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ESTIMATION OF THERMAL STABILITY OF PHENOL STABILIZERS BY MEANS OF THERMOGRAVIMETRIC ANALYSIS

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Abstract

A new method was developed for evaluation of the results of thermal analysis of phenol stabilizers used for the thermal stabilization of light-coloured polymers. The integral observed decomposition temperature obtained by using Doyle's method from the thermogravimetric curves was used as a basis of approach. For this purpose, the computational program TERMOGRAF for PC/AT is suggested. It is considered that the integral observed decomposition temperature is a more reliable and reproducible characteristic of thermal stability than the approach based on the temperature of beginning of decomposition.

Keywords: phenol stabilizers, TG, thermal stability

Introduction

Light-coloured polymer materials are stabilized by the addition of small amounts of phenol stabilizers, which simultaneously prevent the thermal destruction of the polymers during their processing at high temperatures. These additives themselves should be stable under the conditions of thermal treatment of the polymers. The estimated stability of polymers and their additives is an important characteristic that allows determination of the applicability of additives for a particular polymer. Unfortunately, the definition of thermal stability is very vague and it is variously defined by researchers.

Most authors characterize thermal stability by means of the temperature of the beginning of decomposition by using the thermal analysis method; this temperature is determined in different ways. In practice, the beginning of decomposition in the thermogravimetric curves is taken as the temperature at which the substance loses 5, 10 or 15% of its starting mass [1–3]. Fock [4] has sug-

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gested that the beginning of side-chain destruction should be regarded as the beginning of the decomposition of polymers; at that moment, the principal chain remains intact, whereas a further increase of temperature leads to further destruction, and the properties of the materials are radically changed. Wendlandt [5] suggests that the temperature of the beginning of decomposition should be determined by the point of deviation of the tangent from the thermogravimetric curve of mass loss versus temperature. For comparison of the thermal stabilities of compounds, Madorsky [6] uses the temperature at which the sample loses half its mass. There are more complex methods for determination of the temperature of the beginning of decomposition, e.g. by using the temperature at which thermolysis reaches a constant rate [7]. Such a diversity of methods of thermal stability determination is dictated by the essence of the empirical approaches to the complex processes occurring upon the thermal treatment of compounds.

It is seen from the above that it is necessary to find a single approach, and to determine a parameter characterizing the individual thermal properties of a compound. One such parameter is the integral observed decomposition temperature. This index and the calculation method were suggested by Doyle [8] and tested on a series of compounds. Using the thermogravimetric curve of mass loss, Doyle calculated the ratio of areas circumscribed by the curve. The parameter found in the experiment, with the individual properties of the compound taken into account was introduced. It was shown that the integral observed decomposition temperature has the practical sense of the semidecomposition temperature of the compound. In contrast with the ordinary temperature of evaporation (or decomposition) of half of the total amount, the integral observed decomposition temperature is obtained with inclusion of the residual mass. This approach may be used for both one-stage and multistage decomposition; small variations in the rate of heating do not significantly affect the integral observed decomposition temperature.

In this paper we have determined the integral observed decomposition temperatures of a series of phenol stabilizers from thermogravimetric curves. For their calculation, we have suggested a program for the mathematical treatment of thermogravimetric curves: TERMOGRAF.

Experimental

Thermogravimetric curves (TG) of 18 compounds of phenol type were obtained by using the MOM derivatograph (Hungary). The compounds were heated in the temperature range 25–500°C at a rate of 5 deg·min^{-1} in a nitrogen atmosphere. Thermolysis occurred in the compound melt. The mass of the sample was 50 mg, the TG sensitivity was 100 mg, and Al_2O_3 was used as the reference. The crucibles were platinum cups. The TG curves of the melts given in [9] were mathematically processed by software on an IBM PC/AT. For this purpose, we used the programs for approximation of the experimental TG curves and for their graphical display to obtain the tables summarizing the data. The mass change curve was approximated by cubic spline [10], using the program SPLINE developed at the Institute of Theoretical and Applied Mechanics of the Siberian Branch of the Russian Academy of Sciences [11]. Given the argument points and function values at these points, the program develops an array of spline coefficients a_{ik}, $i=\overline{1, 4}$, $k=\overline{1, n-1}$, where n is the number of given points, so that in the k-th region, for which $T_k<T<T_{k+1}$, the function value is calculated via the formula

$$W = a_{1k} + a_{2k}{*}d + a_{3k}{*}d^2 + a_{4k}{*}d^3, \quad d = T - T_{k+1} \tag{1}$$

