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Thermal Analysis of Compounded Poly(Vinyl Chloride)*

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Synopsis

Differential thermal analysis of mixtures of poly(vinyl chloride) and dioctyl phthalate shows a compound endothermic peak due to decomposition of both polymer and plasticizer. The thermal behavior of other plasticizers is similarly affected in the presence of poly(vinyl chloride). The addition of zinc oxide or ferric oxide decreases the thermal stability of the mixture and, under isothermal conditions, a resultant induction period allows the estimation of an activation energy for the dehydrochlorination of poly(vinyl chloride) and of the relative effectiveness of thermal stabilizer systems.

INTRODUCTION

Poly(vinyl chloride) (PVC) is used extensively in modern construction. While it does not burn readily, it decomposes at relatively low temperatures to give toxic and corrosive products.[1,2] The proportion of the time at recent symposium devoted to this plastic[3] reflects the concern with which this aspect of PVC technology is regarded.

There is limited understanding of the mechanism of degradation of PVC. The dehydrochlorination is generally[4] accepted as being a chain radical reaction, but even under favorable conditions it is not possible to exclude contributing nonradical mechanisms.[5] In the presence of the other components necessary to confer processability and serviceability on the polymer, the degradation will certainly be modified, and perhaps completely changed, in ways that are even less understood.[4,6] Accordingly, the screening and evaluation of compounding ingredients and of PVC formulations are largely empirical exercises and, while the ultimate evaluation must be determined by actual service,[7] various aspects of thermal analysis have recently been suggested for evaluation of thermal stability.

Both thermogravimetric analysis and differential thermal analysis of the polymer have been reported; but, while the expected phenomena of glass transition, dehydrochlorination, and ultimate degradation are obvious, the inherent limitations of thermal methods limit the interpretation of the thermograms. For compounded PVC and for PVC copolymers, the inter-

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action of components modifies the thermograms and meaningful comparisons are possible. Thermogravimetric analysis has been employed by Matlack and Metzger[8] to evaluate the thermal stability of PVC formulations and by Weintraub and his co-workers[9] for comparison of vinyl chloride copolymers. Similarly O'Leary and his co-workers[10,11] have utilized differential thermal analysis. Using these techniques, Dudley and Smith[12] have shown the profound effect of metal oxides on the thermal degradation of chlorinated polymers.

In the present communication we present evidence of the interactions that can occur between PVC, plasticizers, stabilizers, and metal oxides. Under conditions of thermal stress ester-type plasticizers are decomposed in the presence of PVC. Precautions are therefore necessary when interpreting thermoanalytical data for PVC formulations, particularly since there is concurrent decomposition of plasticizer and polymer. In the presence of zinc oxide, an induction period prior to decomposition can be determined under isothermal conditions, and there is evidence that activation energies determined in this way can be used to classify and evaluate stabilizer systems.

MATERIALS AND METHODS

The PVC used was Corvic D65/8 (Imperial Chemical Industries of Australia and New Zealand, Melbourne, Australia), a medium-high molecular weight granular polymer, although other grades of Corvic gave similar results; it was used without further purification.

Commercial plasticizers and stabilizers, Analar zinc oxide, and *B.P.C.*-grade ferric oxide were used as received.

Samples were prepared by ball-milling the solid components; the liquid components were then added by hand mixing and the samples were allowed to equilibrate for a week. McKinney[13] has described the rapid dispersion of plasticizer in PVC when "dry mixed" above 120°C. In the present investigation the dispersion of plasticizer was accomplished during the warm-up period, and any incomplete dispersion of solid components was offset by the known thermal history of the sample.

All differential thermal analyses (DTA) were performed on a DuPont 900 Differential Thermal Analyzer using the standard cell (unweighed samples, 1–2 mg) and a heating rate of 20°C/min. When operating in the isothermal mode, there was a warm-up period of 2–3 min and timing was commenced when the heater voltage fell within 3 volts of the operating isothermal voltage. The isothermal temperature was measured in the glass bead reference material and an atmosphere of oxygen-free nitrogen was used to minimize oxidative effects.

A Stanton Automatic Thermo-recording Balance, Model HT-SM, was used, without modification, for the limited thermogravimetric work. Sample size was 50–100 mg and the heating rate was 6–7°C/min.

