

## Poly(vinyl Chloride) Thermal Stability. I. Evaluation by Melt Rheology\*

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### Synopsis

Capillary rheometry is used to characterize the thermal stability of poly(vinyl chloride). By isothermally extruding the polymer melt at constant shear rate, apparent viscosity-time relationships are obtained having three distinct regions: (1) obtainment of equilibrium viscosity, (2) constant viscosity, and (3) rapidly changing viscosity. During regions 2 and 3 the polymer extrudate gradually changes in color from water clear to black. These characteristic regions are related to the temperature of extrusion by Arrhenius plots. An activation energy of 40 kcal./g.-mole was calculated for the decomposition of PVC. Infrared spectroscopy, thermal gravimetric analysis, and intrinsic viscosity experiments are used to corroborate the results of the melt flow data.

### Introduction

The decomposition of poly(vinyl chloride) (PVC) at elevated temperatures has been studied by a number of investigators using a variety of techniques including HCl evolution,<sup>1-3</sup> infrared<sup>4,5</sup> or mass spectroscopy,<sup>6,7</sup> thermal gravimetric analysis,<sup>7-9</sup> oven aging,<sup>10,11</sup> and the Brabender Plastimeter.<sup>12-15</sup> However, only the Brabender or the dynamic thermal stability (DTS) test, utilizes the rheological behavior of the bulk polymer as a criterion of degradation. With this instrument the amount of torque required to shear mix the polymer is measured and is proportional to the melt viscosity of the sample and, as such, should reflect the structural changes occurring in the polymer. Thus, the relative stability of different polymers can be obtained from these torque-time curves.

The DTS test has considerable practical value in that it simulates the mixing action occurring in the milling and extrusion of a polymer. However, for other than routine testing, the test has several deficiencies. The instrument has poor temperature control which prohibits isothermal experiments and the relationship between the torque and shear stress is poorly defined. The normal operating speeds are high enough to cause shear-induced heating, and the shear rate distribution is generally not the same, at constant speed, from sample to sample. Thus, the DTS test shows the results of a number of effects happening simultaneously.

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Many of these objections for a quantitative test can be circumvented by using an instrument of simpler geometry to measure the bulk viscosity. In particular, a capillary viscometer is very suitable because the shear rates are known and controllable, and, at low shear rates, near-isothermal experiments are possible. In this case, a measure of the thermal stability is obtained by measuring, as a function of time, the resistive force opposing the driving plunger. Since this force, at constant shear rate, is proportional to the shear viscosity, changes in the polymer structure will be observed as changes in the force, analogous to the changes in torque measured in the DTS test.

Even though both instruments measure rheological properties, the use of the capillary viscometer has the following advantages: (1) Quantification of the shearing rates in the fundamental unit of time (i.e.,  $\text{sec.}^{-1}$ ) can be made; (2) Isothermal experiments are possible at low shear rates; (3) Continuous monitoring of the extrudate color with time can be made.

The purpose of this work is to study the thermal decomposition of PVC as a function of temperature and stabilizer concentration by using the capillary viscometer.

### Experimental

A constant shear rate type Instron melt rheometer with a  $0.050 \times 2.0017$  in. capillary was used. Although any capillary will work, those with large length/diameter ratios are preferable. The experimental run consists of two operations (1) loading and preheating the polymer and (2) extruding the polymer at a known and constant shear rate and temperature. During the first step the reservoir is loaded with sample, pressured to 10,000 psi by extruding at some relatively high rate of shear for approximately 30 sec., and then allowing the sample to come to equilibrium temperature with the driving force removed. The time for this operation will vary depending on the temperature of extrusion. For example, at an extrusion temperature of  $210^\circ\text{C.}$ , 2 min. is required. The second operation entails the measurement of the resisting load as a function of time and the collection of extrudate samples at appropriate time intervals. The time for the appearance of orange-colored extrudate and the time for the inflection point in the force-time curve serve as measures of the stability.

Dilute solution viscosity measurements were made on the base polymers and extrudates in cyclohexanone at  $30^\circ\text{C.}$ , and the intrinsic viscosities were determined by the conventional double-plot method. Stress-strain measurements were made on the extrudates with an Instron tensile tester at 0.2 in./min.

Infrared spectra were obtained with a Perkin-Elmer Model 521 spectrophotometer. Thermal gravimetric analyses were obtained with an apparatus employing the Cahn electrobalance.

Most of the work reported was done on suspension-polymerized PVC homopolymer (Geon resin 101EP-F24) and an experimental suspension resin having a higher molecular weight (110X212 H468). Some data for

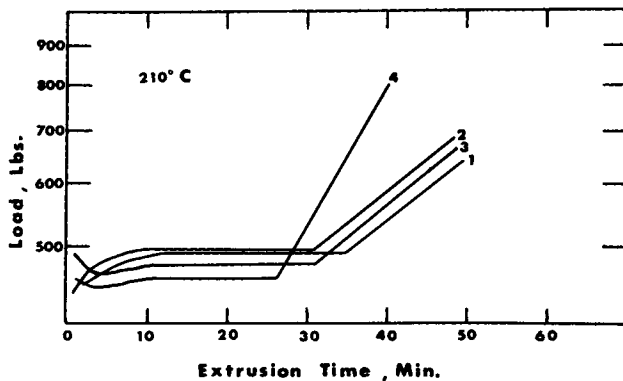


Fig. 1. Typical curves of load vs. extrusion time at 210°C. showing effect of working on PVC thermal stability for Geon resin 101EP-F24 plus 4.0 parts Thermolite-31: (1) Waring Blender mixed; (2) Henschel mixed for 10 min.; (3) Henschel mixed for 10 min. and milled for 2 min. at 300°F.; (4) Henschel mixed for 10 min. and milled for 5 min. at 300°F.

an emulsion PVC homopolymer and a PVC/poly(vinyl acetate) (95/5) copolymer are included for purposes of comparison. The resins were stabilized with dibutyltin dioctylthioglycolate (Thermolite 31,) M&T Chemical, Inc., Rahway, N.J.).

