{f(OIT)}$) values of PE-LLD samples

Calculation results	PE-LLD		
	unmodified	grafted	filled
Activation energy (E_{ad}), kJ/mol	149	150	180
Correlation coefficient (r^2)	0.817	0.924	0.992
$t_{f(OIT)}$ at 210 °C, min	9	4	75
$t_{f(OIT)}$ at 100 °C, min	1.0	0.5	80

The activation energy values (Table 2) were calculated from *OIT* data using logarithmic form of eq. (4) as a respective linear regression equation. Large dissipation of results was observed for unmodified and grafted materials (the correlation coefficients in Table 2, see also Fig. 1) because of matrix (unmodified) material differences (different lots of PE-LLD) and probable variations in subsequent grafting reactions. In the case of filled PE-LLD, the material is expected to be more uniform then in the previous cases since it has been stabilized and homogenized during preparation of the composites.

As regards calculated E_{ad} values, an intrinsic, rather significant, error has to be taken into account as the slope of E_{ad}/R is determined within a narrow range of temperature (in this work 30 °C) and the number of experimental points (n, in this work $n = 4$) is usually limited.

The values of lifetime (or of time to failure $t_{f(OIT)}$) were calculated [from equation (4)] (Table 2) at temperature 210 °C to compare with experimental data under thermooxidative conditions and at arbitrarily taken temperature 100 °C.

The same sequence of increasing thermal stability as for the testing temperature range has been observed for the lifetime values:

PE-LLD grafted < PE-LLD unmodified <
< PE-LLD filled (composites).

CONCLUSIONS

The procedure of *OIT* measurements by DSC method, applied for thermal stability characteristics of polyolefins, can also be used for predictions of their lifetimes. In principle, it can be applied for various polymer materials, in particular those susceptible to the thermooxidative degradation.

The following lifetimes have been predicted for unmodified and modified PE-LLD materials at 100 °C (arbitrarily taken as an example), in years (in parentheses):

PE-LLD grafted (0.5) < PE-LLD unmodified (1.0) < PE-LLD, filled (80). The calculated lifetime values seem to be reasonable, but the experimental data which could confirm the results for tested materials are not available.

REFERENCES

1. PN-EN 728:1999, "Plastic piping systems and ducting systems. Polyolefin pipes and fittings. Determination of oxidation induction time".
2. ISO 11357-6:2002, "Plastics — Differential Scanning Calorimetry (DSC) — Part 6: Determination of oxidation induction time".
3. Mason L. R., Reynolds A. B.: *J. Appl. Polym. Sci.* 1997, **66**, 1691.
4. Bair H. E.: "Thermal Analysis of Additives in Polymers" in: "Thermal characterization of polymeric materials" (Ed. Turi E. A.), 2nd ed., Academic Press, San Diego 1997, pp. 2263—2410.
5. Dobkowski Z.: *Polimery* 2004, **49**, 343.
6. Schmid M., Ritter A., Affolter S.: *Polimery* 2004, **49**, 333.
7. Budrugeac P.: *Polym. Degrad. Stab.* 2002, **68**, 289.
8. Dobkowski Z.: "Activation energy of thermooxidative degradation from OIT for lifetime prediction of polymer materials" in: Proceedings of POLMATIN Workshop "Standardisation, Measurement and Testing of polymer materials for better quality of life", Warsaw, 9—10 October 2003.
9. Jakubowicz I.: *Polimery* 2004, **49**, 321.
10. Montanari G. C.: *IEEE Trans. Electr. Insulat.* 1990, **25**, 1046.
11. Langlois V., Audouin L., Verdu J., Courtois P.: *Polym. Degrad. Stab.* 1993, **40**, 399.
12. Dobkowski Z., Rudnik E.: *J. Thermal. Anal.* 1997, **48**, 1393.
13. Gupta Y. N., Chakraborty A., Pandey G. D., Setua D. K.: *J. Appl. Polym. Sci.* 2004, **92**, 1737.
14. Montanari G. C., Lebok F. J.: *IEEE Trans. Electr. Insulat.* 1990, **25**, 1029.
15. Dobkowski Z., Rudnik E.: *J. Therm. Anal. Cal.* 2002, **69**, 693.
16. Dobkowski Z., Pełka J.: *ICRI Ann. Report* 2001, ICRI Warsaw 2002, 109.

Received 1 IX 2004.