RESULTS AND DISCUSSION

The DTA traces of two typical PVC compounds that differed only in that one contained a small amount of ferric oxide as an additive are shown in Figure 1, together with those of the base polymer and dioctyl phthalate (DOP) plasticizer. It can be seen that the endothermic peak due to the boiling of the plasticizer is absent from the thermogram of the compounded material; that the endothermic peak due to the dehydrochlorination of the polymer has been broadened and the peak position shifted; and that, while the deleterious effect of ferric oxide is obvious, both formulated materials shown an early exothermic effect. Similar results are shown in thermogravimetric analysis. These observations have obvious implications in the application of thermal analysis to evaluation studies of PVC additives.

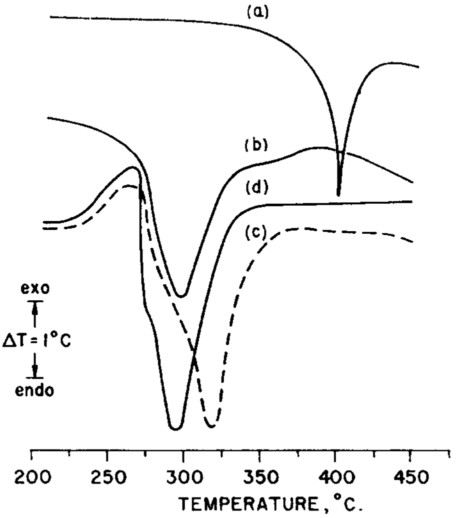

Fig. 1. DTA traces of: (a) dioctyl phthalate on glass beads; (b) PVC (Corvic D65/8); (c) typical PVC compound; (d) same as (c) but containing Fe_2O_3, 1 phr.

PVC–Plasticizer Interaction

A series of mixtures of PVC and DOP were prepared with increasing amounts of polymer in the plasticizer. The DTA traces (Fig. 2) of typical mixtures are shown. As the amount of PVC was increased, the endothermic peak at 400°C, attributed to boiling of the DOP, was weakened and a new endothermic peak appeared, which strengthened as the peak temperature shifted to lower temperatures. When the DOP concentration was 420 parts per 100 parts resin (phr), there was no indication of the original endothermic peak. A sublimate, identified as phthalic anhydride, appeared on the bell jar at temperatures above 320°C.

The new endothermic peak at temperatures about 350°C can be attributed to decomposition of the DOP. Zilberman and his co-workers[14] have shown that DOP is decomposed to phthalic anhydride and octenes by prolonged heating with PVC at 170°C, and Stepec et al.[15] found that the energy of activation for the degradation of PVC is dependent on the concentration of DOP present. Under other conditions the susceptibility of DOP (and other plasticizers) to oxidative attack has been noted.[16] In the present case oxidation is precluded, and the stoichiometry (0.73 mole available HCl/ester group) suggests catalytic decomposition of the DOP to phthalic anhydride and octenes, a contention strengthened by results obtained in the presence of metal oxides.

The observed decomposition of plasticizer during DTA in the presence of PVC is not confined to DOP alone, but has also been shown for dioctyl sebacate and tritolyl phosphate. The reported[10] "boiling off" of trioctyl phosphate (bp 220°C/5 mm Hg)[17] from a PVC compound at 250°C must also be seen as a decomposition of the plasticizer. Since normal PVC formulations contain considerably less DOP than the mixtures we have been considering, the decomposition of the plasticizer in normal compounds is shifted to lower temperatures. It then coincides with the dehydrochlorination of the polymer and modifies both peak position and shape (Figs. 1 and 2) in the thermogram. Any estimation of the relative thermal stability of plasticized PVC from the peak temperature of the dehydrochlorination reaction, as recommended by O'Leary,[11] must be treated with extreme caution. Both energies of activation (derived from peak shape) and enthalpies of decomposition (derived from peak area) can contain an appreciable contribution from plasticizer decomposition.

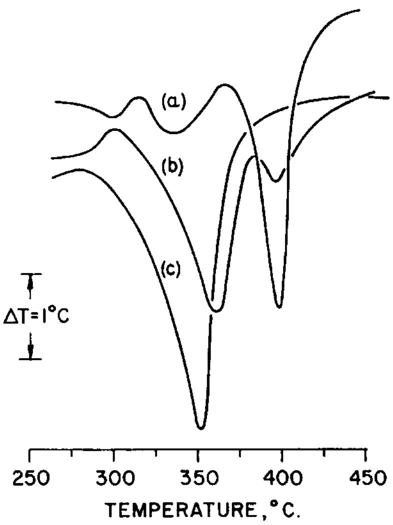

Fig. 2. DTA of PVC–DOP mixtures: (a) DOP, 940 phr; (b) DOP, 520 phr; (c) DOP 420 phr.

