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STUDIES OF DECOMPOSITION OF A FOAMING AGENT IN PVC PLASTISOLS

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ABSTRACT

The preparation of foamed products from paste PVC is an area of great commercial importance. In this work, the decomposition of a blowing agent, azodicarbonamide (ADA), in PVC plastisols has been studied using primarily differential scanning calorimetry (DSC) and thermomechanical analyses (TMA). Some results obtained by thermogravimetric analyses (TGA) and thermosonimetry (TS) are also reported. The results show that DSC and TMA can give very valuable information about the foaming process in PVC plastisols.

INTRODUCTION

A poly(vinyl chloride) (PVC) plastisol is a dispersion of fine particles of a PVC resin in an organic liquid. The particles are typically in the range from about 40 to 0,2 µm and smaller. They consist of primary particles from the polymerization and secondary particles or agglomerates of primary particles formed during the drying process.
Most soft vinyl foams are made from plastisols with azodicarbonamide (ADA) as a foaming agent. The solid ADA is added before mixing the plastisol. By thermal decomposition of ADA blowing gases are released. This reaction is often activated at a lower temperature to avoid thermal destabilization of the PVC. In the production of certain products such as floor coverings and wall papers, the decomposition of ADA is often suppressed to produce profiled patterns. Usually the production of such products from plastisols takes place in four steps:

- Coating a plastisol on a substrate
- Gelatination of the plastisol
- Printing with activator and colour on the gelled plastisol
- Foaming of the gelled plastisol

This procedure will give coloured profiles in the foamed PVC.

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METHODS AND THEORY

We have used the normal thermoanalytical methods DSC, TMA and TGA to study the decomposition reactions of ADA. To get a better understanding of the process from solid ADA to decomposition gases, thermosonimetry (TS) has also been tried. From the DSC measurement it is possible to evaluate the kinetics of the decomposition reaction of ADA. The mathematical model used to describe the kinetics is (ref. 1,2):

$$d\alpha/dt = k(1-\alpha)^n \qquad (1)$$

where $d\alpha/dt$ = rate of reaction, k = reaction rate constant, α = fraction reacted (growing from 0 to 1), t = time of reaction (s), and n = order of reaction. The Arrhenius equation describes the temperature dependence of the reaction rate constant:

$$k = k_o e^{-E_A/RT} \qquad (2)$$

where k_o = frequency factor, E_A = activation energy ($\mathrm{Jmol^{-1}}$), and R = gas constant (8,31 $\mathrm{Jmol^{-1}\ K^{-1}}$). Substituting equation 2 into equation 1, a multiple linear equation is the result:

$$\ln(d\alpha/dt) = \ln k_o + E_A(1/-RT) + n\ln(1-\alpha) \qquad (3)$$

From equation 3 the values for $\ln k_o$, E_A and n can be calculated by multiple linear regression analysis (ref. 1).
We also get from equation 1:

$$n = 1, \quad \alpha = 1-e^{kt} \qquad (4)$$

$$n \neq 1, \quad \alpha = 1-(kt(n-1)+1)^{1-n} \qquad (5)$$

or:

$$n = 1, \quad \lg t = 2{,}3\ \lg(\lg(1-\alpha)) - \lg k_o + E_A/2{,}3RT \qquad (6)$$

$$n \neq 1, \quad \lg t = \lg(((1-\alpha)^{1-n}-1)/(n-1)) - \lg k_o + E_A/2{,}3RT \qquad (7)$$

After a DSC measurement of the decomposition of ADA in a plastisol is performed, an Arrhenius plot of time t to achieve a certain degree of decomposition α can be made as a function of temperature ($1/T$).

EXPERIMENTAL

In most of our experiments a general recipe for foamed PVC products was used (Table 1). To study the effect of various components, one or the other of them was omitted in some experiments as indicated in the legends to the figures.

TABLE 1

Recipe for a PVC plastisol with a foaming agent.

Parts	Component
100	poly(vinyl chloride), PVC
60	di-octyl phtalate, DOP
3	epoxidized soybean oil, ESO
4	dispersion of foaming agent, azodicarbonamide, ADA, in DOP (ADA:DOP = 1:1)
2	dispersion of activator, zinc oxide, ZnO, in DOP (ZnO:DOP = 1:1)

The measurements on DSC, TMA and TGA were performed on a Mettler TA3000 system with built-in evaluation software. The thermosonimetry measurements were done at the University of Trondheim (ref. 3).

RESULTS AND DISCUSSION

Fig. 1 shows results from DSC analyses of plastisols with (Fig. 1a) and without (Fig. 1b) foaming agent. By comparing Figs. 1a and 1b it is clearly seen that the decomposition reaction of ADA is strongly exothermic in the temperature range between 140 and 200^{o}C, with a peak at 187^{o}C.

We have also studied the decomposition of ADA using TMA. Results obtained with a pregelled sample of the same plastisol as that used in Fig. 1a are given in Fig. 2. The derivative of the TMA signal has a peak at 183^{o}C, which is approximately the same temperature as that of the DSC-peak in Fig. 1a.

Hence, we now have two different techniques, DSC and TMA, to study the decomposition reaction of ADA. They give approximately the same optimum mass temperature for foaming a PVC plastisol. This information can be used to control an air heated oven in an industrial process.