## Results

In order to evaluate the usefulness of the capillary viscometer heat stability test (CVHS) to detect incipient instability in thermally degraded PVC, milled and unmilled compounds were studied. The milled samples are excellent for such investigation because they are known to contain some degraded polymer. In one experiment, milled compound, unmilled compound, and the base polymer plus stabilizer were extruded at 210°C. The data obtained for two levels of stabilizer is summarized in Part A of Table I. These data indicate that milling caused, if anything, an increase in the apparent stability of the polymer. Since this observation is in contradiction to other accepted evidence, a second experiment was performed in which the effect of mechanical working was studied in systems containing only polymer and stabilizer. The results of this experiment are given in Part B of Table I. The load-time curves for the samples extruded at 210°C. are shown in Figure 1 and illustrate the type of data obtained from the CVHS test. This latter experiment indicates that milling does have a detrimental effect on polymer stability and that it can be detected with the CVHS test. Since the mixing procedure with the Waring Blender is simple and convenient and does not have a detrimental effect on the polymer, it was used exclusively in all our subsequent work. A temperature of 210°C. was selected as a standard testing temperature for work with PVC polymers primarily to limit the experiment to a practical time scale.

TABLE I  
 Effect of Working on Thermal Stability

Resin and treatment	Time to orange, min.	Time to inflection, min.	$d(\log \eta)/dt$
A. Experimental resin			
Experimental resin + 0.8 parts T-31, extrusion temp. 210°C.			
Milled sheet <sup>a</sup>	7	6-11	0.0154
Powdered compound <sup>a</sup>	4	7	0.0370
Resin + stabilizer	3-4	6	0.0352
Experimental resin + 2.0 parts T-31, extrusion temp. 210°C.			
Milled sheet <sup>a</sup>	13	14	0.0178
Powdered compound <sup>a</sup>	8-9	10-11	0.0398
Resin + stabilizer	8-9	12	0.0371
B. Geon resin			
Geon resin 101EP-F24 + 4.0 parts T-31, extrusion temp. 230°C.			
10 min. Henschel + 5 min. milled	8-9	9.0	0.0547
10 min. Henschel + 2 min. milled	8-9	8.75	0.0521
10 min. Henschel + 0 min. milled	7	7.0	0.0416
Slurried in mineral spirits	8-9	11.0	0.0390
Mixed in Waring Blendor	9.0	9.0	0.0468
Geon resin + 4.0 parts T-31, extrusion temp. 210°C.			
10 min. Henschel + 5 min. milled	30	26	0.0174
10 min. Henschel + 2 min. milled	34	31	0.0085
10 min. Henschel + 0 min. milled	33	31	0.0085
Mixed in Waring Blendor	38	35	0.0078

<sup>a</sup> Includes 5-phr processing aide and 1-phr lubricant.

It has been shown by Druesedow and Gibbs<sup>4</sup> that the intrinsic viscosity of a PVC resin changes during HCl evolution. They found that in a nitrogen atmosphere the intrinsic viscosity increased with continued thermal treatment, whereas in an air atmosphere a decrease in the intrinsic viscosity preceded an eventual increase. It was concluded that this latter observation resulted from chain scission and crosslinking occurring simultaneously. In contrast with such methods as TGA, HCl evolution, and oven aging the polymer in the CVHS test is confined to low air concentrations. The only air present is that which is absorbed on the surface of the resin particle and that which is forced into the reservoir during the loading operation. Intrinsic viscosities  $[\eta]$  were run on the extrudates of two samples (101EP-F24 + 4 part T-31 mixed in the Waring Blendor and 101EP-F24 + 4 parts T-31 mixed 10 min. in the Henschel mixer and subsequently milled at 300°F. for 5 min. The effect of the PVC decomposition on the molecular weight is shown in Figure 2. A summary of the intrinsic viscosity data is contained in Table II. Several important points should be

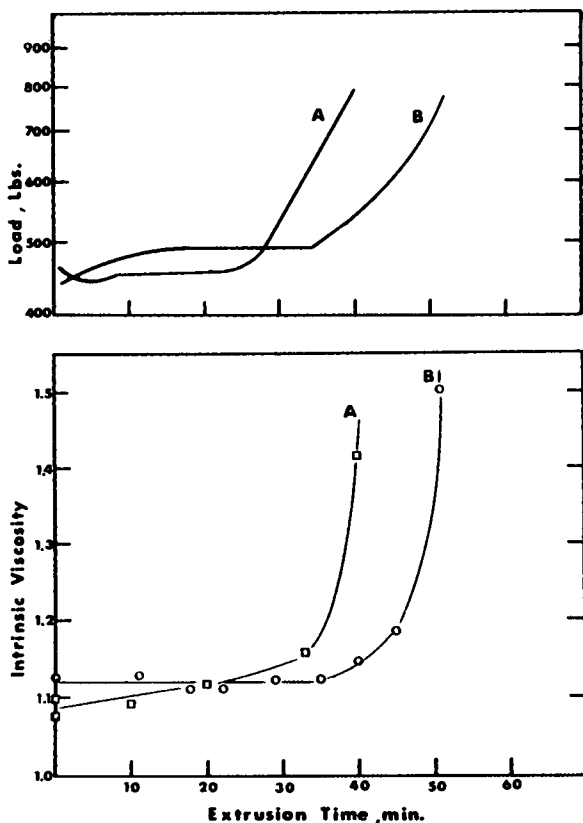


Fig. 2. Curves showing effect of PVC stability on molecular weight for Geon resin 101EP-F24 plus 4.0 parts Thermolite-31 at 210°C. at a shear rate of 15.0 sec.<sup>-1</sup>: (A) is Henschel mixed for 10 min. plus 5 min. milling at 300°F.; (B) is Waring Blendor mixed.