Effect of Metal Oxides

While the deleterious effect of ferric oxide on PVC (Fig. 1) is well known, Smith and Dudley[12] found that, in the presence of ferric oxide, the thermograms of chlorine-containing polymers, including PVC, show an additional exothermic peak before the dehydrochlorination reaction. Further, under isothermal conditions, this peak was subject to an induction period and the derived activation energies could be correlated with the activation energy for dehydrochlorination of the polymers. While we were unable to reproduce these effects for simple mixtures of ferric oxide and PVC, corresponding results were obtained when DOP was added to the mixture.

Repetition of the previous DTA with the addition of small amounts of ferric oxide to the mixture of PVC and DOP showed the extent of the effect of the oxide. Reaction occurred at a much lower temperature and the

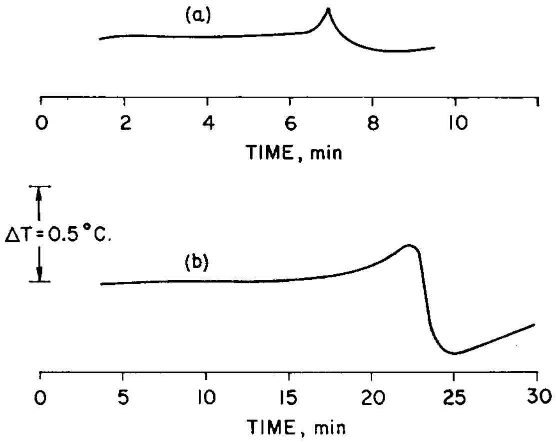

Fig. 3. Isothermal DTA of PVC–DOP (70 phr) mixtures: (a) Fe_2O_3, 2.0 phr, at 204°C (b) ZnO, 3.6 phr, at 164°C.

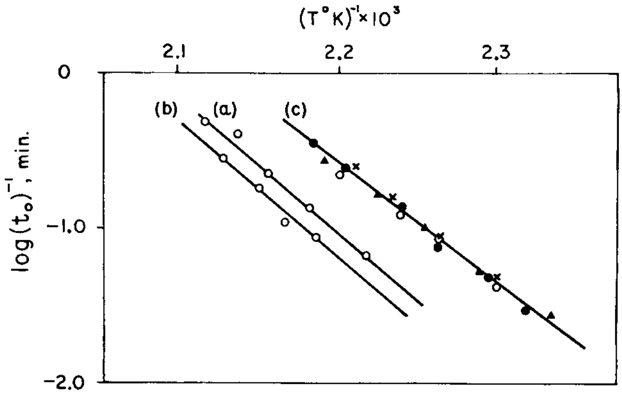

Fig. 4. Arrhenius plot for the induction period of PVC–DOP (70 phr) and metal oxide mixtures: (a) Fe_2O_3, 1.0 phr; (b) Fe_2O_3, 2.0 phr; (c) ZnO: (×), 1.0 phr; (●), 1.8 phr; (▲), 3.6 phr; and (O), 7.8 phr.

boiling of the DOP was completely suppressed by the presence of 0.025 mole ferric oxide and 0.15 mole PVC (monomer equivalent). Similar results were obtained for dioctyl sebacate and tritolyl phosphate plasticizers. Ferric oxide alone, or in conjunction with thermally dehydrochlorinated PVC, was ineffective in promoting decomposition of the plasticizers.

Under isothermal conditions it was found that, after an induction period, mixtures of ferric oxide, PVC, and DOP (70 phr) underwent an exothermic reaction which was immediately followed by an endothermic reaction (Fig. 3). The induction time (t_0) was taken as the time to the initial exothermic departure from the baseline. This gave a straight line for the Arrhenius plot, whereas the time to maximum exotherm or maximum endotherm did not.

Change of DOP concentration in the range 50–100 phr did not affect the induction time; however the Arrhenius plot had the same dependence on ferric oxide concentration (Fig. 4) as was observed by Smith and Dudley[12] in the absence of plasticizer.

When ferric oxide was replaced by zinc oxide, the induction period was reduced and the thermal effects increased in magnitude. The effect of concentration of zinc oxide on the induction period was slight (Fig. 4).

In a very limited thermogravimetric investigation it was found that under isothermal conditions the rate of weight loss from these mixtures was much greater for those containing zinc oxide than for those with ferric oxide, and that in the case of the former it was apparently proportional to the initial concentration of the zinc oxide. However, the induction period could not be determined with the same degree of accuracy as found in differential thermal analysis.

