CHARACTERISATION OF STABILIZERS IN POLYAMIDE USING DSC TECHNIQUE

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Antioxidants are added to the polymers to suppress oxidation during the service life. The paper deals with determination of stabilizer (VANOX–SKT) antioxidant in polyamides using a differential scanning calorimeter. Normally the amount of antioxidants is determined using HPLC method which takes more than 48 hours for sample preparation. A series of polyamide samples with known content of antioxidants (0.0–0.8%) are analysed using DSC form − 50 to 350 °C in oxygen atmosphere keeping Al-crucibles open. For all the compositions a linear relationship was found for ΔH (heat of degradation) and induction time under isothermal conditions at 220 °C which enables the antioxidant VANOX–SKT to be determined in unknown samples.

Recently thermal analysers have found wide application [1–3] in developing new additives for polymers to evaluate expected processing conditions and performance characteristics. Most of the analytical problems with quantitative determination of known additives in polymers arise from separation of the additive from the polymer matrix and its low concentration. However, modern thermal instrumentation is very often useful to assay additives in commercial polymers without extraction. This paper deals with the determination of stabilizer (VANOX–SKT anti-oxidant) in polyamides (PA) using DSC and the results are compared with results obtained from HPLC.

Experimental

Samples of polyamides with different˙ amounts of additives (0–0.8%) VANOX–SKT (trifunctional phenol) were prepared at EMS, Switzerland. The samples were carefully weighed into Al-crucibles using a Perkin–Elmer Micro-balance AD–4. All the samples were subjected to DSC studies in oxygen atmosphere (flow rate 60 ml/min). DSC curves were taken on a Perkin–Elmer

Table 1 Results of DSC scans of polyamides containing different amounts of VANOX–SKT

VANOX–SKT, %	Induction time (isothermal) 220 °C, min	ΔH, J/g	Results obtained form HPLC, %
0.2	0.934	203.4	0.12
0.4	1.606	330.5	0.30
0.6	2.269	410.5	0.47
0.8	0.747	244.9	0.77

Model DSC–7 and calculations regarding enthalpy, onset temperature, curve sloping, addition, substraction etc. were carried out using a Professional Computer Model 7700 with the corresponding software. This is a multi-tasking, multiuser, real time display computer. The samples were also treated isothermally at 220° for 30 minutes.

All the measurements were carried out from −50 to 350°.VANOX–SKT additive was also determined using a Perkin–Elmer Model–410.

Results and discussions

The samples of different compositions of VANOX–SKT with PA were studied using DSC from −50 to 350° in oxygen atmosphere. The measurements were carried out in open Al-crucibles for determining the decomposition characteristics in two different sets.

1) Measurements up to 200° (before decomposition).

2) Measurements up to 350° (after decomposition).

Similarly, isothermal studies at 220° were carried out for 30 minutes to determine the induction period.

The results for all the above compositions are listed in Table 1 along with results obtained from HPLC. The plot of ΔH (heat of degradation) and induction time vs. composition is linear except for the sample with 0.8% of VANOX–SKT. This is due to the fact that the higher quantity of VANOX–SKT (0.8%) is suppressing the degradation to a large extent. It is also clear from the above discussion that unknown amounts of VANOX–SKT can be easily determined using DSC-technique by knowing ΔH, and the induction time. The normal HPLC method takes 48 hours for the preparation of the samples.

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References

1 H. E. Bair, Polym. Engg. Sci., 13 (1973) 435.
2 W. P. Brennen, Perkin–Elmer, Thermal Anal. Appl. Study No. 22 (1977), p. 5.
3 E. A. Turi, Thermal Characterisation of Polymeric Materials, Academic Press. Inc., London, 1984.

Zusammenfassung — Zur Unterdrückung der Oxydation von Polymeren während der Nutzungsdauer werden diese mit Antioxydationsmitteln versetzt. Die vorliegende Arbeit beschäftigt sich mit der Bestimmung von Stabilisatoren (VANOX–SKT Antioxydans) in Polyamiden mit Hilfe eines Differential-Scanning-Kalorimeters. Auf herkömmliche Art und Weise wird der Antioxydansgehalt mittels HPLC bestimmt, was jedoch wegen der Probenvorbereitung mehr als 48 Stunden dauert. Mittels DSC von − 50 bis 350 °C in Sauerstoffatmosphäre in offenen Aluminiumtiegeln wurde eine Reihe von Polyamidproben mit bekanntem Antioxydansgehalt (0,0–0,8%) untersucht. Für alle Zusammensetzungen konnte zwischen der Zersetzungswärme ΔH und der Induktionszeit unter isothermen Bedingungen bei 220 °C ein linearer Zusammenhang festgestellt werden, welcher die Bestimmung des VANOX–SKT Antioxydansgehaltes von unbekannten Proben erlaubt.

Резюме — Антиоксиданты подавляют окисление полимеров в процессе их использования. Статья касается определения стабилизатора (антиоксидант ВАНОКС–СКТ) полиамидов с помощью дифференциальной сканирующей калориметрии. Обычно для количественного определения антиоксидантов используется метод высокоэффективной жидкостной хроматографии, требующий более чем 48 часов для приготовления пробы-образца. Ряд образцов полиамидов с известным содержанием оксидантов (0–0,8%) был изучен методом ДСК в открытых алюминиевых тиглях в атмосфере кислорода и в интервале температур от − 50 до + 350 °C. Для всех образцов в изотермических условиях при 220 °C была найдена линейная зависимость между ΔH (теплота распада) и индукционным периодом, которая позволила количественно определить антиоксидант ВАНОКС–СКТ в образцах полиамидов.