(1) is used to obtain the formula for calculating the integral:

$$I = \int_{T_1}^{T} W(T)\mathrm{d}T = -\sum_{j=1}^{k} \left(a_{1j}d_j + \frac{1}{2}a_{2j}d_j^2 + \frac{1}{3}a_{3j}d_j^3 + \frac{1}{4}a_{4j}d_j^4\right)$$

$$d = \begin{cases} T_j - T_{j+1}, & \text{if } j < k, \\ T - T_{k+1}, & \text{if } j = k, \end{cases}$$

Here K is the serial number of the interval with T, so that $T_k \le T \le T_{k+1}$.

The data file for calculations was formed. It contains the following data for each experimental curve (according to Doyle's notation [8]):

$n$exp= the experiment number;
W_o= the initial mass;
n= the number of points;
T_j, $j=\overline{1, n}$ are n temperature values in °C;
W, $j=\overline{1, n}$ are n values of mass loss.

After the program had read the data, it fulfilled the following operations: calculating the values:

1) the spline coefficients;

2) $I = \int_{T_1}^{T_n} W\,\mathrm{d}T$, where $W = W_o - \overline{W}$;

3) $A = I/[W_o(T_n - T_1)]$;

4) $T_a = 475A + 25$;

5) $B = \int_{T_1}^{T_n} W\,\mathrm{d}T\ W\,\mathrm{d}T$;

6) $K=B/[W_n(T_a-T_1)]$;

7) $T_{ia}=475AK+25$;

8) entering the string of the resulting data into the file representing the table of results.

In Table 1, T_{ia} are the integral observed temperatures of decomposition of the phenol stabilizers. Table 2 lists the phenol stabilizers and their melting points ($T_{m.p.}$) and the calculated integral observed decomposition temperatures (T_{ia}). For comparison, Table 2 gives the temperatures of beginning of decomposition (T_W) found from the 5% loss in mass of the compound and from the deviation of the tangent from the TG curve (T_t).

Table 1

No.	i	A	T_a/°C	B	K	T_{ia}/°C
1	18134.22	0.6297	324.09	16778.73	0.9196	300
2	14511.38	0.5375	280.29	13299.11	0.9625	270
3	19465.06	0.8651	435.93	18537.07	0.9606	419
4	17479.57	0.6775	346.81	16646.88	0.9348	325
5	12608.87	0.5604	291.19	11857.23	0.9832	286
6	15814.42	0.7029	358.86	14681.50	0.9507	342
7	16767.03	0.7452	378.97	15506.91	0.9428	358
8	13708.64	0.6093	314.41	12531.28	0.9479	299
9	12443.26	0.5530	287.69	11333.87	0.9537	275
10	13277.02	0.5901	305.29	11375.87	0.8912	274
11	13787.17	0.6894	352.45	13528.46	0.8946	317
12	13221.37	0.5876	304.12	12064.76	0.9495	290
13	16159.84	0.7182	366.15	15143.26	0.9580	351
14	20044.77	0.7424	377.64	18819.70	0.9573	362
15	24366.29	0.6768	346.50	23106.24	0.9741	338
16	18264.21	0.5798	300.41	16183.71	0.9233	279
17	16874.27	0.7031	358.97	14594.18	0.9447	340
18	13647.50	0.6066	313.11	11722.72	0.8911	281

The errors in the decomposition point determination from the TG curves have been estimated. The standard deviation is 2.97. For 5 measurements and a confidence level of 0.95, the confidence range of the random error is 1.47.