The derived energies of activation from the Arrhenius plots (Fig. 4) are 36 and 33 kcal/mole for reactions in the presence of ferric oxide and zinc oxide, respectively. Both values are of the expected order for the dehydrochlorination of PVC.[12]

The DTA results can be interpreted as being determined by the initial thermal degradation of PVC. The evolved hydrogen chloride, and metal halide when metal oxide was present, is seen as acting as an acid catalyst for the decomposition of the polymer[12] and the plasticizer[14] and perhaps for the interaction of both. Since they are less volatile, both ferric and zinc chlorides will maintain a higher concentration in the system than hydrogen chloride and thus be more effective. The absence of exothermic effects when there is no plasticizer present is considered to be predominantly a transport effect which would be overcome by the use of sufficiently finely dispersed oxide in the polymer. The interpretation requires an unmodified thermal degradation to proceed until there is some critical catalyst concentration, at which time vigorous reaction of both plasticizer and polymer ensues. While there is unreacted oxide (or stabilizer in the more general case), the net effect is an exothermic reaction; however when these are reacted, the true endothermic nature of the dehydrochlorination is manifested (Figs. 1 and 3 and thermogram[10]).

The pronounced exotherm suggests that very little degradation has occurred at the time of the initial exothermic departure from the isothermal baseline (Fig. 3). If the efficiency of formation of zinc chloride is greater than that of ferric chloride, or if the catalytic effectiveness is greater, than the point of departure will correspond to a smaller degree of decomposition of the PVC. Since the chlorine atoms first eliminated are the most labile, this could account for the decreased energy of activation observed in the presence of zinc oxide.

Evaluation of Stabilizers

With constant plasticizer and metal oxide concentrations, a reproducibly small degree of decomposition of the PVC should have occurred at the end of the induction period. This period will be influenced by the presence of stabilizers in the system and would therefore be expected to reflect their effectiveness.

A mixture was chosen such that induction periods could be determined in the range 160°–220°C, and calcium stearate, dibasic lead phosphite, and dibutyltin dilaurate, representing poor, moderate, and good stabilizers, respectively, were incorporated into the formulation, as follows: PVC (Corvic D65/8), 100 parts by weight; dioctyl phthalate, 70 parts by weight; zinc oxide, 1.8 parts by weight; and stabilizer, equivalent weights, as shown. Arrhenius plots were constructed from the induction times determined for different levels of stabilizer concentration.

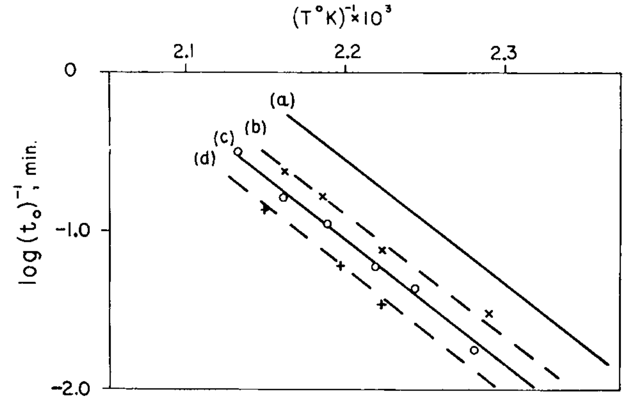

Fig. 5. Arrhenius plot for PVC–DOP (70 phr), ZnO (1.8 phr), and calcium stearate mixtures: stabilizer concentration (a) 0.0 phr; (b) 1.1 phr; (c) 2.1 phr; (d) 3.2 phr.

Straight-line relationships with both calcium stearate (Fig. 5) and dibasic lead phosphite (Fig. 6) were obtained, and the displacement of the graphs showed a marked concentration dependence. The apparent activation energy was the same as in the unstabilized mixture in each case; however the stearate was marginally less effective in increasing the induction period. This suggests that these stabilizers have little effect on the initiation reac-

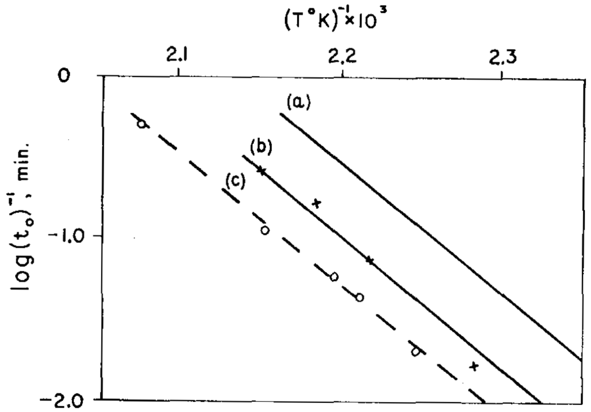

Fig. 6. Arrhenius plot for PVC–DOP (70 phr), ZnO (1.8 phr), and dibasic lead phosphite mixtures: stabilizer concentration (a) 0.0 phr; (b) 1.0 phr; (c) 1.8 phr.

