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Assessment of polyethylene stability using the standardized *OIT* procedure by DSC method

Summary — The standardized procedure for determination of oxidation induction time (*OIT*) using the differential scanning calorimetry (DSC) method has been described. A Perkin-Elmer DSC7 instrument was used and it was calibrated with indium and tin certified reference materials (CRMs). Measured values of melting temperature were consistent with the certified values within ± 0.3 °C. The procedure was validated using commercially available PE samples. Relative standard deviation (*RSD*) values were calculated and compared with the published data. The values obtained were lower than those quoted in literature for particular PE grades. Then chemically modified (grafted) PE matrices and composites with a flame retardant filler were investigated. *OIT* values were measured at various temperatures and the optimum measurement temperature for modified PE composites was determined. It was equal to 220 °C as compared with 200 °C for unmodified PE. Thus, it has been found that the thermal stability of investigated composites in thermooxidative degradation conditions is higher than that of unmodified PE material. **Key words:** thermal stability, polyethylene materials, flame retardants, oxidation induction time, relative standard deviation.

Oxidation induction time (*OIT*) is a parameter used for assessment of thermooxidative stability of some polymeric materials, their lifetime and quality in practical applications. *OIT* values are usually measured for polyethylene (PE) and polypropylene (PP) used for the ducts, pipes and fittings, as well as an electrical insulating material for wires and cables. In this case the procedure of *OIT* determination using the differential scanning calorimetry (DSC) method is described in standards [1–5]. *OIT* measurements are applied not only for routine testing of polyolefin products, but also in research works. In such cases, various techniques of thermal analysis (TA) can be applied, including DSC method [6, 7].

Recently, the *OIT* method was applied in our Institute for chemically modified PE and its compositions. The method was checked and an example of application for modified PE materials is given in this paper.

EXPERIMENTAL

Materials

The following PE materials were used in this work:
— commercially available various types of PE, listed in Table 1;

Table 1. Investigated commercial PE samples

PE type	Symbol	Density kg/m ³	Producer/ Supplier
PE-HD	HE3366	945	Borealis
PE-MD	ME1244	934	Borealis
	ME6032	928	
	ME6060	934	
PE-LD	Malen E KAPC33	928	Orlen
	Malen E KGAP27	922	
PE-LLD	LE8707	920	Borealis
	LE6040	920	
	1. "Stamylex 1026F"	919	DSM
	2. "Stamylex 08-026F"	910	
	3. "Stamylex TMX 1000F"	902	

— PE-LLD, chemically modified (grafted)*;

— mixtures of grafted PE-LLD with flame retardants.

A typical composition contained: grafted polymer, flame retardant filler, processing aids, and antioxidants in amounts of 100, 150, 11, and 0.6 parts.

* Preparation of grafted PE-LLD and its compositions, and investigations of their selected properties were supported by the State Committee for Scientific Research, research project No. 3 T09B 041 16, and were described elsewhere [8].

Instrument

DSC 7 Perkin-Elmer differential scanning calorimeter with GSA 7 Perkin-Elmer automatic gas flow switch was used for *OIT* measurements. A computer programme was applied for data acquisition and calculations for *OIT*.

The instrument was calibrated using two certified reference materials (CRMs):

- SRM (standard reference material) 758 Indium, NIST, delivered by Perkin-Elmer, $T_m = 156.6\text{ }^{\circ}\text{C}$ and $\Delta H = 28.45\text{ J/g}$, and
- SRM 2200 Tin, NIST, $T_m = 231.92\text{ }^{\circ}\text{C}$ and $\Delta H = 60.21\text{ J/g}$.

Procedure

The procedure was checked for commercially available PE polymers, and thus it was validated using the precision parameters for comparison. Routinely, at least 3 replicates were measured for each sample using standard open Al sample pans; N_2 purge gas and O_2 gas contained less than 5 ppm and less than 24 ppm of impurities, respectively.