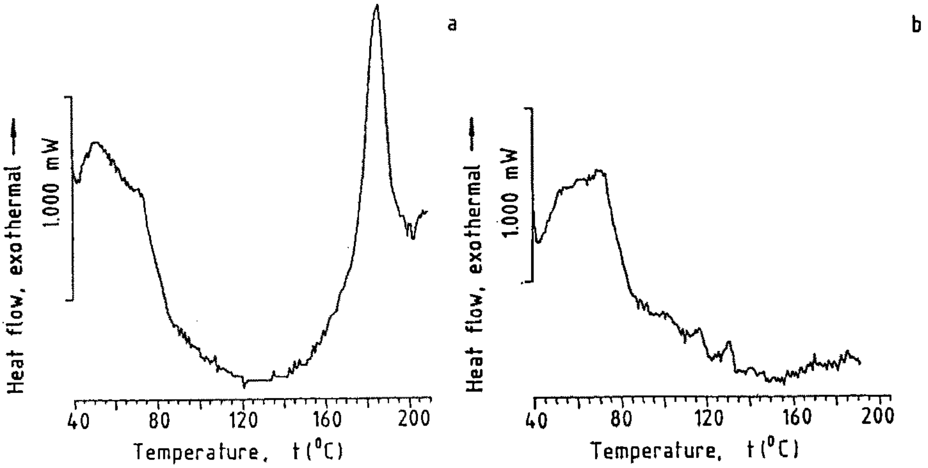

Fig. 1. DSC analyses of PVC plastisols.
(a) With foaming agent (ADA) and activator (ZnO).
(b) Without the foaming agent; the other components being the same as for (a). Heating rate = 10 K/min.

The comparison between the two techniques also gives some information about the reproducability of the measurements. Since relatively small samples (10-15 mg) are measured, it is necessary to make parallel measurements, using either the same plastisol on the same instrument, or the same plastisol on DSC and TMA before any conclusions can be made.

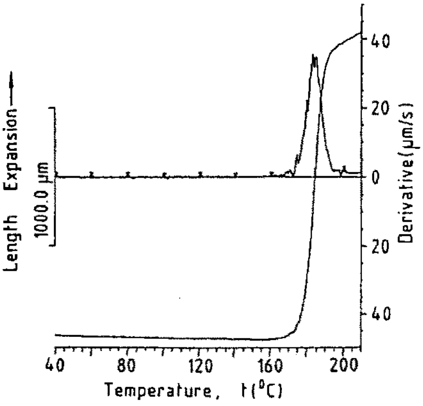

Fig. 2. TMA analysis of pregelled plastisol with foaming agent (ADA) and activator (ZnO). Heating rate = 10 K/min. (Pregelling: 120 s at 130°C in an air heated oven (Werner Mathis).

In an earlier study, thermogravimetric analyses (TGA) (ref. 4) and thermosonimetry (TS) (ref. 3) were also used to see what happens to the solid ADA particles during the heating process. In these measurements no PVC was added. In Fig. 3 these results are compared with results from a DSC measurement on the plastisol (ref.4).

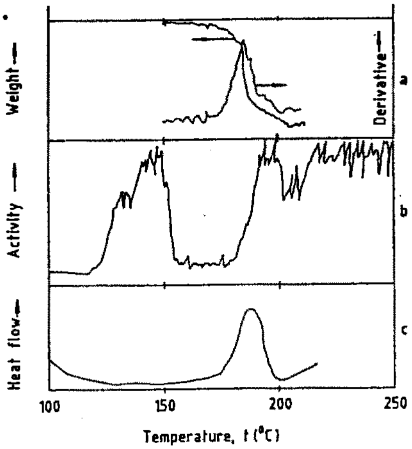

Fig. 3. Comparison of signals from different techniques (a) TGA of a "plastisol" dispersion without PVC. (b) TS of the same dispersion. (c) DSC of a PVC plastisol with all components added (reproduced after ref. 4).

From the TS measurement (Fig. 3b) the solid ADA particles seem to start disintegrating at 120°C, i.e. before the decomposition reaction starts in the temperature range between 150 to 170°C, as can be seen from TGA (Fig. 3a) and DSC (Fig. 3c) measurements.

A comparison of three different activating systems is given in Fig. 4. As can be seen, at 190°C the lead phosphite gives the fastest decomposition of ADA, then follows zinc octoate and finally zinc oxide. Experiments in an air heated oven at the same temperature gave the same result (ref. 5).

CONCLUSIONS

Thermoanalytical methods seem to be very useful tools for studying the decomposition of a foaming agent in PVC plastisols. However, the sample size is usually very small (10-15 mg), so that many parallel measurements have to be done before conclusions can be made.

The optimum mass temperature for decomposition of ADA with ZnO as activator seems to be about 185-190°C. This mass temperature is often used in industrial processes.

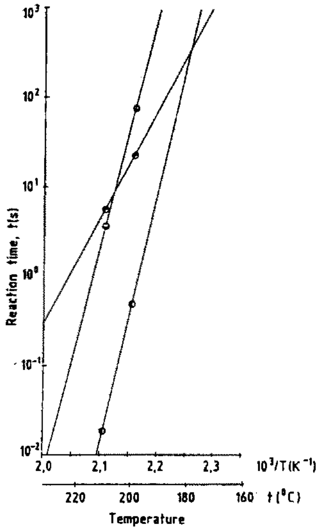

Fig. 4. Reaction time to achieve 90% decomposition of blowing agent as a function of temperature for three different activator systems:

◒ Zinc oxide
◓ Zinc octoate
◐ Lead phosphite

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