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Studying Stabilization of PVC by Differential Thermal Analysis

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ABSTRACT

A method for studying the thermal stability of PVC compounds by using differential thermal analysis (DTA) is presented. At isothermal conditions and in an oxygen-free nitrogen atmosphere, an exothermal maximum is observed at the moment when all stabilizer is consumed. The time until this maximum appears is taken as a measure of stability of the tested sample. Earlier DTA investigations on the thermal stability of PVC were done by Dunn and Ennis. They needed the addition of a destabilizer, such as ferric or zinc oxide to the PVC compound to get an easily determinable exothermal maximum. This means that applications of their method to industrial PVC compounds or end products were impossible, as neither should contain any of these oxides. Probably due to more sensitive equipment it is now possible to obtain an exothermal maximum without any destabilizer. A stabilizer such as tribasic lead sulfate (TBLS), for example, is still needed though. Plasticized or rigid compounds may be investigated. High amounts of some fillers cause the maximum to broaden, and the evaluation becomes more difficult. The method is easy and time saving. The very small amount of sample required (a few milligrams only) makes the sample preparation possible for all kinds of products.

INTRODUCTION

The heat stability of PVC is important to everyone working with this polymer. One way to measure the heat stability is by using DTA (differential thermal analysis). At isothermal conditions and in a nitrogen atmosphere, an exothermal maximum appears when all stabilizer is consumed. The time until maximum appears is taken as an induction time. PVC stability measurements by DTA were earlier carried out by Dunn and Ennis [1], but they needed addition of a destabilizer, like ferric or zinc oxide, which made it impossible to test industrial compounds.

EXPERIMENTAL

The DTA equipment used was a Mettler TA2000 instrument. The PVC was a commercial product, Pevikon S687 (Kema Nord, Sundsvall, Sweden), a suspension type PVC with a K value of 68. Dioctyl phthalate (DOP), tribasic lead sulfate (TBLS), and China clay were also used for compounding.

Samples were prepared by hand-mixing and milling at 160°C for 10 min. Plasticized and rigid compounds were tested. Table 1 shows the formulations of some plasticized compounds with increasing amount of stabilizer. These are the compounds used in the following investigations.

SCANNING DTA

A few milligrams of each sample were analyzed by scanning DTA. A nitrogen atmosphere was used to avoid oxidizing effects. The rate of temperature increase was 5°C/min. In Fig. 1 the resulting curves are shown. Prior to the endothermal breakdown of the PVC compounds,

TABLE 1. PVC Formulations

	Parts					
PVC S 687	100	100	100	100	100	100
DOP	50	50	50	50	50	50
TBLS	0	1	2	4	6	8
China clay	8	8	8	8	8	8

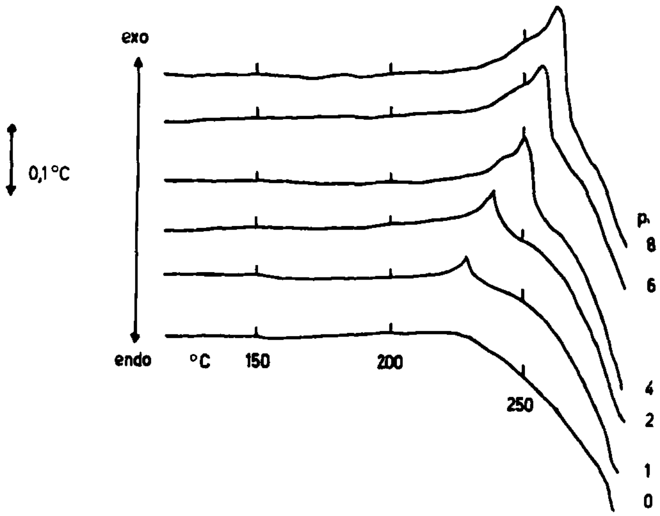

FIG. 1. Scanning DTA of formulations containing 100 parts PVC, 50 phr DOP, 8 phr China clay, and 0, 1, 2, 4, 6, or 8 phr TBLS. 5°C/min, N_2 atmosphere.

all compounds containing stabilizer show an exothermal maximum. This maximum is shifted to higher temperatures as the amount of stabilizer is increased.