RESULTS AND DISCUSSION

Harmonization of *OIT* procedures

The routine procedures for PE, described in standards [1–5], were checked and harmonized. In the case of PE the following crucial conditions are recommended: (1) measurement temperature $200\text{ }^{\circ}\text{C}$, (2) calibration of instrument with indium and tin at the heating rate 1 deg/min near the melting point (*i.e.*, above $145\text{ }^{\circ}\text{C}$ or above $220\text{ }^{\circ}\text{C}$ for indium or tin, respectively), (3) inert gas (nitrogen) flow $50\text{ ml/min} \pm 10\%$ and oxygen gas flow $50\text{ ml/min} \pm 10\%$, (4) heating rate 20 deg/min during flushing with nitrogen from $50\text{ }^{\circ}\text{C}$ to the testing temperature, (5) maintaining the measurement temperature constant within $\pm 3\text{ }^{\circ}\text{C}$.

Calibration results

Calibration results are given in Table 2. The results are consistent with the standard recommendation, *i.e.*, that the temperature difference should be less than $0.30\text{ }^{\circ}\text{C}$.

Table 2. Calibration measurements

CRM	Melting temperature, $^{\circ}\text{C}$		Difference, $^{\circ}\text{C}$	
	certified	measured (onset)	measured	allowed
Indium	156.60	156.37 156.44	-0.23 -0.16	± 0.30
Tin	231.92	231.60	-0.32	± 0.30

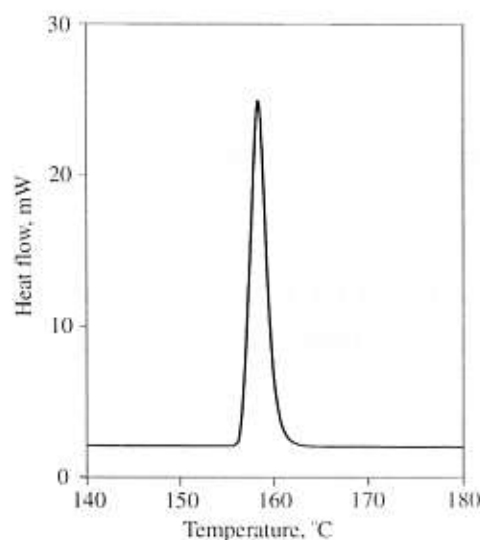


Fig. 1. The calibration peak of indium CRM as an example: conditions — sample wt. 5.100 mg, scanning rate $20.0\text{ }^{\circ}\text{C/min}$; results — onset $156.44\text{ }^{\circ}\text{C}$, peak 158.15 , $\Delta H = 28.23\text{ J/g}$

$^{\circ}\text{C}$. The calibration peak is shown in Fig. 1 for indium as an example.

Procedure

The repeatabilities of parameters of precision, *i.e.* the standard deviation (SD) and the relative standard deviation (RSD) are shown in Table 3.

Thus, the RSD values obtained in our laboratory are consistent with, and even lower than published data [5]. Therefore, our procedure conforms to the actual regional (ASTM, EN) and international (ISO) standards and to requirements for measurement quality.

Application for PE-LLD and compositions of grafted PE-LLD with a flame retardant

In the case of other than “pure” PE polymers, adequate testing conditions have to be found, the testing temperature in particular. *OIT* of compositions of grafted PE-LLD with a flame retardant, prepared in ICRI [8], was measured according to the recommended procedure, with an exception concerning the testing temperature. Various testing temperatures were applied (*cf.* Table 4) to choose the optimum testing temperature for investigated type of compositions. A typical *OIT* measurement curve is shown in Fig. 2.

It has been found that the testing temperature $200\text{ }^{\circ}\text{C}$ can be applied for matrices, *i.e.* the same as usually recommended for PE. In the case of mixtures, however, the temperature of *OIT* measurements has to be higher, namely $220\text{ }^{\circ}\text{C}$. According to EN and ISO standards [4, 5], it is recommended that testing temperature should enable measurement of *OIT* values higher than 10 min.