Table 2 Destruction and melting temperature of phenol stabilizers

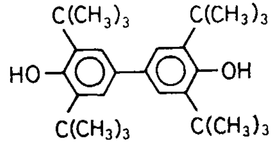
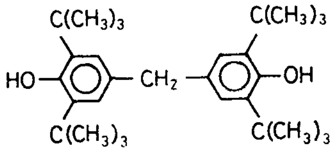
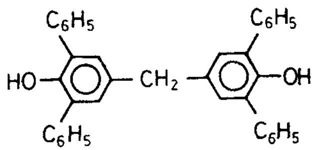
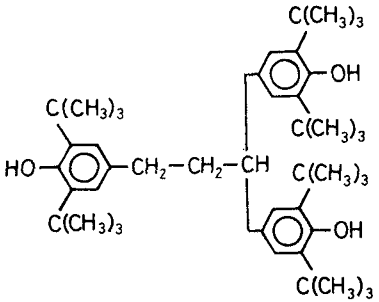
No.	Compound	Formula	$T_{m.p.}$°C	T_{ia}°C	T_w°C	T_t°C
1	3,3',5,5'-Tetra-terbutyl-4,4'-hydroxyphenyl		170	300	230	195
2	Di-(3,5-di-tert-butyl-4-hydroxyphenyl)methane		140	270	200	160
3	4,4-Bis-(3,5-diphenyl-4-hydroxyphenyl)methane		195	419	365	340
4	1,1,3-Tris-(3,5-di-tert-butyl-4-hydroxyphenyl)-propane		210	325	280	240

Table 2 Continued

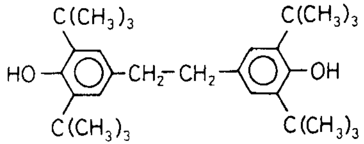
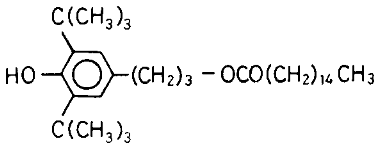
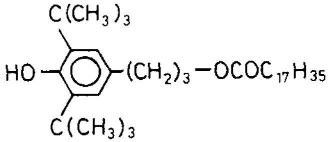
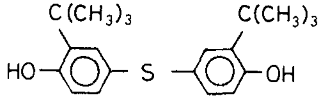
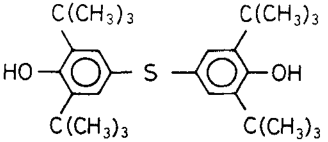
No.	Compound	Formula	$T_{m.p.}$°C	T_{ia}°C	T_w°C	T_t°C
5	Bis-1,2-(3,5-di-tert-butyl-4-hydroxyphenyl)ethane		100	286	250	220
6	3-(3,5-Di-tert-butyl-4-hydroxyphenyl)propylpalmetate		20	342	270	255
7	3-(3,5-Di-tert-butyl-4-hydroxyphenyl)propyl-stearate		50	358	345	290
8	Di-(3-tert-butyl-4-hydroxyphenyl)sulfide		110	299	240	225
9	Bis-(3,5-di-tert-butyl-4-hydroxyphenyl)sulfide		135	275	235	180