noted about these data. (1) The increase in the intrinsic viscosity occurs at approximately the same extrusion time as does the increase in the shear viscosity of the melt. (2) The process of milling lowered the intrinsic viscosity. (3) For the milled polymer there is a gradual increase in the intrinsic viscosity that is not reflected in the shear viscosity of the melt. (4) Very little, if any, chain scission is occurring in the Waring Blendor mixed sample. The Waring Blendor data shows an initial decrease followed by an increase as observed by Druesdow and Gibbs<sup>4</sup> for their samples in air.

The effect of PVC decomposition can also be characterized using infrared spectroscopy and thermal gravimetric analysis. In this case the extrudates of Geon (101EP-F24 + 4 parts T-31) extruded at 210°C. were analyzed. The absorbance at six frequencies were measured — 1725 cm.<sup>-1</sup> (C=O), 1670 cm.<sup>-1</sup> (C=C), 2910 cm.<sup>-1</sup> (CH<sub>2</sub>), 1430 cm.<sup>-1</sup> (CH<sub>2</sub> atactic), 1420 cm.<sup>-1</sup> (CH<sub>2</sub>-tactic), and 2960 cm.<sup>-1</sup> (C—H). Absorbance

TABLE II  
Intrinsic Viscosity Data on PVC Extrudates  
(Geon Resin 101EP F24 and 4 parts T-31)

Sample extrusion time, min.	$[\eta]$ (Reduced)	$[\eta]$ Inherent	$[\eta]$ Average	$k_1^a$	$-k_1'^b$	$k_1 + (-k_1')$	Insoluble polymer, %
Waring Blendor mixed							
0	1.128	1.120	1.124	0.3264	0.1506	0.4770	0.0
11	1.128	1.128	1.128	0.3600	0.1431	0.5031	0.26
18	1.107	1.115	1.111	0.4211	0.1203	0.5414	3.35
20	1.050	1.050	1.050	0.3665	0.1399	0.5064	0.0
22	1.105	1.115	1.110	0.4226	0.1218	0.5444	3.35
29	1.123	1.121	1.122	0.3470	0.1486	0.4956	2.5
35	1.121	1.123	1.122	0.3736	0.1393	0.5129	4.2
40	1.143	1.144	1.144	0.3727	0.1380	0.5107	0.3
45	1.177	1.193	1.185	0.4952	0.0908	0.5860	0.0
51	1.497	1.509	1.502	0.4284	0.1187	0.5471	26.7
10 min. Henschel mixed 5 min. milling 300°F.							
0	1.092	1.100	1.096	0.4175	0.1225	0.5400	3.78
0	1.073	1.075	1.074	0.3804	0.1336	0.5130	0.0
10	1.087	1.094	1.090	0.4174	0.1219	0.5393	1.99
20	1.116	1.119	1.118	0.3740	0.1372	0.5112	2.8
33	1.148	1.165	1.156	0.4607	0.1112	0.5719	0.0
40	1.413	1.415	1.414	0.3853	0.1320	0.5173	—

<sup>a</sup> Slope of reduced viscosity curve.

<sup>b</sup> Slope of inherent viscosity curve.

ratios relative to the absorption at  $2960\text{ cm.}^{-1}$  (C—H) were calculated. They are shown graphically in Figure 3 along with the load-time data from the CVHS test. For each absorbance ratio-time curve a radical change occurs in the same region as the change in load. From the absorbance at  $2910$ ,  $1430$ , and  $1420\text{ cm.}^{-1}$ , it appears that very little hydrogen as HCl is lost until the stabilizer is consumed. This is confirmed by the facts that very little color is developed until after the break in the load-time curve occurs and that no evidence of gas evolution is observed in the extrudate samples until well after the increase in load.

The absorbance at  $1725\text{ cm.}^{-1}$  is due to carbonyl structure. The presence of dibutyltin dioctylthioglycolate stabilizer accounts for the initial carbonyl structure. The increase in the absorbance ratio must come from reaction of the PVC polymer with oxygen. The decrease in the ratio may result from volatilization of the stabilizer or its reaction product, or splitting out of  $\text{CO}_2$ .

Finally, the absorbance at  $1670\text{ cm.}^{-1}$  due to isolated  $\text{C}=\text{C}$  structure shows that an initial concentration of this structure exists and that the concentration eventually diminishes. Whether or not the apparent minimum is real cannot be presently answered. These isolated  $\text{C}=\text{C}$  structures

probably reflect the formation of double bonds from early evolution of HCl, the decrease being a result of the competing reaction of the C=C with oxygen to form carbonyl structure. Because this C=C is not observed in untreated Geon 101EP resin it cannot be associated with terminal double bond structure.

