

Thermal Stability of Modified Poly(vinyl Chloride) by TGA

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Synopsis

The stability of poly(vinyl chloride), as measured by thermogravimetric analysis, is significantly different from that of other thermoplastics. It is shown that the onset of weight loss can be correlated with the development of color in a processed resin. It is further shown that the ingredients within a rigid polyvinyl chloride compound drastically alter its thermal behavior. The effect of lubricant and stabilizer on the degradation of poly(vinyl chloride) is stressed.

The processing of thermoplastic materials usually requires reasonably high temperature stability (up to 300°C.) of polymers. It is apparent that all resins do not behave similarly (Fig. 1) and, since this is also true of single resins from different sources or of different batches of a resin from the same source, it is necessary to be able to distinguish or determine the differences in thermal stability. Thermogravimetric analysis (TGA) affords an excellent method by which this may be accomplished. Most of the common resins (e.g., polyethylene and polystyrene) have a single weight-loss mechanism or reaction. This is not true, however, of resins such as polyvinyl chloride (PVC). PVC is especially vulnerable to changes in thermal conditions due to the chlorine groupings, and thus its weight-loss process is somewhat different (see Fig. 1).

The thermal instability of PVC can be followed by a three-step weight-loss thermogram on the TGA. This degradation procedure is identified as follows (Fig. 2): A is the region of dehydrochlorination (weight loss of 50-60%), B is the evolution of simple hydrocarbons formed by cyclization and chain scission (weight loss of 15-30%), and C is a gradual evolution of the more complex degradation compounds.^{1,2}

The initial formation of conjugated bonds (caused by the evolution of HCl) imparts a coloring to the PVC compound that is quite unfavorable to the processor. Since PVC compounds are mixtures of PVC resin and additives such as lubricants, stabilizers, and modifiers, it is necessary to understand the influence of these additives on the stability of the material. It is the purpose of this paper to demonstrate the use of the TGA technique

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in differentiating between materials as to the influence of additives on the thermal stability and development of color.

In order to examine the effect of the variables on the stability of PVC, a series of compounds was formulated in which only that variable which was under investigation was altered. Earlier work³ has indicated the change in

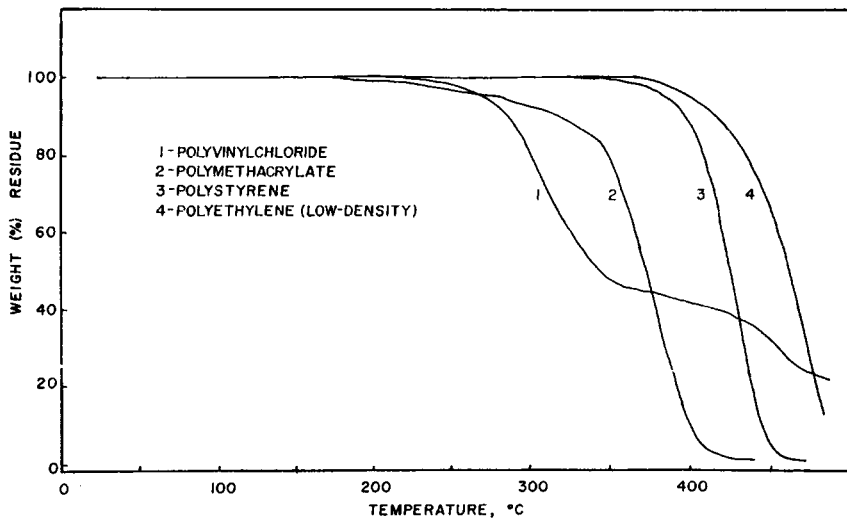


Fig. 1. Tracings of TGA thermograms of common extrusion-grade thermoplastic materials.

