Processing of Poly(vinyl Chloride) Polymers Correlated with Composition, Glass Transition, and Viscosity

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Synopsis

Correlations between processing characteristics and measurable physical properties were investigated for 16 commercial poly(vinyl chloride) polymers and acetate copolymers. Processing was evaluated with the Brabender Plasti-Corder. The glass transition temperature and dry blending procedure were examined by differential thermal analysis. The polymers included high and low molecular weight materials and examples of suspension, emulsion, and solution methods of polymerization. Effects due to the amount of plasticizer, stabilizers, and other additives were measured and are discussed.

I. EVALUATION IN THE PLASTI-CORDER

In recent years the Brabender Plasti-Corder (Brabender Instruments, Inc., South Hackensack, N. J.) has been used extensively for the study of processing variables. The instrument and its use in evaluating the processing of elastomers was described in detail by Blake.[1] At the 20th Annual Technical Conference, Touchette, Seppala, and Darby[2] presented an evaluation of many plasticizers with a single poly(vinyl chloride) polymer. The present study includes a variety of both homopolymers and copolymers of vinyl chloride with a single plasticizer. It has been possible to examine the behavior of resin and plasticizer without stabilizer or other additive as well as the effect of each additive. Premixed blends, aged blends and dry blends have also been investigated.

The Plasti-Corder is Model PL-V3AA and the mixing head used was the roller type, which approximates the action of the Banbury mixer. A constant volume of sample was used, sufficient when fused to fill the mixing chamber. The weighed components were charged directly to the mixer without prior mixing and with the mixer chamber and oil reservoir at room temperature. Heating and circulating of the heating oil was then started and continued until the temperature was well above the fusion point of the sample. The heating rate was from room temperature to 140°C. in 1 hr. (average 2°C./min.) Unless specifically stated, all values are for a rotor speed of 30 rpm.

In the Plasti-Corder it is possible to measure the forces involved in mixing in the dry state, during fusion, and finally in the highly viscous melt.

Although the rotors in the mixing chamber are shaped for intensive mixing such as those in a Banbury and, therefore, would be expected to produce turbulent flow, it seemed of interest to attempt correlations with melt viscosity measurements on the same polymers. In the case of Newtonian liquids the temperature dependence of viscosity follows a simple exponential relationship.[3]

$$\eta = A e^{E/RT}$$

for which the plot of log η versus $1/T$ is a straight line. For this reason, the data were plotted as the log of torque measurements versus the reciprocal of absolute temperature. The assumption is that above the fusion temperature, the viscous shearing forces between the large polymer molecules is the
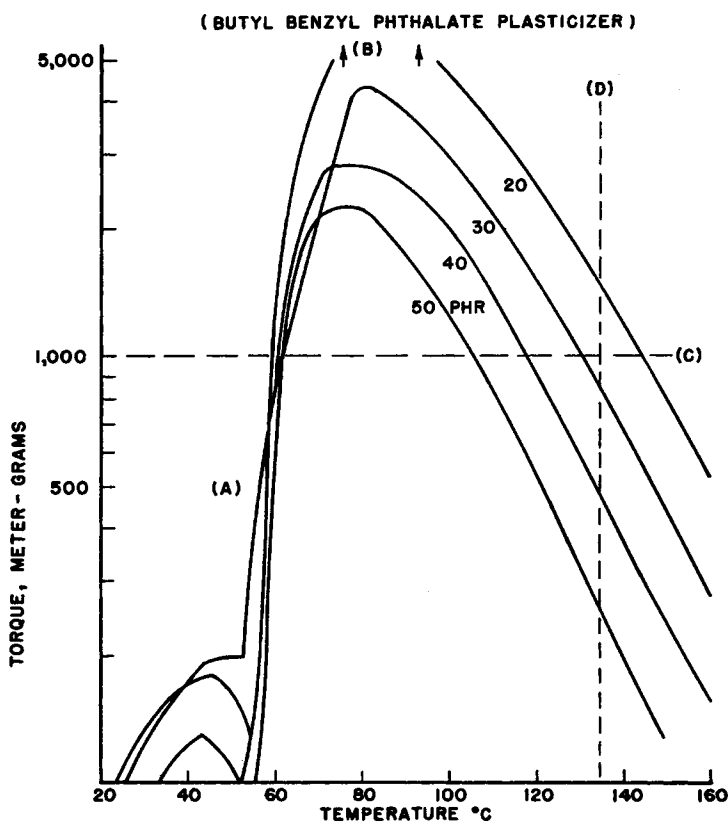

