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OXIDATION STABILITY OF POLYMERIC MATERIALS DYNAMIC DSC/DTA METHOD

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The dynamic DSC/DTA method was observed to give better selectivity and reproducibility than the isothermal method when estimating relative oxidation stability of plastics materials. The dynamic DSC/DTA method is in this survey exposed to a round robin test. Results of various instruments and test stations are compared, and their compatibility is unexpectedly good. Subsequently the dynamic DSC/DTA method was chosen as the quality control method and will be published as Finnish standard SFS 3449.

The methods used for evaluating oxidation stability of plastics materials have been object of great interest during the past few years. Oxidation has been studied in the first place by means of two methods of thermal analysis: the isothermal method to measure isothermal induction time and the dynamic method to measure the temperature of the onset of oxidation. In order to establish the reproducibility and adaptability of the method in current quality control use, in this survey the dynamic method is exposed to a round robin test.

EXPERIMENTAL

Materials

The test materials consisted of various grades of commercial polyolefines, polyethylene /HD-PE/ and polybutylene /PB/, which

were either granules or pieces taken out of plastics pipes. For the round robin test, the material was homogenized by driving it through the melt flow index procedure, according to standard ISO 1133-1981. The test samples for various test stations were cut-offs of the extrudate, adapted to the sample holder in question.

Method

The method was developed for the purpose of publishing it as a Finnish standard. The use of the standard for processing control was the reason for fixing the experimental parameters, partially even in spite of loss of information. The test specimen, 10 $\pm$ 5 mg, was cut off the extrudate. The thermal analysis was carried out by starting the DSC or DTA run at +50°, under oxygen or air flow, at a constant heating rate of 10 deg/min. Expecially in the case of some instruments, smaller sample mass and lower heating rate would have given a more precise result. The relatively high heating rate was favoured with regard to the time saved. The starting temperature was fixed so as to ensure the flushing of the sample with test atmosphere during the run. The sample holders varied in construction, and efforts were made to find a procedure adequate in all instruments. The covering of sample pans with lids was considered to hamper the change of atmosphere, but was necessary to establish a reasonable base line. Participating test stations and their instruments are given in Table 1.

Table 1

Test stations and instruments

Stations	Instrument
1. Oy Wiik & Höglund Ab	Mettler, DSC20
2. Oy Finlayson Ab	Mettler, DSC20
3. Oy Uponor Ab, Upo-Pipe	DuPont 990
4. VTT, Chemical Laboratory	Perkin-Elmer, DSC-2
5. VTT, Laboratory of Structural Engineering	Netzsch, STA 429
6. Instrumental demonstration	DuPont 1090

RESULTS AND DISCUSSION

The output varies considerably from one commercial thermal instrument to another. Some instruments are computer aided. The SI-units are not built-in in all systems. To demonstrate the differences and difficulties faced in connection of this work, the main types of instrumental results are produced in Figs la - e.

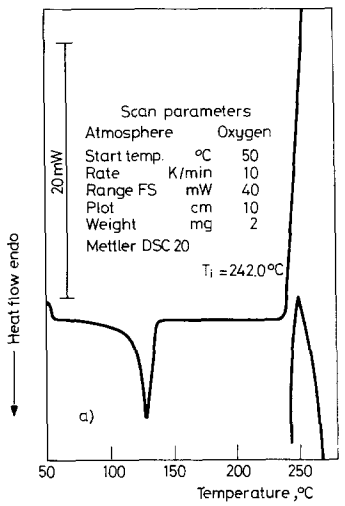

Fig. 1. Examples of the output of instruments in the round robin test. a) Mettler, DSC20/Oy Wiik & Höglund Ab

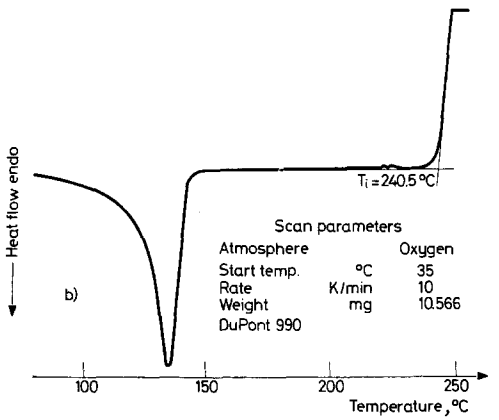

Fig. 1. b) DuPont 990/Oy Uponor Ab, Upo-Pipe

The illustrations from Fig. la to le follow the order of instruments in Table 1, and the curves are chosen to give an

example of the working condition at the moment of the round robin test.