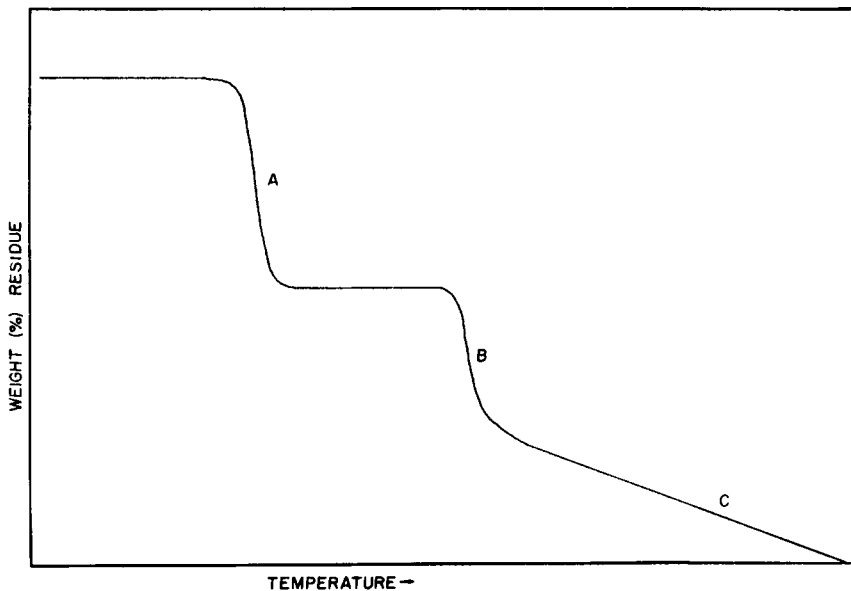


Fig. 2. TGA thermogram (idealized drawing) of the thermally active regions of PVC.

stability of a PVC compound, as defined by the dehydrochlorination temperature, as the quantity of lubricant was varied. It was also shown that endothermic behavior (observed by DTA) in the 450°C. region was not significantly affected by changes in the formulation of the compound. This

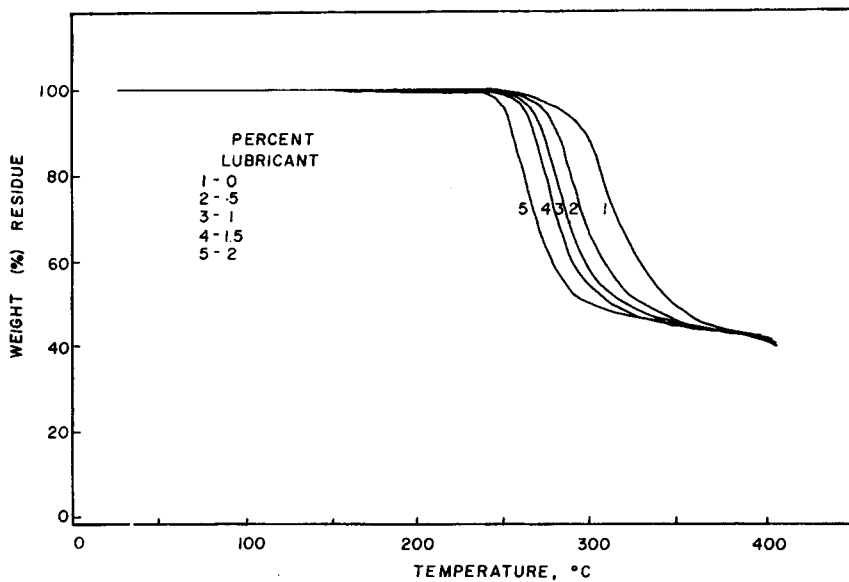


Fig. 3. Tracings of TGA thermograms as the concentration of lubricant is varied in a PVC compound.