Fig. 1. Plasti-Corder evaluation of copolymer (Exon 487, butyl benzyl phthalate plasticizer); torque vs. temperature, materials charged individually to mixer.

dominant factor in the torque measurement and therefore the torque reading is treated as a viscosity value. The resultant charts have proved to be very informative. In some charts, for ease of reading, the torque values on a logarithmic scale are shown plotted directly against temperature rather
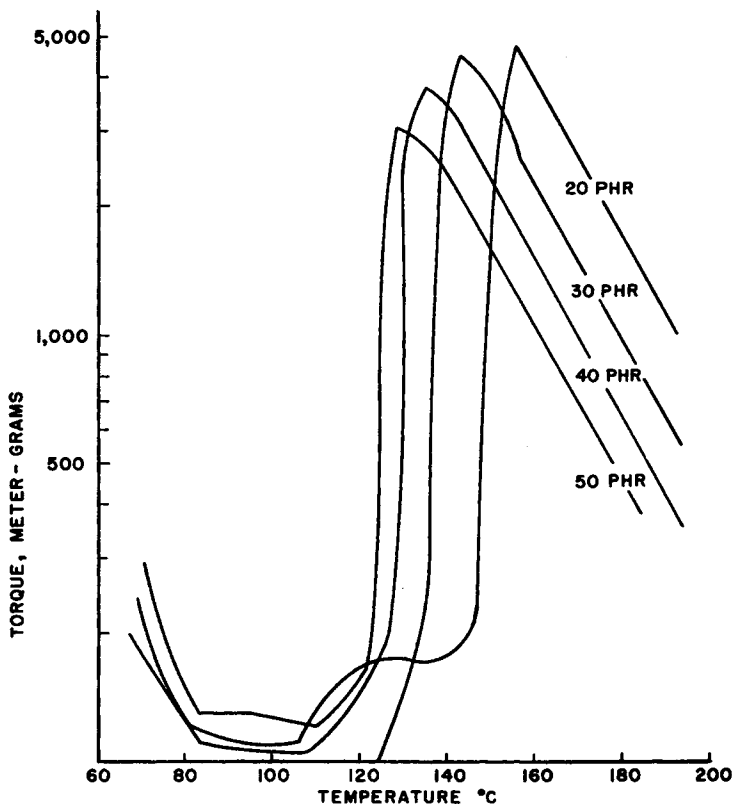
Fig. 2. Plasti-Corder evaluation of dry blending homopolymer (Escambia 3185, butyl benzyl phthalate plasticizer); torque vs. temperature, materials charged individually to mixer.

than the reciprocal, since this introduces only minor changes in the shape of the curves.

Typical curves are shown for the evaluation of the effect of varying the amount of the plasticizer butyl benzyl phthalate. The data plotted in Figure 1 are for a 13% acetate copolymer (Exon 487). Initial fusion is evidenced by a rapid increase in torque as at (A) in Figure 1. The fusion temperature is specific in this procedure but can be varied by change in some physical variable such as in the rate of heating, rotor speed, and the use of ram pressure. For purpose of comparison, the temperature at which the increasing torque is 500 m.-g. is arbitrarily tabulated as the "initial fusion" temperature. In the case of the Exon copolymer (Fig. 1), it is evident that the fusion temperature is not changed appreciably by the amount of plasticizer in the blend. However, this "initial fusion" temperature is quite low, and this behavior will be correlated later with the plasticizing action of the acetate content of the copolymer and the phenomenon of the glass transition. In the case of the Escambia and Opalon homopolymers (Fig. 2, Table I), the initial fusion temperature increases as the amount of plasticizer is

TABLE I
Effect of Plasticizer on Initial Fusion Temperature of Homopolymers in Plasti-Corder

Plasticizer, phr	Initial fusion temperature, °C.	
	Opalon 610	Escambia 3185
20	153	148
30	144	136
40	140	129
50	132	124

reduced and occurs at much higher temperatures. This initial fusion temperature can also be read from the inflection of the time–temperature chart as described by Touchette, Seppala, and Darby.[2] However, they used a closed system and ram pressure so that their relative fusion temperatures differ.

The maximum torque (B) increases as the amount of plasticizer is reduced for both homopolymer and copolymer. After the maximum torque is reached and fusion is completed, the viscosity of the melt decreases regularly with increase in temperature. In this temperature range the torque readings of the Plasti-Corder have the attributes of melt viscosity values and for the purpose of comparing polymers and polymer compositions can be treated as viscosity readings. They cannot be easily converted into absolute viscosity values, since the irregular shape of the rotors and mixing chamber do not permit calculation of shear rates.