Although the infrared data suggest that rapid evolution of HCl does not begin until the stabilizer is consumed, thermal gravimetric analysis (TGA)

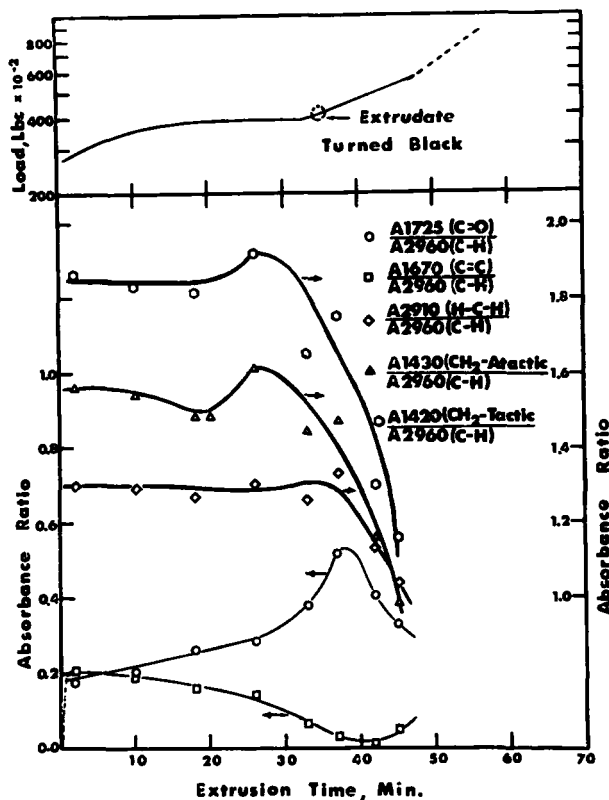


Fig. 3. Infrared analysis of extrudates obtained at  $210^{\circ}\text{C}$ . and a shear rate of  $7.5 \text{ sec.}^{-1}$  for Geon resin 101EP-F24 plus 4.0 parts Thermolite-31.

(Fig. 4) indicates that no HCl is lost from the extrudates over the time interval of the test. The possible explanations of this are: (1) very little HCl was evolved even after 50 min. of heating at  $210^{\circ}\text{C}$ ., or (2) considerable HCl was evolved between 35 and 50 min. but was trapped in the extrudate during the TGA experiment.

The activation energy calculated from TGA rate curves in a manner previously reported<sup>16</sup> confirms that decomposition occurs after the viscosity breakpoint. The agreement between TGA and the CVHS test is encouraging.

The physical properties of material reflect its molecular structure and vice versa. Since a number of structural changes can be occurring during the degradation process, it is important to know their effect on the physical behavior of the material. With this in mind, the stress-strain relationships for the extrudates from an extrusion at 210°C. were determined with an Instron tensile tester. The extrudate rods were held in position with smooth-faced clamps and stressed with a crosshead speed of 0.2 in./min. The tensile stresses at 100% elongation and at fracture were calculated and

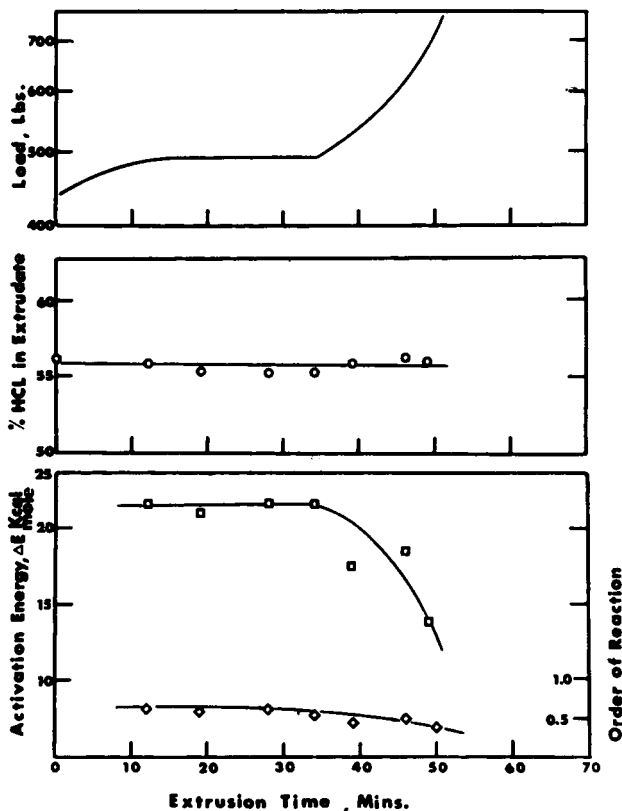


Fig. 4. Thermal gravimetric analysis of extrudates obtained at 210°C. and a shear rate of 15.0 sec.<sup>-1</sup> for Geon 101EP-F24 resin plus 4.0 parts Thermolite-31.

are plotted in Figure 5. Both measures of the tensile strength suggest a maximum with extrusion time, but the tensiles at fracture appear to have considerably more error associated with them.

The increase in tensile strength at short times can result from the polymer coming to thermal equilibrium and achieving a state of complete particle boundary disappearance. The subsequent mild decrease indicates that the thermal decomposition is now the controlling process. The radical drop at 45–50 minutes extrusion time supports intrinsic viscosity data