ISOTHERMAL DTA

On the basis of the scanning DTA measurement, a temperature of 220°C was chosen for isothermal measurements. The temperature was brought up to 220°C at a rate of 25°C/min. The results are shown in Fig. 2. After reaching 220°C, the baseline is fairly straight again. The unstabilized sample showing no maximum is omitted from Fig. 2. The times from reaching 220°C until the maxima appear (stability time) are noted in the figure and also in Table 2. In Fig. 3 the stability times or induction times at 220°C are plotted against amount of stabilizer.

Similar measurements were carried out at other temperatures, and the resulting curves are shown in Fig. 4. Arrhenius plots of log stability time over 1/T give straight lines, and the activation energy was calculated to be 32 kcal/mole.

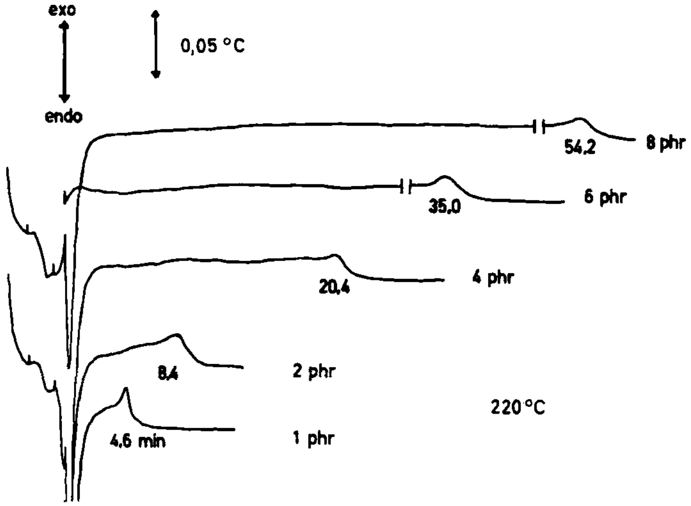

FIG. 2. Isothermal DTA of formulations containing 100 parts PVC, 50 phr DOP, 8 phr China clay, and 1, 2, 4, 6, or 8 phr TBLS. 220°C, N_2 atmosphere.

TABLE 2. Times until Maxima Appear

TBLS (phr)	Stability time at 220°C (min)
1	4.6
2	8.4
4	20.4
6	35.0
8	54.2

CONFIRMING EXPERIMENTS

It now seems obvious that the exothermal maximum denotes the total consumption of the stabilizer but some experiments will confirm this. As a simultaneous test to the DTA measurement, the nitrogen gas having passed the DTA cell was passed into distilled water and the pH was continuously recorded. At the same time as the exothermal

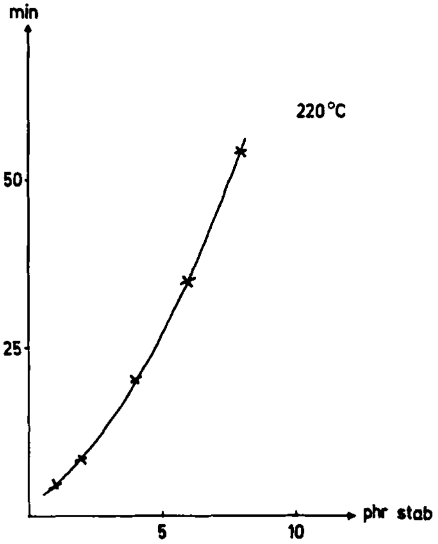

FIG. 3. Stability time as function of amount of TBLS for formulations containing 100 parts PVC, 50 phr DOP, 8 phr China clay, TBLS as shown; 220°C.