The fluidity or viscosity of the melted resin composition can be compared either as (C) Figure 1, the temperature at a specified torque (e.g., 1000 m.-g.) or as (D), the torque at a specified temperature (e.g., 135°C.). If comparisons are to be made with other physical constants it is essential that these values be read from linear portions of the curves.

A specific procedure for the Plasti-Corder has been defined in this investigation. Furthermore, in the present case processing has been measured only in the Plasti-Corder, although extensive experience indicates that the same conclusions will apply to other processes with comparable shear rates.

Effect of Plasticizer on Relative Melt Viscosity for Various Polymers

Above the fusion temperature the regularity of the decrease of torque (relative melt viscosity) as the amount of plasticizer is increased is evident in the first two figures. This fundamental relationship of viscosity and temperature is shown more accurately by the plot of the log of torque versus the reciprocal of absolute temperature as shown in Figure 3 for both a copolymer and a homopolymer. The only difference between copolymer and homopolymer is that the viscosity curves for the latter are at a higher temperature for equal flow, that is, for equal ease of processing. The change of relative melt viscosity with increasing molecular weight is shown in the series of Opalon polymers, each at one plasticizer level (30 phr) in
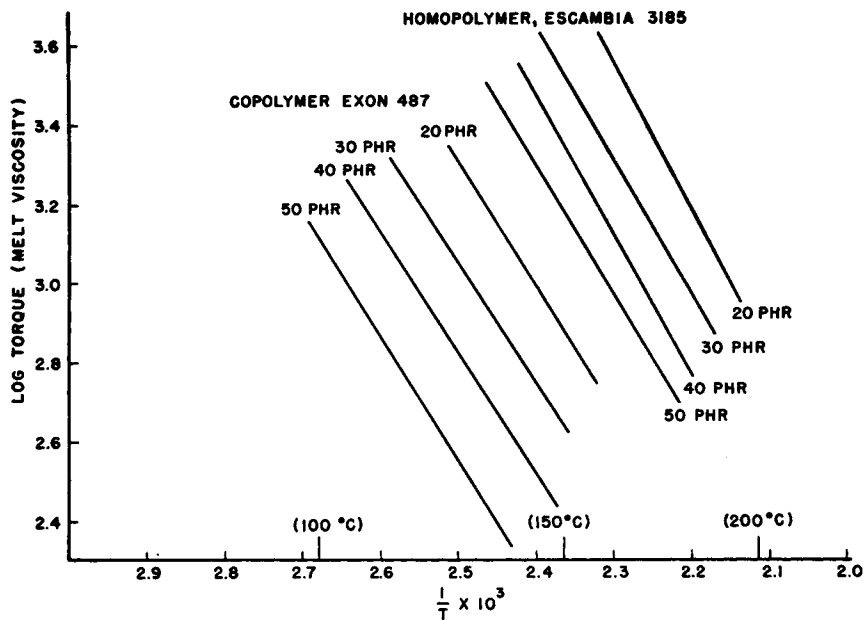
Fig. 3. Temperature dependence of melt viscosity of poly(vinyl chloride) polymers and copolymers at various plasticizer levels.
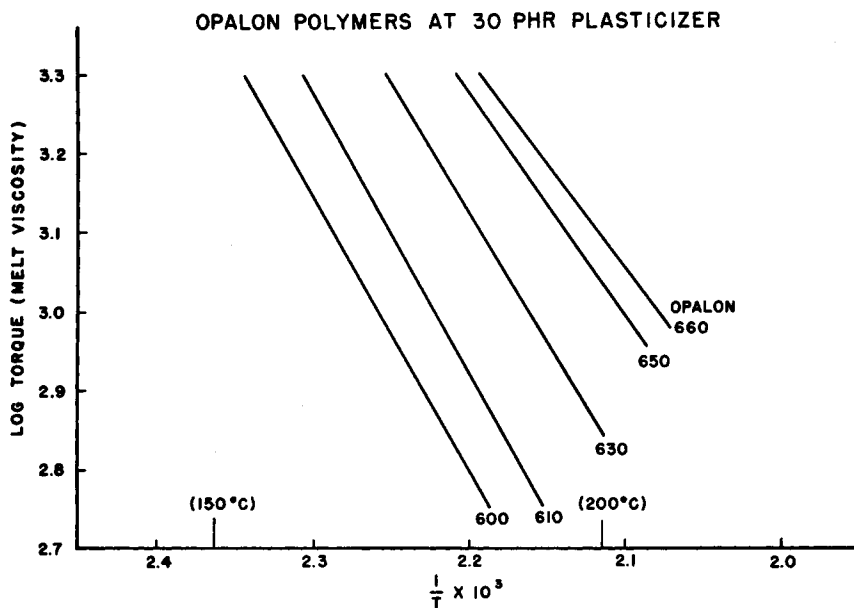

Fig. 4. Temperature dependence of melt viscosity of Opalon poly(vinyl chloride) polymers of differing molecular weight at 30 phr plasticizer.