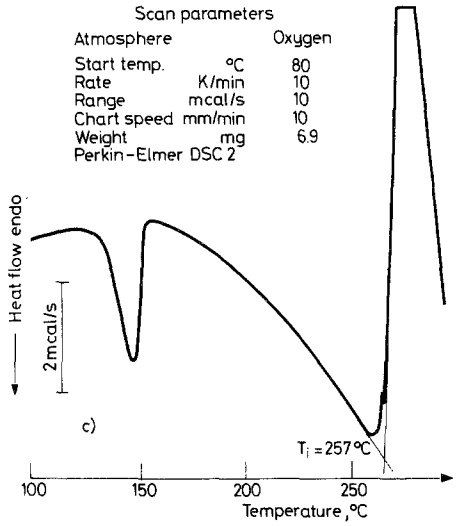

Fig. 1. c) Perkin-Elmer, DSC-2/VTT, Chemical Laboratory

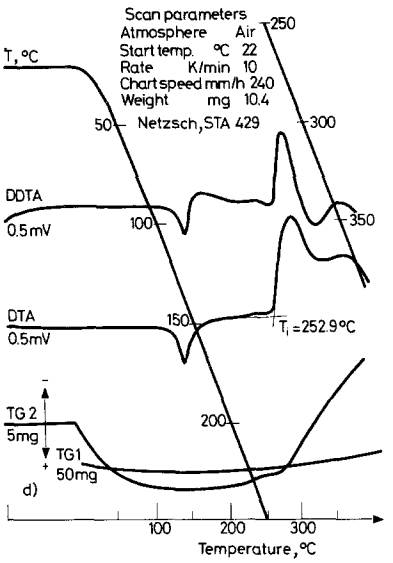

Fig. 1. d) Netzsch, STA 429/VTT, Laboratory of Structural Engineering

Table 2 lists some results obtained when oxygen atmosphere was used. The results are averages of two runs and in fair agreement. The method is selective enough to separate the materials

HD-PE 1 and HD-PE 2 with low oxidation stability as well as the polyethylenes with higher oxidation stability. The method is presumably applicable to polyolefines in general.

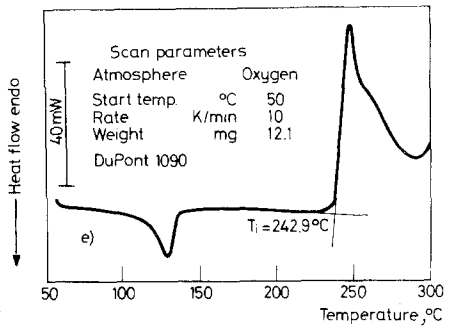

Fig. 1. e) DuPont 1090/Instrumental demonstration

The variation of results in Table 2 was considered to have its origin partially in experimental conditions, and a further refinement was gained by studying the influence of gas flow rate. An increase in the oxygen flow rate resulted in a lower induction temperature of oxidation until certain saturation was reached.

Table 2
Temperature of thermal oxydation, in centigrade

Material	Test station			
	1	2	3	4
HD-PE 1	202.8	203.4	201.6	208.0
HD-PE 2	211.1	212.1	209.5	218.5
HD-PE 3	246.5	247.7	245.4	255.5
HD-PE 4	243.4	238.5	239.3	252.5
HD-PE 5	244.3	244.7	241.7	250.5
PB 1	249.5	250.4	260.0	259.0
PB 2	202.8	197.4	192.4	216.0

Results from runs with varying flow rate are given in Table 3. Table 3 indicates that the influence of flow rate is to some extent due to instrument. All instruments were not equipped with equal facilities.

Table 3
Induction temperatures measured at test stations, using varying gas flow rates

Gas	flow cm^3/min	Induction temperature T_i, °C					
		Oy Finlayson Ab	Oy Uponor Ab, Upo-Pipe	Oy Wiik & Höglund Ab	VTT Chemical Laboratory	VTT, Laboratory of Structural Engineering	Others
Air	33					252.9	
"	0			252.7			
Oxygen	20			248.3	249		
"	25	245.6	240.75	245.9			
"	40			244.4	249		
"	50	243.8	241.0	243.9			
"	60			242.3			
"	75	242.0	241.0	242.5			
"	80			243.1	250		242.9
"	90			242.8			
"	100	240.7	241.2	242.9			242
"	110			242.1			

The selectiveness and reproducibility of the dynamic DSC/DTA method were considered adequate, and subsequently the method in question was chosen as the quality control method for polyolefines. The scatter of results is larger between test stations than it is within the results of a single station. The scatter must be specially considered when fixing the limits for quality control.

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Thanks are due to the Finnish Plastics Industries Federation and its member companies for the helpful interest in the course of this survey.

ZUSAMMENFASSUNG - Bei der Bestimmung der relativen Oxydationsbeständigkeit plastischer Materialien wurden mit der dynamischen DSC/DTA-Methode eine bessere Selektivität und Reproduzierbarkeit als mit der isothermen Variante beobachtet. Die dynamische Methode wurde in verschiedenen Laboratorien getestet. Die mit verschiedenartigen Geräten in verschiedenen Laboratorien erhaltenen Testergebnisse stimmen überraschend gut überein. Die dynamische DSC/DTA-Methode wurde deshalb als Qualitätskontrollmethode gewählt und wird als finnische Norm SFS 3449 herausgegeben.

Резюме - Установлено, что динамический ДСК/ДТА метод показывает лучшую избирательность и воспроизводимость, чем изотермический метод при установлении относительной устойчивости пластических материалов к окислению. В представленном обзоре этот метод всесторонне проверен. Сопоставлены результаты, полученные в различных лабораториях и на различных приборах. Оказалось, что совпадение результатов неожиданно хорошее. Впоследствии динамический метод ДСК/ДТА был принят как качественный контрольный метод и будет опубликован как финский стандарт SFS 3449.