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THERMAL ANALYSIS OF STABILIZED POLYMERS

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ABSTRACT

The influence of a number of amine and phenol type stabilizers on the value of the activation energy (E) of thermal-oxidative degradation of polyethylene (PE), polyethylene therephthalate (PET) and polycaproamide (PCA) has been investigated. The dependence of the activation energy of PE thermal-oxidative degradation on the concentration of such stabilizers as 2,6-di-*tert*-butyl-4-methylphenol; 2,2-methylene-bis(6-*tert*-butyl-4-methylphenol); N,N-di(naphthyl-2)phenylenediamine-1,4; bis[(3,5-di-*tert*-butyl-4-hydroxyphenyl)ethoxycarbonylethyl] sulfide is of an extreme character, the maximum activation energy being observed at a stabilizer concentration of 0.1–0.5%. Dispersion of the stabilizer introduced to molecular level, achieved during its chemical addition to macromolecules, provides an increasing effect on thermal stability. The results of thermal analysis of the stabilized polymers have been used to explain their stress–strain properties.

INTRODUCTION

Stabilizers introduced into polymers, to extend their lifetime and to improve the time and temperature conditions of operation of materials and products based on them, influence the kinetics of thermal and thermal-oxidative degradation of macromolecules [1]. Through thermal analysis, the inhibiting efficiency of additives introduced into stabilized polymers can be characterized. The aim of the present paper is to estimate the efficiency of different stabilizing additives in the processes of thermal-oxidative degradation of polyethylene (PE), polyethylene terephthalate (PET) and polycaproamide (PCA) according to their effect on the activation energy value of thermal-oxidative degradation.

EXPERIMENTAL

Commercial samples of low-density PE, PET and PCA were studied. 2,2-Methylene-bis(6-*tert*-butyl-4-methylphenol) (**I**); bis[(3,5-di-*tert*-butyl-4-hydroxyphenyl)ethoxycarbonylethyl] sulfide (**II**); 2,6-di-*tert*-butyl-4-methylphenol (**III**); N,N-di(naphthyl-2)phenylenediamine-1,4 (**IV**); 4,5-dimethoxy-

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1,2-benzoquinone (**V**); 4-(4′-phenylazophenylamino)-5-methoxy-1,2-benzoquinone (**VI**); 2,6-di-*tert*-butyl-1,4-benzoquinonediazide (**VII**); 1,4-benzoquinone (**VIII**); bis(4-phenylaminophenoxyethyl)ester (**IX**); and phosphonic acid (**X**), were used as stabilizing additives.

The additives (compounds **I**–**VI**) were introduced into PE by mixing with the polymer melt during milling. The stabilizer content ranged from 0.1 to 5%. Compound **VII** was introduced into PE by means of diffusion from its 2% solution in chloroform. The PE film was kept at 293 K for 5 min, and was then heated at 408 K for 10 min. The content of stabilizer introduced under these conditions comprised 0.4%. Compound **IX** was introduced into PCA by adding it to a polymer solution prior to film formation. Introduction of compound **VIII** into unstretched films and oriented fibres of PCA was performed by leaving samples in 1.5% water solution of stabilizer at 348 K for 60 min. The contents of compounds **VIII** and **IX** in PCA samples under investigation were both 0.1%. Compounds **VI** and **X** were introduced into PET at the stage of inter-esterification, their concentration in the samples under study was 0.1%.

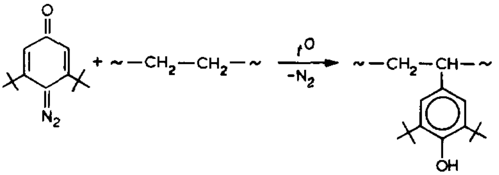
Thermogravimetric analysis was carried out under dynamic conditions with a MOM derivatograph (type OD-103, Hungary). The value of E was determined by the known methods [2,3].

RESULTS AND DISCUSSION

Introduction of stabilizers into PE is accompanied by a change in E value (Fig. 1, Table 1). The dependence of E on stabilizing additive concentration is of extreme character, the E maximum being observed at a stabilizer concentration of 0.1–0.5%. The inhibiting activity of the amine type stabilizer (**IV**) is close to that of diatomic space-hindered phenol (**I**). Compound **I** is more effective than monoatomic phenol (**III**). Compound **V** is the most effective thermal stabilizer. Introduction of **V** into the PE melt provides an E increase from 95 to 116 kJ mol^{-1}.

The determination of E for PET with additives of compounds **VI** and **X** (used in industry) has shown that compound **VI** is a more effective thermal stabilizer than **X** (Table 2). E values are independent of the extension ratio of the sample under investigation.