TABLE II
Physical Specifications of Polymers

Polymers[a]	Specific viscosity η_{sp} (c = 0.4, cyclohexanone, 30°C.)	Intrinsic viscosity $[\eta]$ (cyclohexanone, 30°C.)	Calculated molecular weight		Melt viscosity of 30 phr blends as torque at 180°C., m.-g.
			$\bar{M}_n$	$\bar{M}_w$	
Homopolymers					
Opalon 660	0.55[b]	1.18[c]		106,200	2300
Geon 101EP	0.54	1.128		100,100	2700
Escambia 2250	0.50	1.060	58,700	94,200	2400
Opalon 650	0.48[b]	1.05[c]	53,900	94,500	2000
Borden VC-32	0.39	0.908		81,100	1300
Diamond PVC 40	0.39	0.893	44,300	79,700	1450
Escambia 2200	0.39	0.866	43,400	77,300	1400
Opalon 630	0.38	0.836	41,700	75,000	1450
Exon 924	0.37	0.840	40,300	75,000	1200
Escambia 3185	0.32	0.720	40,300	64,800	960

Polymer					
Opalon 610	0.29	0.653	28,900	58,300	870
Opalon 600	0.251	0.59[c]		53,100	610
Exon 965	0.22	0.50[c]	19,800	43,600	490
Emulsion Polymers					
Marvinol VR-10	0.63	1.34[c]			3300
Geon 121	0.56	1.280			2400
Marvinol VR-53	0.425	0.93[c]			1700
Copolymers					
VYNW (3% Ac)	0.51	1.100	56,800	98,200	2200
VYNS (10% Ac)	0.33	0.735	33,700	65,600	560
VYHH (13% Ac)	0.22	0.525	21,900	47,100	105
VYFS (13% Ac)	0.23	0.548	23,000	49,000	120
Exon 487 (13% Ac)	0.21	0.495	20,200	44,200	100

[a] Polymers: Opalon, Monsanto Chemical Company; Geon, B. F. Goodrich Chemical Company; Escambia, Escambia Chemical Corporation; Exon, Firestone Plastics Company; Marvinol, U. S. Rubber Company; VYNW, VYNS, VYHH, VYFS, grades of Vinylite resins, Union Carbide Plastics Company.

[b] Manufacturer's published data.

[c] Interpolated from a plot of $[\eta]$ versus η_{sp} values of all remaining PVC polymers.
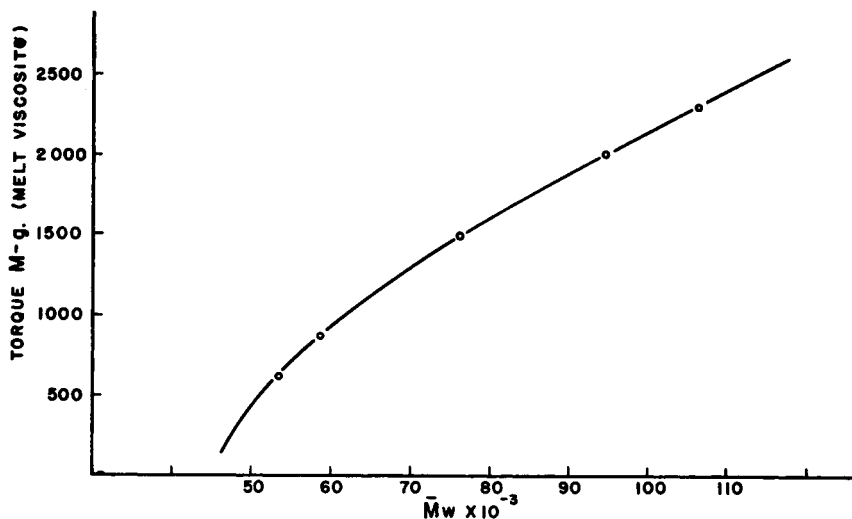
Fig. 5. Variation of melt viscosity of Opalon series of homopolymers (30 phr blend) with molecular weight. Torque at 180°C.