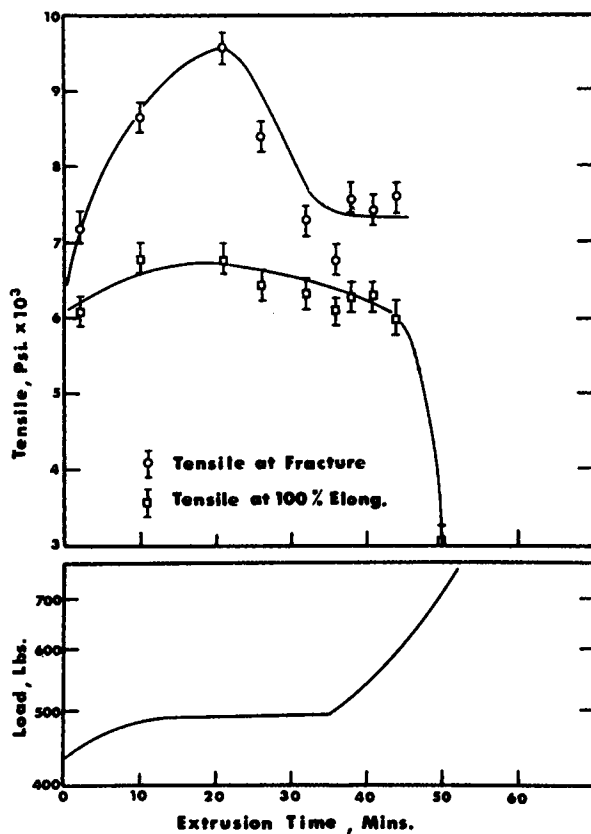


Fig. 5. Tensile strength of extrudates obtained at 210°C. and a shear rate of 15.0 sec.<sup>-1</sup>.

TABLE III  
Some Properties of Geon Resin 101 EP-F24  
(4 Parts Stabilizer T-31)<sup>a</sup>

Extrusion time, min.	Diameter of extrudate, in.	Maximum elongation, %	Elongation at complete necking, %	Tensile strength at 100% elongation, psi	Tensile strength at fracture, psi
2	0.056	350	288	6080	7200
10	0.053	393	270	6780	8650
21	0.053	420	258	6780	9560
26	0.054	369	256	6440	8400
32	0.054	313	273	6330	7300
36	0.055	286	272	6120	6780
38	0.055	352	265	6280	7590
41	0.055	312	260	6320	7420
44	0.057	342	250	6000	7600
50	0.075	28	—	3040	3040

<sup>a</sup> Testing conditions 0.2 in./min. crosshead speed, 50 lb. load, 1 in. jaw space.

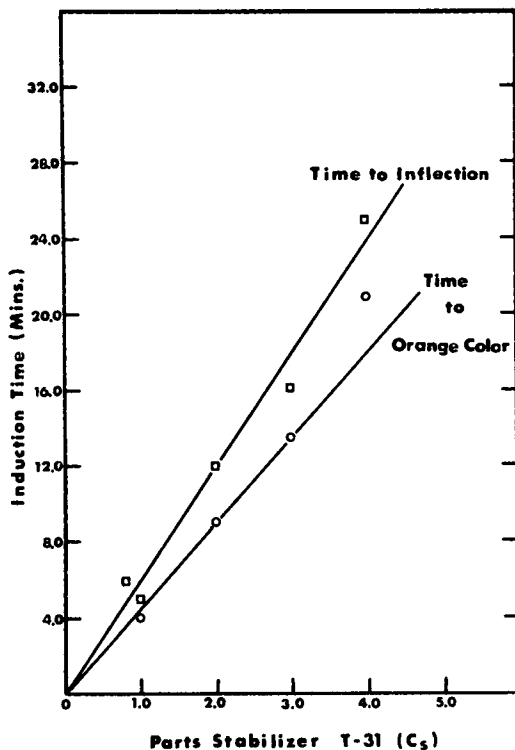


Fig. 6. Effect of the stabilizer level on thermal stability of PVC experimental resin.

which suggest that crosslinking is occurring and is the dominating event at these conditions.

The pertinent properties obtained from the uniaxial stress experiments are given in Table III.

By using the CVHS test the effect of concentration of stabilizer, 0-4 phr T-31 was determined. The induction times on both the color and viscosity basis were found to vary linearly for this particular stabilizer as shown in Figure 6. The effect of temperature on the induction time and on the rate of decomposition  $d(\ln \eta)/dt$  was studied at two stabilizer concentrations, (2 and 4 phr) and three shear rates (7.5, 15, and 30 sec.<sup>-1</sup>). Arrhenius plots were used to represent these data. Figures 7 and 8 show the temperature dependency of the color and viscosity induction periods, respectively. Figure 9 shows the temperature dependency of the rate of decomposition.

From the results of Figures 7-9 the following conclusions can be made: (1) the shear rate, for the range covered, does not effect the rate of decomposition; (2) the concentration of T-31 stabilizer affects the induction period but not the rate of decomposition; (3) little difference can be seen between Geon resin 101EP F24 and the PVC experimental resin of higher molecular weight. This last conclusion is not surprising as there is little