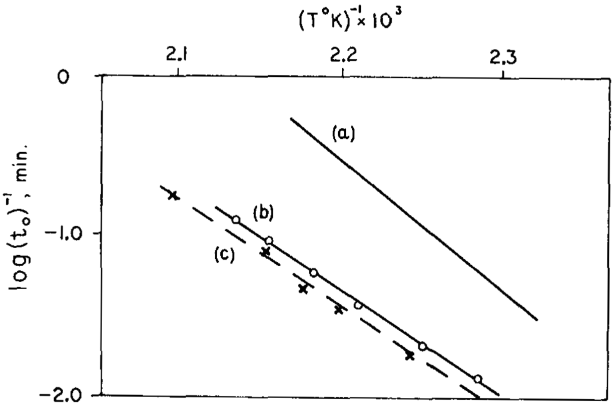

Fig. 7. Arrhenius plot for PVC–DOP (70 phr), ZnO (1.8 phr), and dibutyltin dilaurate mixtures: stabilizer concentration (a) 0.0 phr; (b) 1.1 phr; (c) 2.2 phr.

tions in the degradation, but function as simple hydrogen chloride acceptors.

In contrast, the compound containing dibutyltin dilaurate showed a lower energy of activation (31 kcal/mole) than the unstabilized mixture (33 kcal/mole) (Fig. 7). Also an increased concentration of the organotin stabilizer had much less effect than the former stabilizers. O'Leary et al.[11] reported decreased heat of dehydrohalogenation for PVC in the presence of organotin stabilizers, and Metzger[8] noted that, while the onset of weight loss was delayed by organotin stabilizers, the ultimate reaction was more vigorous. It is therefore apparent that these stabilizers function directly at the initiation of degradation.

The synergism of a mixture of calcium stearate and dibutyltin dilaurate was also shown (Fig. 8) by this method. The observed induction period was longer than that predicted by simple addition of the increments due to each component. It is interesting to note, however, that the gradient of the line approximated closely to that predicted.

In the absence of the "destabilizing" zinc oxide, DTA of the above mixtures, at linear heating rates, gave traces in which it was difficult to pick with certainty the onset of degradation. The traces showed only small differences in endothermic peak temperature and isothermal studies were not attended by sufficiently pronounced thermal effects to be useful.

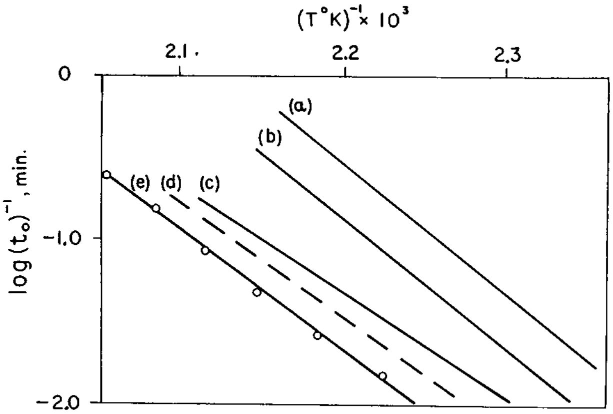

Fig. 8. Arrhenius plot for PVC–DOP (70 phr), ZnO (1.8 phr), dibutyltin dilaurate, and calcium stearate mixtures: (a) no stabilizer; (b) calcium stearate, 1.1 phr; (c) dibutyltin dilaurate, 1.1 phr; (d) calculated (nonsynergistic) value for (b) and (c); (e), measured values for (b) and (c).

On the other hand, the isothermal method using a "destabilizer," such as zinc oxide, gives easily determined endpoints, allows estimation of concentration dependence, and indicates qualitative differences between stabilizer systems. The effect of stabilizers on the decomposition of ester-type plasticizers, leading to flammable by-products during the decomposition of PVC compounds, can also be studied by these techniques.

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