

# Effect of Diester Type Plasticizers on the Differential Thermal Spectrum of a Polyvinyl Chloride System

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One of the most successful formulated plastics for medical and paramedical applications is the polyvinyl chloride (PVC) family. A variety of excellent properties is possible by incorporating other agents such as plasticizers into PVC. Plasticized systems are currently being used for flexible tubings, blood bags, various types of catheters, and protective materials. Because of the lack of published information on the effects of plasticizers on the thermal spectra of PVC and the paucity of data on this polymer using differential thermal analysis, a study was initiated to note what effects a group of plasticizers would have on the thermal behavior of formulated PVC systems. A group of diester plasticizers was used to note how each member of the series would influence the depolymerization process. Results of this study suggest a method of predicting whether a plasticizer will increase or decrease the tendency of the polymer to degrade.

THE RAPID increase in the use of polymeric materials to replace glass, rubber, and metals is very evident by observing the multitude of plastic products now in use in medicine and paramedical applications. Advancements in plastic technology have brought forth certain polymeric materials which require the introduction of an appreciable quantity of plasticizers to impart specific desired physicochemical and mechanical properties. Polyvinyl chloride, cellulose acetate, polyvinyl acetate, and nitrocellulose are a few examples of plastic materials which may contain one or more plasticizers.

In medical practice the plasticized polyvinyl chloride (PVC) has been and is currently being used widely for the construction of blood bags, tubings, devices for the administration of drug products, as collection devices for body fluids, and as storage containers for one or more products. This widespread acceptance of PVC has required much scrutiny in selecting plasticizers which will produce the desired processing and performance characteristics in the finished medical product. It is also understood that the plasticizers should be nontoxic when used for a medical application which might have contact with tissue or with a product to be administered to a patient (1, 2).

The addition of a plasticizer to polyvinyl chloride reduces the glass transition temperature ( $T_g$ ) and thereby imparts various degrees of softness and flexibility. Since polyvinyl chloride materials must also contain a stabilizer to prevent

or hinder degradation of the material during processing, it was felt that the various plasticizers might have different effects on influencing the stability of the plastic when thermal conditions are imposed. Few reports of a quantitative nature, however, have appeared in the literature in regard to the role of the plasticizer as a stabilizing agent in polyvinyl chloride. For this reason a study was undertaken to assess the relative heat stabilizing properties of a group of plasticizers on polyvinyl chloride when exposed to thermal treatments using differential thermal analysis (DTA).

## EXPERIMENTAL

**Materials and Apparatus**—(a) Polyvinyl chloride.<sup>1</sup>

(b) Plasticizers: dimethyl phthalate, dibutyl phthalate, dioctyl phthalate, ditridecyl phthalate (W. R. Grace & Co., Hatco Chemical Division, Fords, N. J.), dioctyl adipate, didecyl adipate (Eastman Chemical Products, Inc., Kingsport, Tenn.), dihexyl azelate, dioctyl azelate (Emery Industries, Inc., Cincinnati, Ohio), dibutyl sebacate, dioctyl sebacate (Reichhold Chemical Co., Deecy Products Division, Cambridge, Mass.), dibenzyl sebacate, dibutyl suberate, dibutyl dodecanedioate (Wallace & Tiernan, Inc., Harchem Division, Belleville, N. J.), trioctyl trimellitate (Rubber Corporation of America, Hicksville, N. Y.), and trioctyl phosphate (Monsanto Co., St. Louis, Mo.).

(c) Stabilizer: a barium-cadmium carboxylate type stabilizer.<sup>2</sup>

(d) Polyvinyl chloride films: the films of the polymer are prepared by the plastisol fusion technique, *i.e.*, a colloidal dispersion of a high molecular weight vinyl chloride resin in the desired plasticizer is heated until all the plasticizer in the liquid phase is absorbed into a fused polymer. The loss of separate phases and interfacial boundaries produces a translucent plastic with a high tensile strength.

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<sup>1</sup> Geon 121. High molecular weight. B. F. Goodrich Chemical Co., Cleveland, Ohio.

<sup>2</sup> Advastab BC-100 S-I, Advance Division, Carlisle Chemical Works, Inc., New Brunswick, N. J.

The formulation used in this study was: 100 Gm. PVC, 60 Gm. plasticizer, and 1.5 Gm. stabilizer.