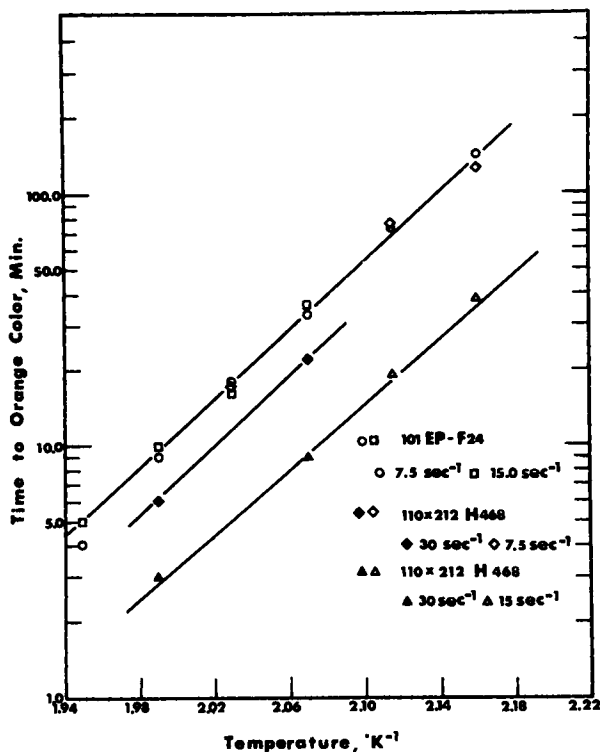


Fig. 7. Temperature dependence of induction period: Geon resin 101EP-F24 plus 4.0 parts Thermolite stabilizer (○) at 7.5 sec.<sup>-1</sup> and (□) at 15.0 sec.<sup>-1</sup>; PVC experimental resin plus 4.0 parts Thermolite stabilizer (◆) at 30 sec.<sup>-1</sup> and (◇) at 7.5 sec.<sup>-1</sup>; PVC experimental resin plus 2 parts Thermolite stabilizer (▲) at 30 sec.<sup>-1</sup> and (△) at 15 sec.<sup>-1</sup>.

difference in their molecular weights (1.163 and 1.270 intrinsic viscosity in cyclohexanone at 30°C., respectively). Crosato-Arnaldi and co-workers<sup>18</sup> have found no dependence of molecular weight on the rate of dehydrochlorination of PVC having intrinsic viscosity above 0.83.

Finally, the temperature effect on the stability of a PVC emulsion polymer and a PVC copolymer (95/5 vinyl chloride-vinyl acetate) was studied and compared with the suspension-polymerized Geon resin 101EP-F24 as shown in Figures 10 and 11.

### Discussion

As shown in Figure 12, a typical CVHS curve can be divided into three parts. In region I the polymer is brought to equilibrium conditions of shear and temperature. The time to reach the equilibrium viscosity (region II) for PVC is quite temperature-dependent, being as long as 90 min. at 160°C. For the higher temperatures 220–240°C. the time is about 2 or 3 min., and one observes a decrease in the viscosity as contrasted to a

gradual increase found at low temperatures. It is believed that this effect reflects the time for the particulate structure to break down. The increase in tensile strength of the extrudates at the short extrusion times supports this belief. The milled sample illustrated in Figure 1 shows an initial decrease in viscosity because incomplete melting was obtained before the actual extrusion was begun, and thus, elastic energy was stored during the pressuring part of the charging procedure. No change in molecular weight is observed in Region I.

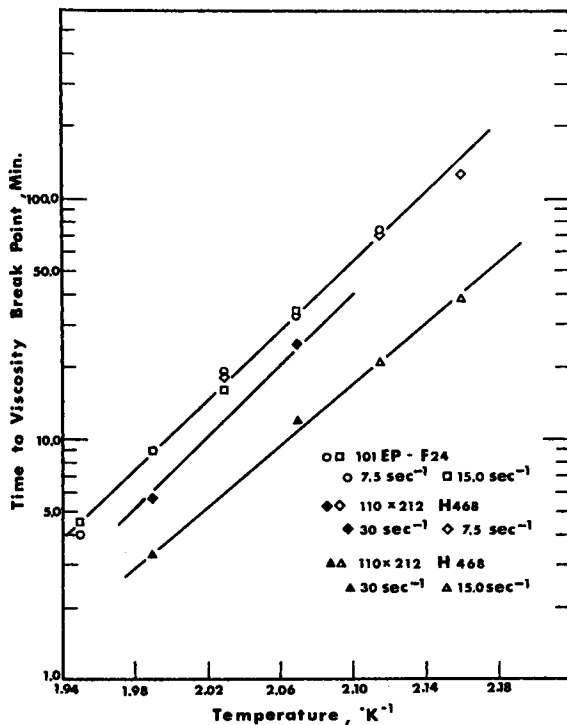


Fig. 8. Temperature dependence of induction period: Geon resin 101EP-F24 plus 4.0 parts thermolite stabilizer (O) at 7.5 sec.<sup>-1</sup> and (□) at 15.0 sec.<sup>-1</sup>; PVC experimental resin plus 4.0 parts Thermolite stabilizer (◆) at 30 sec.<sup>-1</sup> and (◇) at 7.5 sec.<sup>-1</sup>; PVC experimental resin plus 2 parts Thermolite stabilizer (▲) at 30 sec.<sup>-1</sup> and (△) at 15 sec.<sup>-1</sup>.

Region II is a region of constant viscosity provided decomposition does not occur before equilibrium has been reached. This points out the need to pick the proper temperature and shear rate for routine analysis. We have found that 210°C. and a shear rate of 15 sec.<sup>-1</sup> meets these requirements. The time required to reach the end of region II is considered as an induction time for the main decomposition reaction and indicates the lifetime of the stabilizer. During region II little, if any, change of molecular weight is taking place. At the same time the tensile strength of the extrudates is at a maximum.