Table 2 Continued

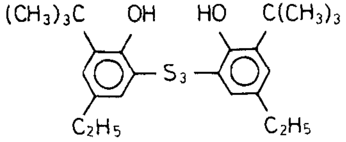
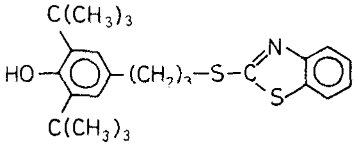
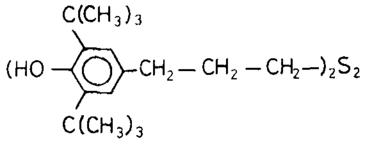
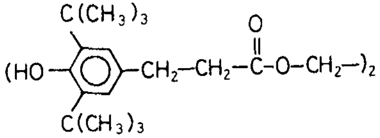
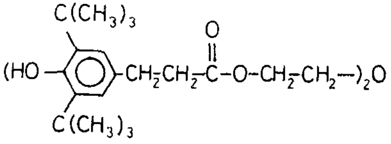
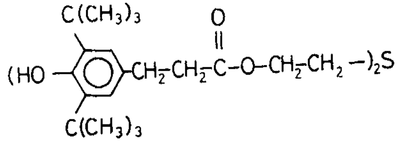
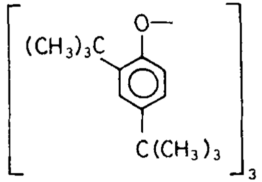
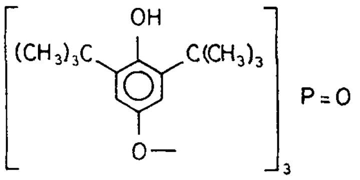
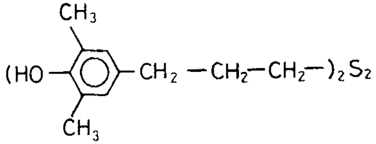
No.	Compound	Formula	$T_{m.p.}$°C	T_{ia}°C	T_w°C	T_t°C
10	Bis-(3-ethyl-5-tert-butyl-6-hydroxyphenyl)trisulfide		82	274	210	180
11	2-[(3,5-Di-tert-butyl-4-hydroxyphenyl)propylthio]benzothiazol		90	317	235	225
12	Di-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propyl]disulfide		100	290	230	220
13	2-(3,5-Tert-butyl-4-hydroxyphenyl) propionic acid-1,2-ethanedioldiester		135	351	300	245
14	2-(3,5-Di-tert-butyl-4-hydroxyphenyl)propionic acid-2,2'-oxybis-ethanoldiester		85	362	250	240

Table 2 Continued

No.	Compound	Formula	$T_{m.p.}$°C	T_{ia}°C	T_w°C	T_t°C
15	2-(3,5-Di-tert-butyl-1-hydroxyphenyl)propionic acid-2,2'-thiobisethanol-diester		60	338	290	280
16	Tris-(2,4-di-tert-butylphenyl)-phosphite		165	279	250	180
17	Tris-(3,5-di-tert-butyl-4-hydroxyphenyl)phosphate		200	340	305	275
18	Di-[3-(3,5-dimethyl-4-hydroxyphenyl)propyl]disulfide		80	281	225	220

$T_{m.p.}$°C is the melting points of phenol stabilizers; T_{ia}°C is the integral observed decomposition temperature; T_w°C is decomposition temperature determined by 5% mass loss of a compound; T_t°C is decomposition temperature determined by deviation of the tangent from TG curve.

Conclusions

From the TG curves, we have calculated the integral observed decomposition temperatures of 18 compounds of phenol type with the properties of thermal stabilizers. For the calculations, we have suggested the software for treatment of the TG curves to obtain the necessary integral characteristics and for graphic display of the approximations on an IBM PC/AT.

In our opinion, the integral observed decomposition temperature is the most informative characteristic of the specific features of organic compounds of complex structure. This characteristic is convenient since it can be determined with good reproducibility and precision and may be calculated from the data of one experiment only.

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Zusammenfassung — Es wurde eine neue Methode zur Auswertung der Resultate der thermischen Analyse von Phenolstabilisatoren ausgearbeitet, wie sie für die thermische Stabilisierung von leichtgefärbten Polymeren verwendet werden. Als Grundlage der Untersuchung wurde die wesentlichste beobachtete Zersetzungstemperatur verwendet, die unter Einsatz der Doyle'schen Methode an TG-Kurven ermittelt wurde. Hierfür wird das Computerprogramm TERMOGRAF für PC/AT empfohlen. Man stellte fest, daß die wesentlichste beobachtete Zersetzungstemperatur eine weitaus sinnvolleres und reproduzierbareres Merkmal der thermischen Stabilität ist, als bei der Betrachtung, die auf der Temperatur für das Einsetzen der Zersetzung basiert.