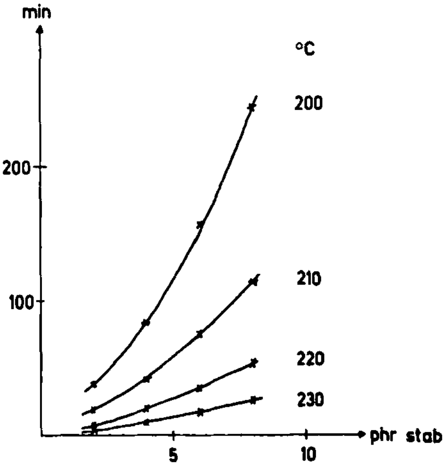

FIG. 4. Stability time as function of amount of TBLS at different temperatures for formulations containing 100 parts PVC, 50 phr DOP, 8 phr China clay, TBLS as shown.

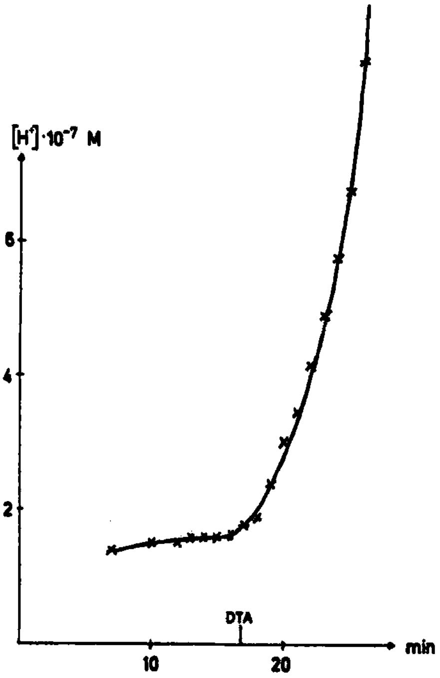

FIG. 5. Hydrogen ion concentration as function of time at 230°C for a formulation containing 100 parts PVC, 50 phr DOP, 8 phr China clay, 6 phr TBLS. DTA stability time noted.

maximum appeared on the DTA recorder, the pH value decreased fairly rapidly (Fig. 5).

The DTA stability time was also compared with the time measured according to ASTM 793-49 in which the amount of HCl evolved from a PVC sample into a carrier gas (nitrogen) is determined by titration. At 180°C, the temperature required by the ASTM method, a sample containing 2 phr TBLS showed a DTA stability time of 166 min; and the time by ASTM measurements is 168 min, indeed a good agreement.

APPLICATIONS

The DTA method of measuring PVC stability is useful in a number of ways. Whenever it concerns thermal stability the method is suitable. It is of interest to see how different additives affect the thermal stability.

TABLE 3. Effect of Stabilizers

Stabilizer	Source	Stability time at 220°C (min)
TBLS	Asso Lead	31.6
Lead carbonate	Asso Lead	45.8
Lead phthalate	Asso Lead	34.0
Barium-cadmium	Akzo	24.2
Barium-lead	Durham	13.0
Barium-cadmium-zinc	Ferro	6.7
Barium-zinc	Meister	5.4
Sulfur-free organic tin	Meister	-[a]
Aminocrotonate	Ciba-Geigy	7.2

[a] The organotin gives no well defined maximum.

Stabilizers

Formulations containing 100 parts PVC, 50 parts DOP, 8 parts China clay, and 6 parts of various stabilizers were mixed on the mill. Their DTA stabilities were measured and are listed in Table 3. On changing from one stabilizer to another makes it possible to optimize the compound technically and economically by use of the DTA stability values.

Plasticizers

The influence of two plasticizers, dioctyl phthalate (DOP) and a chlorinated paraffin (Cerechlor S52) on the thermal stability is shown in Figs. 6 and 7. The DOP compounds contain 100 parts PVC, variable DOP, 2 parts TBLS and 8 parts China clay. The Cerechlor compounds contain 100 parts PVC, variable Cerechlor, and 5 parts TBLS. The effects of the two plasticizers are obvious.