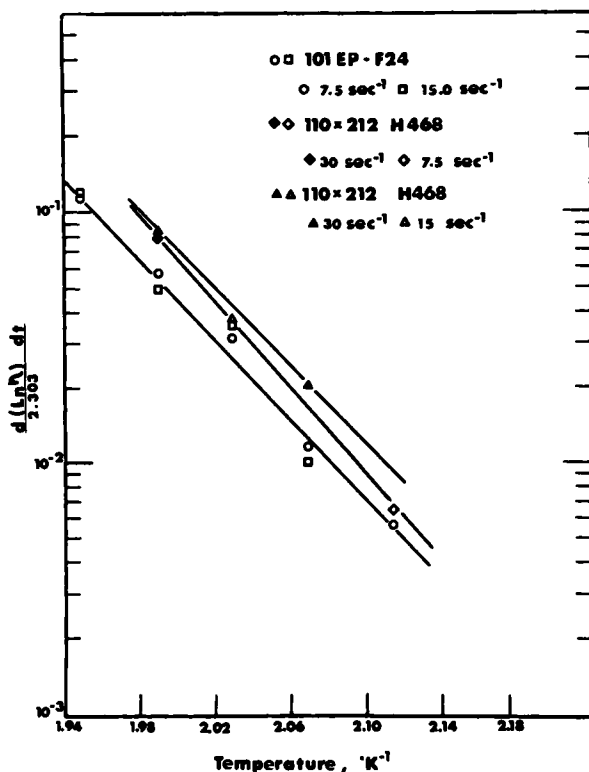


Fig. 9. Temperature dependence of rate of decomposition: Geon resin 101EP-F24 plus 4.0 parts Thermolite stabilizer (O) at 7.5 sec.<sup>-1</sup> and (□) at 15.0 sec.<sup>-1</sup>; PVC experimental resin plus 4.0 parts Thermolite stabilizer (◆) at 30 sec.<sup>-1</sup> and (◇) at 7.5 sec.<sup>-1</sup>; PVC experimental resin plus 2 parts Thermolite stabilizer (▲) at 30 sec.<sup>-1</sup> and (△) at 15 sec.<sup>-1</sup>.

In region III the shear viscosity increases rapidly and the extrudates become black, ultimately the polymer will decompose and will cause the extrudate to have rough surfaces. During this period shear viscosities are very erratic.

In Figure 12 the logarithm of the viscosity is plotted against time. The linear relationship shown in region III indicates that the degradation reactions are first order. Hence, the rate of reaction can be expressed by eq. (1):

$$d\eta/dt = k\eta \quad (1)$$

Integrating eq. (1) gives:

$$\ln \eta - \ln \eta_0 = k(t - t_0) \quad (2)$$

where  $\eta_0$  is the viscosity at time zero.

Differentiating eq. (2) results in:

$$d(\ln \eta)/dt = k \quad (3)$$

Hence, the slopes of the curves in regions II and III are rate constants. If these are kinetic rate constants, they should be related to the temperature by an Arrhenius equation. This is the case, as is shown in Figure 9. The activation energies calculated for the Geon resin, the copolymer, and the emulsion PVC are 41.8, 43.1, and 28.0 kcal./mole, respectively. These values refer to the overall decomposition reaction occurring in an environment of low oxygen concentration. Both dehydrochlorination and cross-linking contribute to this reaction. Activation energies of 26–36 kcal./mole

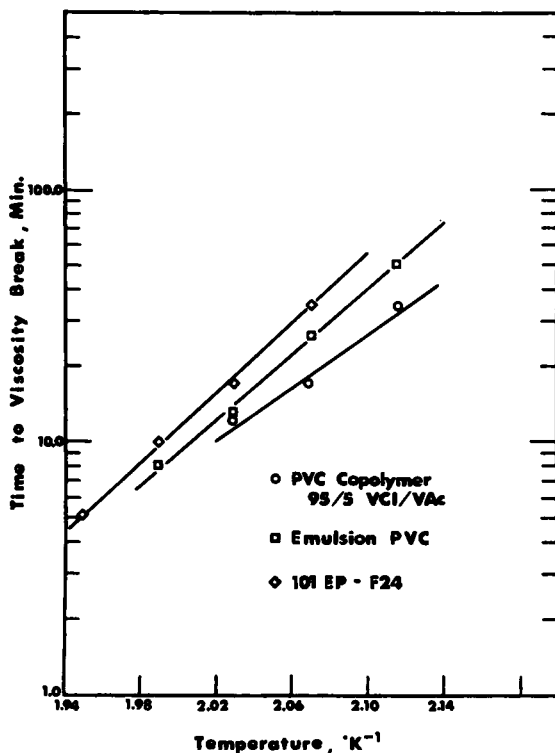


Fig. 10. Temperature dependence of induction period for (O) PVC copolymer (95/5 vinyl chloride/vinyl acetate); (□) emulsion PVC; (◇) Geon resin 101EP-F24.

have generally been reported for PVC from dehydrochlorination studies.<sup>7,19,20</sup>

As stated before, the slope of the curve in region II is generally zero and, therefore, the rate constant is zero. This being the case, it means either no reaction is occurring or that the reaction that is occurring does not have a significant affect on the shear viscosity. The latter definitely is the case, as color changes occur prior to region III. This suggests that the reaction of PVC with T-31 is not a substitution reaction involving the octylthioglycolate ion, as the addition of this ion as a side chain should cause an increase in viscosity.

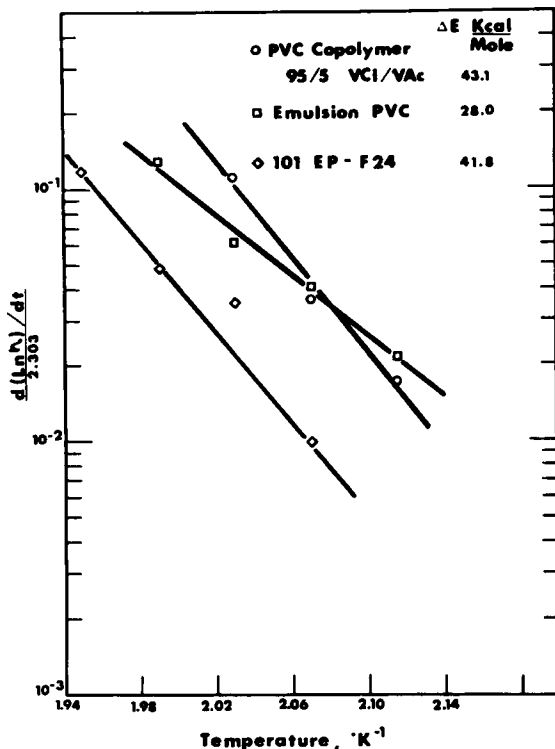


Fig. 11. Temperature dependence of rate of decomposition for (O) PVC copolymer (95/5 vinyl chloride/vinyl acetate); (□) emulsion PVC; (◇) Geon resin 101EP-F24.