The particular PCV<sup>1</sup> was chosen because its molecular weight is high enough to prohibit undue solvation by the plasticizer at normal temperatures, though assuring proper solvation at increased temperatures. Lower molecular weight resins were avoided because they are solvated at room temperatures such that the swelling resin particles raise the volume concentration of solid phase and the plastisol becomes an unworkable plastigel. The barium-cadmium carboxylate type was chosen as the stabilizer system for this study because it provides excellent heat and light stabilization in closed mold plastisol processing. Prior to molding the formulation, the plasticizer and stabilizer were placed in a Hobart model K45 mixer,<sup>3</sup> and the vinyl chloride resin added slowly until a uniform dispersion was produced (approximately 45 min. to 1 hr.). The formulations were stored for 24 hr. to achieve partial deaeration and then poured into preheated (165°) 40-mil thick molds and processed on a Dake press model 44-325<sup>4</sup> for 3.5 min. at 35,000 lb. pressure. The molds were then cooled to 120° and the films removed. All the formulations were conditioned 48 hr. at 22° and 50% relative humidity.

(e) Differential thermal analysis apparatus: the apparatus consists of a controlled atmosphere differential thermal analyzer with a quick cool furnace model F-1DF and two L&N Speedomax H strip chart recorders. This instrument is manufactured and described by Robert L. Stone Co., Austin, Tex. (3, 4).

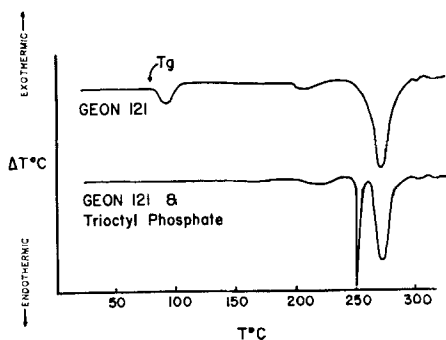


Fig. 1—DTA thermograms of plasticized and unplasticized polyvinyl chloride.

**Effect of a Group of Plasticizers on the Dehydrohalogenation of PVC**—One-milligram samples of each of the PVC formulas were run in the differential thermal analysis apparatus at a heating rate of 6.0°/min., using highly calcined, 80 mesh  $Al_2O_3$  as the inert reference. Nitrogen was used as the dynamic gas in order that purely thermal effects might be distinguished from the oxidative transitions which will occur in an air atmosphere. In each instance four determinations were made for each plastic formula to insure the reliability of the results. Figure 1 illustrates the thermograms for an unplasticized PVC and for a plasticized PVC (trioctyl phosphate). As may be noted from the unplasticized PVC, a main glass transition temperature

is apparent at 86.0° and a small depolymerization temperature occurs at 200.6°. No glass transition temperatures were noted for the plasticized resins in the temperature range studied (ambient to 300°). Figure 1 also reveals that in the plasticized PVC, the plasticizer (trioctyl phosphate) apparently "boils" off the plastic immediately prior to the dehydrohalogenation. None of the other plasticized resins followed this trend.

From each of the thermograms, the following information was derived: (a) the temperature of onset of dehydrohalogenation, (b) the peak temperature of dehydrohalogenation, and (c) the area under the curve corresponding to the dehydrohalogenation reaction. This area was then utilized to calculate the heat of dehydrohalogenation ( $\Delta H^\circ$ ) in a manner described in a previous report (5). Table I includes the onset and peak temperatures for all of the plastic formulas as well as the calculated heats of dehydrohalogenation.

In all experiments actual weights of the plastic samples were determined after dehydrohalogenation had occurred, and from this information it was possible to calculate the percentage weight loss included in Table I.

## DISCUSSION

As has been indicated, the plasticized polyvinyl chlorides, at least in the temperature range studied, did not reveal any glass transition temperatures as the pure polymer did. In these cases, however, it may be assumed that the  $T_g$  values were present but occurred below ambient temperature or if they did occur above ambient temperature, they may not have been detected by the instrument.

A review of the results in Table I clearly reveals that the structure of the plasticizer can play a very important role in helping to stabilize the PVC resin. In the phthalate ester series, an increase in stability can be noted as the molecular weight of the plasticizer is increased. The most "protective" phthalate ester, and in fact the most protective plasticizer in the whole series, was the ditridecyl phthalate which had peak temperatures for dehydrohalogenation of 289.2° and a heat of dehydrohalogenation of 26.9 Kcal./mole, a value of 7 to 8 times that of the other phthalate esters and considerably higher than the  $\Delta H^\circ$  for any of the other plasticizers. Dibenzyl sebacate and trioctyl trimellitate had also high heats of dehydrohalogenations, 15.6 Kcal./mole and 20.6 Kcal./mole, respectively. Generally, these high heats of dehydrohalogenations indicate that greater stability is afforded the PVC resins when these are subjected to high processing temperatures. However, in the case of the dibenzyl sebacate there appeared to be an anomalous situation where the actual temperature for onset of dehydrohalogenation was depressed to a slight extent as compared to the other plasticized systems having high  $\Delta H^\circ$  values. Exact reasons for this depression are still not known.