Table 3. Repeatability of *OIT* measurements for various types of PE at temperature 200 °C

PE type	Results of this work, <i>OIT</i> , min				Round robin test [5]			
	sample	mean	SD	RSD	sample	mean	SD	RSD
PE-HD	HE3366	157	2.6	1.7	PE-HD	163	8.3	5.1
PE-MD	ME1244	192	6.2	3.2	—	—	—	—
	ME6032	105	6.7	6.4	—	—	—	—
	ME6060	68	2.8	4.1	—	—	—	—
PE-LLD	LE8707	165	3.9	2.4	PE-LLD	120	7.8	6.5
	LE6040	108	1.8	1.7	—	—	—	—
PE-LD	KAPC33	41	2.9	7.1	PE-LD	24.0	2.8	11.7
	KGAP27	98	2.9	3.0	—	83.4	9.2	11.0

Table 4. *OIT* results for PE-LLD and modified PE-LLD compositions

Sample		Measurement temperature, °C					
type	No.	190	200	210	220	230	240
PE-LLD	1	50	28	13	7.6	—	—
	2	83	24	12	4.7	—	—
	3	30	11	5.1	2.8	—	—
Compositions	1k	—	—	79	32	12	5.7
	2k	—	—	70	32	14	5.9
	3k	—	—	70	30	13	4.4

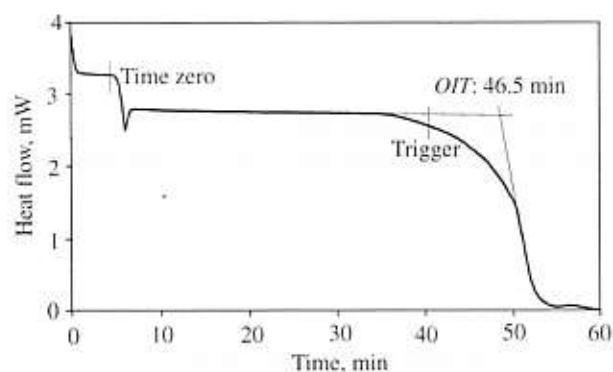


Fig. 2. DSC thermogram of *OIT* determination: conditions — sample wt. 4.800 mg, start temp. 30.0 °C, scan rate 20 °C/min, testing temp. 200.0 °C, final time 65 min, result — *OIT* = 46.5 min

CONCLUSIONS

The procedure of *OIT* determination was checked and validated. It has been found that the procedure is consistent with recommendations of actual regional (ASTM, EN) and international (ISO) standards and with requirements for measurement quality.

Compositions of chemically modified (grafted) PE-LLD with the flame retardant filler were investigated using *OIT* method. The optimum testing temperature 220 °C was found for compositions. So, it was confirmed that thermal stability of compositions in thermooxidative degradation conditions is higher than that of matrix PE materials (200 °C).

REFERENCES

1. IEC 811-4-2:1990: "Common test methods for insulating and sheathing materials of electric cables. Part 4: Methods specific to polyethylene and polypropylene compounds. Section 2, Appendix B: Test method for copper-catalyzed oxidative degradation of polyethylene insulated conductors (*OIT* test)".
2. ISO TR 10837:1991: "Determination of the thermal stability of PE pipes for use in gas pipes and fittings".
3. ASTM D 3895-94: "Standard test methods for oxidation induction time of polyolefins by differential scanning calorimetry".
4. PN-EN 728:1999: "Plastic piping systems and ducting systems. Polyolefin pipes and fittings. Determination of oxidation induction time".
5. ISO 11357-6:2002: "Plastics — Differential Scanning Calorimetry (DSC) — Part 6: Determination of oxidation induction time".
6. Bair H. E.: "Thermal Analysis of Additives in Polymers" in "Thermal Characterization of Polymeric Materials" (ed. Turi E. A.), Academic Press, Orlando 1981, p. 845—909; 2nd edition, Academic Press, San Diego 1997, p. 2263—2420.
7. Mason L. R., Reynolds A. B.: *J. Appl. Polym. Sci.* 1997, 66, 1691.
8. Pelka J., Kucharski M.: *ICRI Ann. Report '99*, ICRI Warsaw 2000, 93.