Filler

The influence of clay on the thermal stability of a PVC compound was studied. Compounds containing 100 parts PVC, 50 parts DOP,

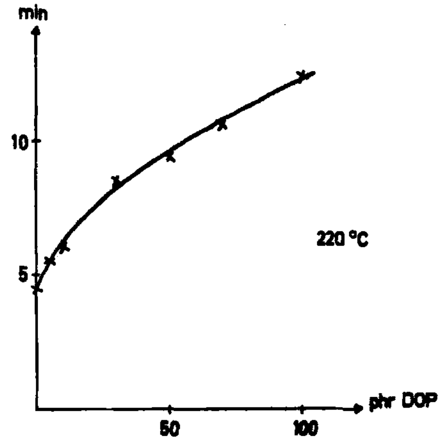

FIG. 6. Stability time as function of amount of DOP for formulations containing 100 parts PVC, 2 phr TBLS, 8 phr China clay, DOP as shown. 220° C, N_2 atmosphere.

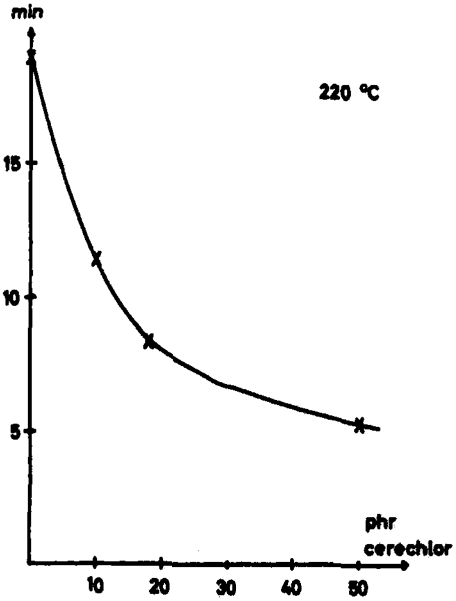

FIG. 7. Stability time as function of amount of Cerechlor S52 for formulations containing 100 parts PVC, 5 phr TBLS, Cerechlor as shown. 220° C, N_2 atmosphere.

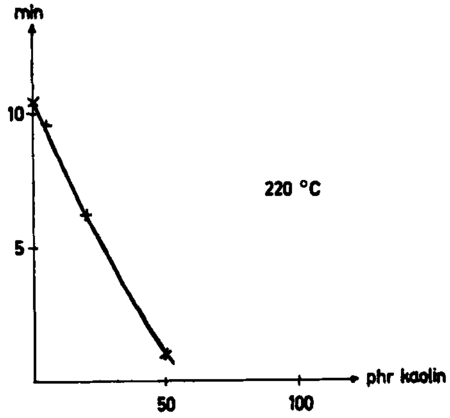

FIG. 8. Stability time as function of amount of China clay for formulations containing 100 parts PVC, 50 phr DOP, 2 phr TBLS, China clay as shown. 220°C, N_2 atmosphere.

2 parts TBLS, and variable China clay were analyzed by DTA at 220°C. The stability times are seen in Fig. 8. The China clay drastically reduces the thermal stability. The reason for this probably is that the China clay contains small amounts of ferric oxide, which is known to catalyze the decomposition of PVC.

Color Masterbatch

Different color concentrates give different stability properties to a PVC compound. Some compounds, of which the red one often caused trouble in production, were tested by DTA. The results are shown in Fig. 9. The red colored compound has a much lower stability time than the others. On testing a compound prepared with a new red masterbatch the stability time was found to be even longer than for the other colors. The masterbatch producer confirmed our suspicions that the old red masterbatch contained ferric oxide as a color base.

DISCUSSION

Using DTA to determine PVC stability is a convenient method. It is quick, easy, and reproducible. Because of the small amount of sample required, most PVC products may be tested. Problems may arise with some kinds of stabilizers showing no or several maxima.