It may be noted from the table that most of the plasticizers increase the temperature where dehydrohalogenation takes place, but for the most part once this temperature is reached, less energy ( $\Delta H^\circ$ ) is needed to bring about complete dehydrohalogenation.

The results of this study appear to demonstrate that higher molecular weight plasticizers have a

<sup>3</sup> Hobart Mfg. Co., Troy, Ohio.

<sup>4</sup> Dake Corp., Grand Haven, Mich.

TABLE I—EFFECT OF SELECTED ESTER TYPE PLASTICIZERS ON THE DEHYDROHALOGENATION TRANSITION OF POLYVINYL CHLORIDE

Plasticizer	Mol. Wt.	Onset <sup>a</sup> Temp., °C.	Peak <sup>b</sup> Temp., °C.	Heat of Dehydrohalogenation		Polymer Wt. Loss, %
				cal./Gm.	Kcal./mole	
Pure polymer		243.4	278.8	30.9		
Dimethyl phthalate	194.18	258.2	266.9	16.2	3.15	76.4
Dibutyl phthalate	278.34	262.3	271.4	13.8	3.85	75.8
Diethyl phthalate	390.53	271.4	277.9	10.9	4.27	75.9
Ditridecyl phthalate	530.0	273.8	289.2	50.7	26.9	65.5
Diethyl adipate	370.56	271.2	275.9	10.6	3.95	76.0
Didecyl adipate	426.67	277.3	280.7	16.0	6.85	77.4
Dibutyl sebacate	286.3	260.7	269.0	15.3	4.39	75.3
Dihexyl azelate	356.0	270.2	276.1	18.4	6.57	76.0
Diethyl azelate	412.0	275.0	282.1	17.4	7.20	75.3
Dibutyl sebacate	314.0	263.5	271.7	12.6	3.95	76.0
Diethyl sebacate	426.0	276.1	283.3	19.1	8.18	73.0
Dibenzyl sebacate	382.0	264.2	272.2	39.6	15.6	72.5
Dibutyl dodecanedioate	342.0	267.8	273.1	11.9	4.08	75.5
Triethyl trimellitate	546.0	272.4	292.4	37.4	20.5	75.7
Triethyl phosphate	362.40	265.4	269.6	16.7	6.07	75.5

<sup>a</sup> Onset temperature at which dehydrohalogenation takes place. <sup>b</sup> Peak temperature at which dehydrohalogenation takes place.

greater protective effect than the lower ones and that an increase in the hydrophobic moiety of the plasticizers plays an important role in the protective mechanism afforded to the PVC.

The use of differential thermal analysis for the evaluation of a group of plasticizers in regard to their protective effects under purely thermal conditions reveals that this technique can give considerable information in a relatively short period of time which should be helpful when a new plasticizer

is to be considered for a polyvinyl chloride formula.

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## Application of 1-(*N*- $\beta$ -Hydroxyethyl-4-piperidyl)-3-(4-piperidyl)- propane in the Mannich Reaction I

### Substituted $\beta$ -Aminoketones

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The Mannich reaction has been successfully performed using 1-(*N*- $\beta$ -hydroxyethyl-4-piperidyl)-3-(4-piperidyl)propane (4-DI-PIP-OL). A series of Mannich bases has been prepared employing 4-DI-PIP-OL and various ketones. Characteristic

infrared absorption bands for OH, NH,  $\overset{\text{O}}{\parallel}\text{C}$  groups are recorded. The compounds are to be screened for possible pharmacological activity.

**M**ANNICH BASES have been prepared (1-25) for pharmacological testing as antispas-

modics, analgesics, local anesthetics, or chemotherapeutic agents. Such compounds are usually prepared by the condensation of formaldehyde (paraformaldehyde) with ammonia, a primary or secondary amine, and a compound containing at least one active hydrogen atom. The condensation reaction may be illustrated as in Scheme I.

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