Compounds **I**–**V**, when introduced into PE, do not add to it chemically. Compound **VII** is known to add to PE under heating or UV irradiation according to the following scheme [4] thus eliminating its volatilization.



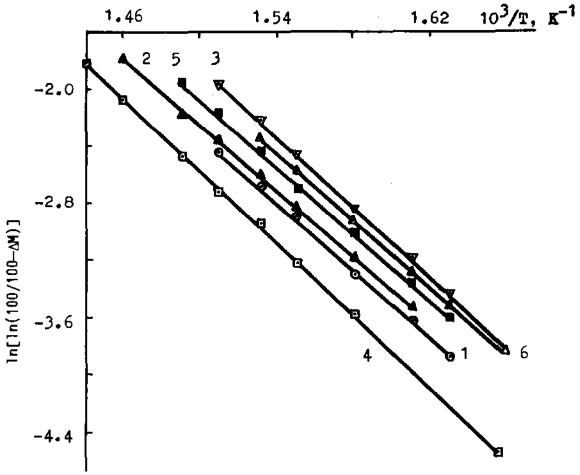


Fig. 1. Dependence of the ln[ln(100/100 − Δ*M*)] value on 1/*T* for PE stabilized by **I**. Stabilizer content (%): 1–0.1; 2–0.25; 3–0.5; 4–1.0; 5–3.0; 6–5.0.

TABLE 1

Dependence of *E* on stabilizer nature and concentration.

Stabilizer concentration (%)	E (kJ mol^{-1})				
	I	II	III	IV	V
0	95	95	95	95	95
0.1	101	95	96	97	102
0.25	102	100	98	101	–
0.5	103	97	97	104	116
1.0	101	97	95	102	–
3.0	99	95	–	100	–
5.0	97	94	–	99	95

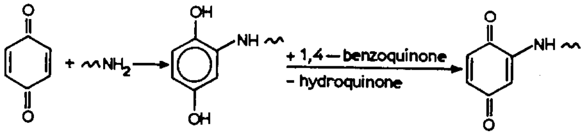
TABLE 2

Dependence of *E* on the stabilizer nature and extension ratio of the samples

Stabilizer	Extension ratio	E (kJ mol^{-1})
–	1.0	191
–	4.6	191
–	5.2	191
X	1.0	193
	4.6	193
	5.2	193
VI	1.0	210
	4.6	210
	5.2	210

The thermal analysis results of PE stabilized by compound **VII** provide evidence for a substantial increase of PE resistance to thermal-oxidative degradation. In particular, E increases from 95 to 104 kJ mol^{-1}. By finding the concentration dependence of E in the system PE–compound **II** we have shown that the maximum value of E is achieved at a stabilizer concentration of 0.25%, further increase of concentration results in the E value decreasing to that of the initial PE. The sample of PE with stabilizer **VII** contains the same stabilizing functional groups as does compound **III**. Though the stabilizer content in the polymer does not exceed 0.25% the E value of the sample with compound **VII** appears to be higher not only in comparison with the initial PE but also with PE containing an optimal quantity of compound **III**. The highly efficient stabilizing effect of compound **VII**, demonstrated by a substantial increase in E, seems to be due to its chemical addition to PE resulting in dispersion of the stabilizer to molecular level.

Compounds **VIII** and **IX** were chosen as stabilizers for PCA. Compound **VIII** is a highly efficient thermal stabilizer for PCA, provided that the diffusion mode of introduction is used [5,6]. According to refs. 5 and 6, PCA treatment with a water solution of compound **VIII** is accompanied by addition of **VIII** to the end amino groups of the polymer by the following scheme.



Over 90% of the total amino groups available in the polymer react. Aminoquinone, formed according to this scheme, successively adds molecules of **VIII**, resulting in a block copolymer of PCA and polyoxyphenylene, the latter being a product of the thermal polymerization of **VIII** in water solution.

The most resistant samples to thermal oxidation are those stabilized by products of interaction of compound **VIII** with PCA macromolecules. It is

TABLE 3

Dependence of E on sample type and nature of stabilizer introduced for PCA

Stabilizer	Sample type	E (kJ mol^{-1})
–	fibre	125
–	film	125
VIII	fibre	142
	film	142
IX	film	138

essential that the thermal-oxidative stability of samples of unstretched film-type and high-oriented fibres, estimated by E values, is the same, i.e., that it is determined by the chemical composition of the sample rather than by peculiarities of its submolecular organization (Table 3).

The results of thermal analysis of the stabilized polymers have been used [7,8] to explain their stress–strain properties.

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