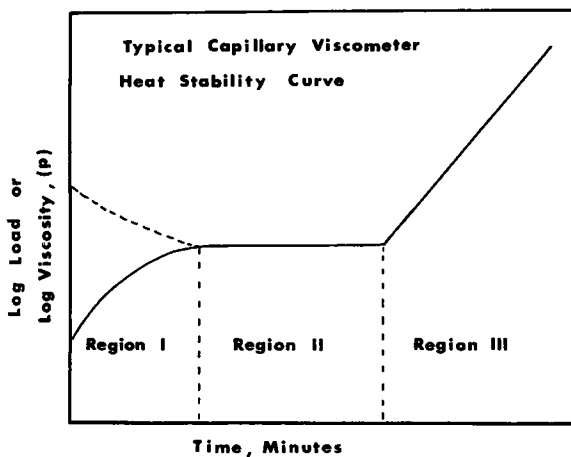


Fig. 12. Typical capillary viscometer heat stability (CVHS) curve.

The fact that  $k = 0$  refers only to PVC stabilized with T-31. Whether  $k = 0$  for other stabilizers must be investigated.

The reaction of the stabilizer and polymer can also be treated kinetically. The results shown in Figure 6 indicate that this reaction is zero order and accordingly follows the rate equation

$$-dC_s/dt = k \quad (4)$$

where  $C_s$  is concentration of stabilizer.

Integration of eq. (4) over the limits of  $(C_s)_0$  to  $C_s$  yields eq. (5):

$$C_s - (C_s)_0 = -k(t - t_0) \quad (5)$$

Then, at the induction time  $\theta$ , that is, the time required for the consumption of stabilizer,  $C_s$  should then equal zero. Hence, eq. (5) becomes

$$(C_s)_0 = k\theta \quad (6)$$

Again,  $k$  is a kinetic rate constant related to the temperature through an Arrhenius equation. Since  $(C_s)_0$  is the initial concentration of stabilizer and therefore a constant, eq. (6) can be rearranged.

$$\theta = (C_s)_0/k = k_1$$

Hence,

$$\theta = k_1 = Ae^{-\Delta E/RT} \quad (8)$$

$$\ln \theta = \ln A - \Delta E/RT \quad (9)$$

The fact that the data of Figures 7 and 8 can be fitted by eq. 9 confirms the assumption that the order of reaction for the stabilizer is zero order.

An activation energy of about 30 kcal./mole is calculated for stabilizer T-31. The fact that  $A$  is linear with concentration confirms the data of Figure 6.

In summary, it has been demonstrated that the CVHS test is a useful method for studying the decomposition of PVC. Extending this technique to other stabilizer systems should prove to be a useful tool in studying stabilizer efficiency as well as to permit reliable stability predictions to be made for any given time, temperature, shear rate, and stabilizer concentration conditions. It has been shown that the results from the CVHS test are in accord with those obtained from other acceptable methods such as TGA, infrared spectra, and intrinsic viscosity. In addition, it has been shown that the data from the CVHS test can be treated kinetically.

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### Résumé

La rhéométrie capillaire est utilisée pour caractériser la stabilité thermique du chlorure de polyvinyle. En extrudant isothermiquement le polymère fondu à vitesse de cisaillement constante, on obtient une relation viscosité apparente-temps qui présente trois régions distinctes. (1) l'obtention de la viscosité d'équilibre, (2) la viscosité constante et (3) une viscosité rapidement changeante. Durant les régions 2 et 3 les extrudats de polymères changent graduellement de couleur, de limpide comme l'eau jusque noir. Ces régions caractéristiques sont reliées à la température d'extrusion par des diagrammes d'Arrhénius. Une activation de 40 Kcal/g. mole a été calculée pour la décomposition du PVC. La spectroscopie infrarouge, des analyses gravimétriques et des mesures de viscosité intrinsèque ont été utilisées pour comparer les résultats de ces données d'écoulement à l'état fondu.

### Zusammenfassung

Die thermische Stabilität von Polyvinylchlorid wird durch das kapillare Fließverhalten charakterisiert. Durch isotherme Extrusion des Polymeren mit konstanter Schubgeschwindigkeit wird die Zeitabhängigkeit der scheinbaren Viskosität in drei deutlich verschiedenen Bereichen erhalten: (1) Einstellung der Gleichgewichtviskosität, (2) konstante Viskosität und (3) rasch sich ändernde Viskosität. In den Bereichen zwei und drei ändert sich die Farbe des extrudierten Polymeren kontinuierlich von wasserklar zu schwarz. Diese charakteristischen Bereiche hängen von der Extrusionstemperatur nach Art eines Arrheniusdiagramms ab. Für die Zersetzung von PVC wurde eine Aktivierungsenergie von 40 kcal/Mol berechnet. Zur Bestätigung der Ergebnisse der Schmelzflussversuche werden Infrarotspektroskopie, thermogravimetrische Analyse sowie die Messung der Viskositätszahl herangezogen.

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