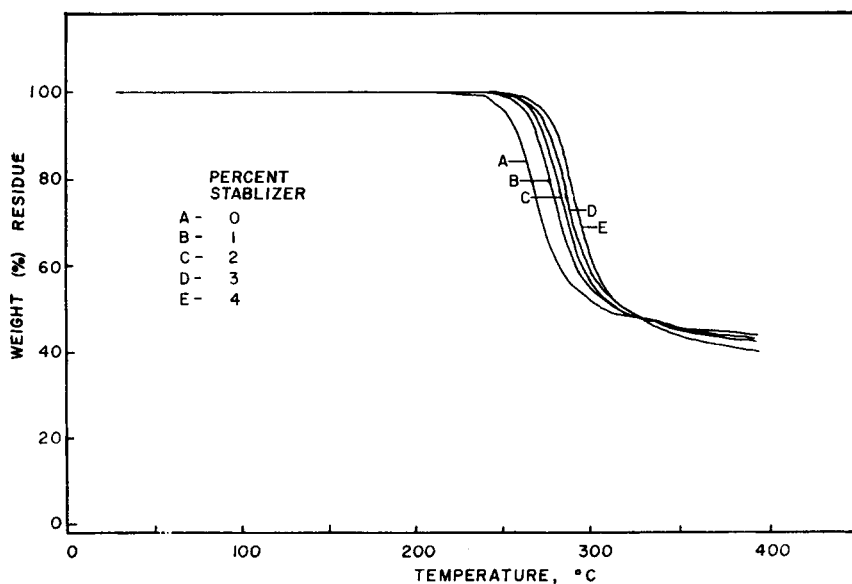


Fig. 4. Tracings of TGA thermograms as the concentration of stabilizer is varied in a PVC compound.

thermal response was considered to be the result of depolymerization of the PVC resin. With the aid of TGA the thermally active areas have been further defined.

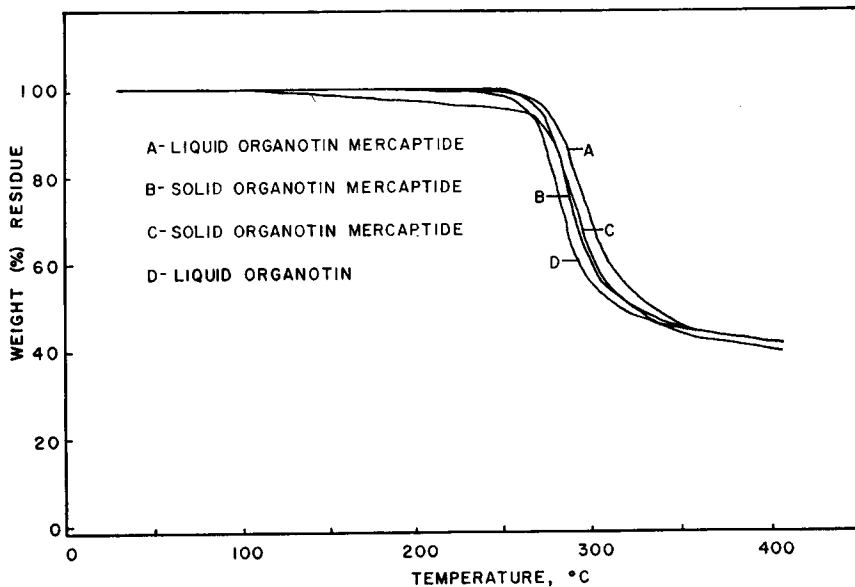


Fig. 5. Tracings of TGA thermograms as the stabilizer type and state are varied in a PVC compound (A, B, and C from source 1 and D from source 2).

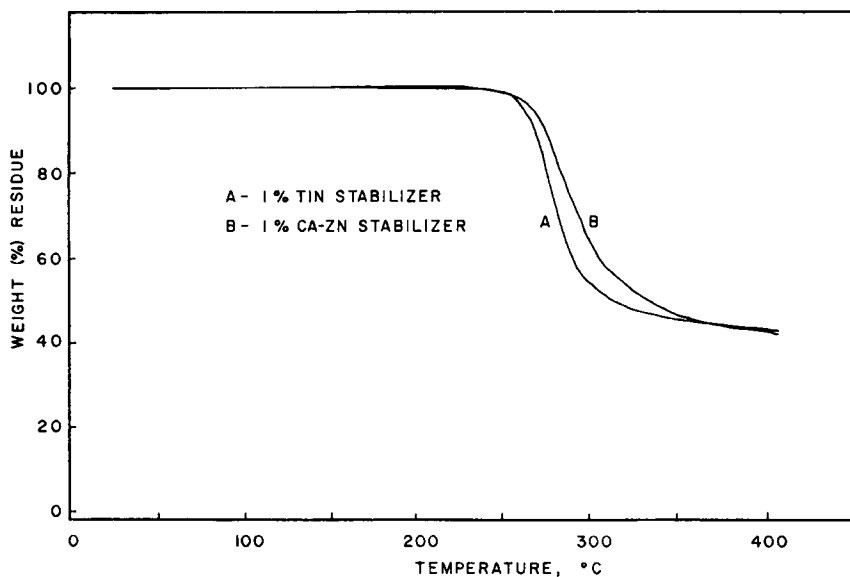


Fig. 6. Tracings of TGA thermograms of a PVC compound, comparing the difference between tin-stabilized and non-tin-stabilized systems.