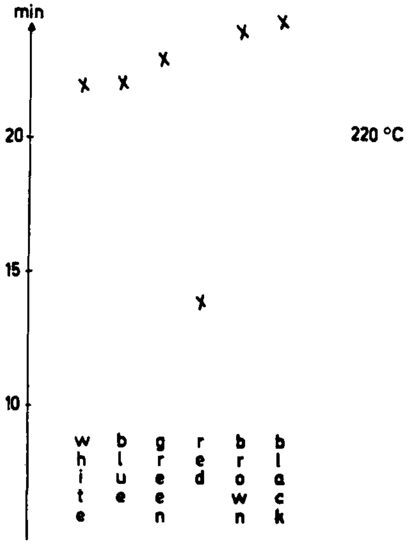

FIG. 9. Stability times for differently colored compounds. 220° C, N_2 atmosphere.

The method is thought to work only with stabilizers consumed during reaction with hydrogen chloride. The experience so far is that these DTA measurements are very useful both for research, development, control, and troubleshooting.

The exact mechanism responsible for the exothermal maximum is unknown to us. It is probably due to changes in heat of reaction when the stabilizer no longer reacts with hydrogen chloride.

REFERENCES

[1] P. Dunn and B. C. Ennis, J. Appl. Polym. Sci., 14, 355 (1970).

DISCUSSION

Dr. A. Guyot (Centre National de la Recherche Scientifique, Villeurbanne, France): I was greatly interested in Fig. 1 of Dr. Westerberg's paper. She both mentioned and showed that there is some exothermic effect which probably reflects a reaction between the stabilizer and the PVC or perhaps a reaction with the hydrochloric acid.

Is there any real possibility of a quantitative measurement of this exothermic effect? If it were possible to have such a quantitative measurement that would be an easy way in which to estimate the amount of stabilizer remaining in the PVC after either processing or irradiation. Secondly is there a sizable variation in the sensitivity of this exothermal peak depending on the kind of stabilizer system? For instance, is there a difference if calcium-zinc, cadmium-barium, lead, or organotin systems are used?

Dr. Westerberg: In answer to your first question, I think on the scanning curves it would be possible to measure the amount of the still active stabilizer content by determining the energy evolved. From my point of view it is easier, however, to determine the remaining amount of stabilizer by measuring the induction time on the isothermal curve. Comparing the induction times for two samples, one of which has been partly degraded, will show to what extent active stabilizer remains in the degraded sample. Concerning your second question, I suppose what is meant by the question is if there is a difference in peak height according to the stabilizers used. To some extent there is a difference, but the peaks are all about the same height. The height might vary a little, but not much.

Dr. A. Jungk (Metallgesellschaften, Frankfurt, Germany): Let me make an additional comment as a reply to Prof. Guyot's remarks and the DTA analysis of Dr. Westerberg. I think the suggestion is a good one and that it does explain why DTA does not work so well for tin- or barium/cadmium stabilizer systems. The peak obtained in DTA is easily explained via the enthalpy of neutralization of the basic components of the lead salts present. This concept does explain the different peak heights linked to different stabilizer levels. Since the stabilizing mechanisms of tin and barium/cadmium systems differ substantially from the lead systems, different peak maxima correspondingly will appear in DTA; these maxima are not as easily interpreted as with lead systems.

NOTE ADDED IN PROOF

During the period of the Symposium, our attention was drawn by Prof. D. Smith (Queen Mary College, University of London, and QMC Industrial Research Ltd) to his paper, Reaction of Halogenated Polymers with Ferric Oxide (M. A. Dudley and D. A. Smith, Society of Chemical Industry Monograph, No. 26, London, 1967 pp. 49-62). Dudley's and Smith's results are in good agreement with our own, both with respect to the temperature range for observed exotherms with isothermal DTA and also the calculated activation energy (30-32 kcal/mole) for the chemical reaction determining the induction period for poly(vinyl chloride), polychloroprene, and chlorosulfonated polyethylene, each containing various concentrations of added ferric oxide. However, the investigations of Smith are limited to PVC compounds containing ferric oxide as a destabilizer.