The work reported here was carried out with the DuPont Thermal-gravimetric Analyzer (Model 950), which is a modular attachment to the du Pont Model 900 DTA. The instrument is a semimicro analyzer based on a null-balancing system and uses the DTA temperature-controller programmer recorder.⁴ TGA runs were made with a heating rate of 20°C./min. and a nitrogen atmosphere flowing (35 ml./min.) through the furnace and over the sample. The thermocouple was placed inside the sample pan above the sample. The sample sizes were of the order of 10–12 mg., and reproducibility was excellent.

The samples previously characterized¹ by DTA were subjected to TGA; the thermograms are shown in Figure 3 (all figures except Fig. 2 are tracings of the actual scans). These compounds are rigid blow-molding materials formulated with a PVC base resin, lubricant, stabilizer, flow modifier, and impact modifier. The region below 400°C. appears to show the greatest thermal response and is, as mentioned previously, the region important to the processor. Essentially all the PVC materials examined had nearly the same thermal behavior above the completion of dehydrochlorination. Since the second weight loss (Fig. 2, B) is a function of the conjugated backbone of the polymer itself, it seems reasonable that any difference observed in the operative stability is seen below this region. Therefore, the reported work will be limited to the range of ambient temperature to 400°C. Figure 3 confirms the DTA observation that an increase in lubricant additive creates a decrease in the onset of thermal response.

With the same formulation as that described above the stabilizer quantity was varied and resulted in the thermograms seen in Figure 4. The influence of a 0–4% variation in the organotin mercaptide stabilizer creates a temperature difference in the weight loss equal to about half that caused by only a 2% variation in lubricant. However, the initial departure from the baseline is seen to occur at a higher temperature with the stabilizer (this may indicate that the lubricant is more volatile).

The effect of stabilizer was further examined by altering the type of stabilizer and the supplier but retaining the same compound. The thermograms in Figure 5 show how the onset of weight loss and dehydrochlorination is affected by the variation and state of the stabilizer. For example, curve A in Figure 5 is a liquid organotin mercaptide and curve C is a solid organotin mercaptide from a common supplier. The ability to distinguish between resins of "good" and "bad" stability is important and necessary. Dehydrochlorination is somewhat of a clue to the characteristic processibility of a resin, and the onset of weight loss apparently is directly related to the development of color in the resin. In the compounds examined the material exhibiting the lowest temperature of onset of weight loss also had the most rapid color development in processing. This occurrence of color development can be altered with changes in the lubricant, stabilizer, or other additives or in the quantity of any one of these.

There has been considerable difficulty in making a nontin stabilizer that works as well as the tin. Figure 6 is a typical comparison of the two

systems. Curve A is that of an organotin-mercaptide, and curve B is that of the same basic formulation but of a calcium-zinc stabilizer substitute. At first glance the tin system may seem inferior, if judged by the temperature of dehydrochlorination, but when the onset of weight loss (although small, it is reproducible both with this formulation and others tested) is examined, the tin is seen to have a stability better by nearly 125°C. Therefore, one would expect the nontin system to develop a higher degree of color when held at constant temperature (as on processing operation), and this is the case. The extreme is observed in the tin-stabilized compounds remaining a clear, nearly transparent sheet after 5 min. at 154°C., whereas the nontin sheet developed a very yellow color under identical conditions. There also appears to be a direct relationship between the stabilizer system and the slope of the dehydrochlorination loss. In general, the nontin systems show 5-8% less loss than the tin system and have slopes of -2.9 as compared with the -3.8 of the tins.

It has been attempted in the foregoing results to indicate the usefulness of thermogravimetric analysis in providing the processor with information concerning possible process problems and relative color development. TGA can aptly describe the relative stability of a compound without a pilot plant study or extensive examination, thereby increasing the economic value of the technique. The technique is quite sensitive to small formulation changes and therefore, when combined with other techniques such as DTA, provides an excellent method of laboratory "screening" of PVC formulations.

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