Figure 4 and for one temperature in Figure 5. Molecular weights and related properties for all polymers investigated are discussed in a later section and are listed in Table II. Correlations have all been made with plasticized blends, since the Plasti-Corder procedure used is not adapted to the measurement of melt viscosities of most unplasticized polymers. The effect of plasticizer on reducing the mixing torque is directly proportional to the parts per hundred of plasticizer used in the case of the low molecular weight copolymer (Figure 6). It was possible to process this copolymer without any plasticizer present and obtain the value shown. It appears that initial amounts of plasticizer have proportionally greater effect in reducing the torque, a factor reported for other physical measurements with poly(vinyl chloride). A similar plot of the higher molecular weight homopolymers is not entirely linear. However, if the comparison of polymers is made at equal viscosity, that is at equal ease of processing by plotting the plasticizer level versus the reciprocal of the temperature at, for example, 1000 m.-g. torque, the variation is linear, as shown in Figure 7. Thus 50 phr of plasticizer are required to reduce the "melt viscosity" of the homopolymer Exon 965 to that of a 20 phr plasticized copolymer Exon 487. Since these two polymers are closely equal in molecular weight (data of Table II) the 13% acetate in the copolymer acting as an internal plasticizer is roughly equal to 30 phr of externally added plasticizer, the amount necessary to produce an equal torque in processing the homopolymer at the same temperature.

The melt viscosity as measured by mixing torque in the Plasti-Corder is lowered by the acetate monomer as it is by addition of plasticizer, whereas it is known and is indicated by the present data that the presence of this co-
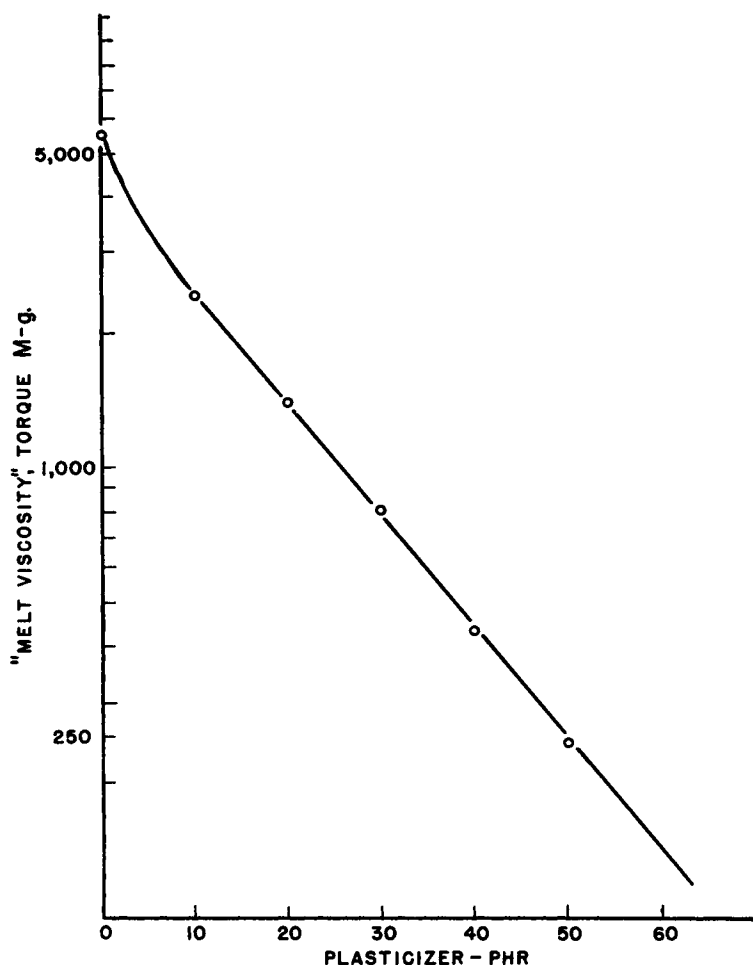
Fig. 6. Relation of melt viscosity to plasticizer content of blends for Exon 487 acetate copolymer at the same processing temperature (135°C.).

monomer does not affect the measurement of molecular weight by the usual solution methods.

Relation of Plasti-Corder Torque Values to Specific Viscosity and Molecular Weights of Unplasticized Polymers

Each of the polymers evaluated in the Plasti-Corder has been identified by measurement of specific viscosity in cyclohexanone solution at 30°C. (Table II) by ASTM viscosity method D-1243-60. Intrinsic viscosities have been determined by graph from these solution viscosities and from them the number-average $(\bar{M}_n)$ and weight-average $(\bar{M}_w)$ molecular weights. The equation of Danusso[4]

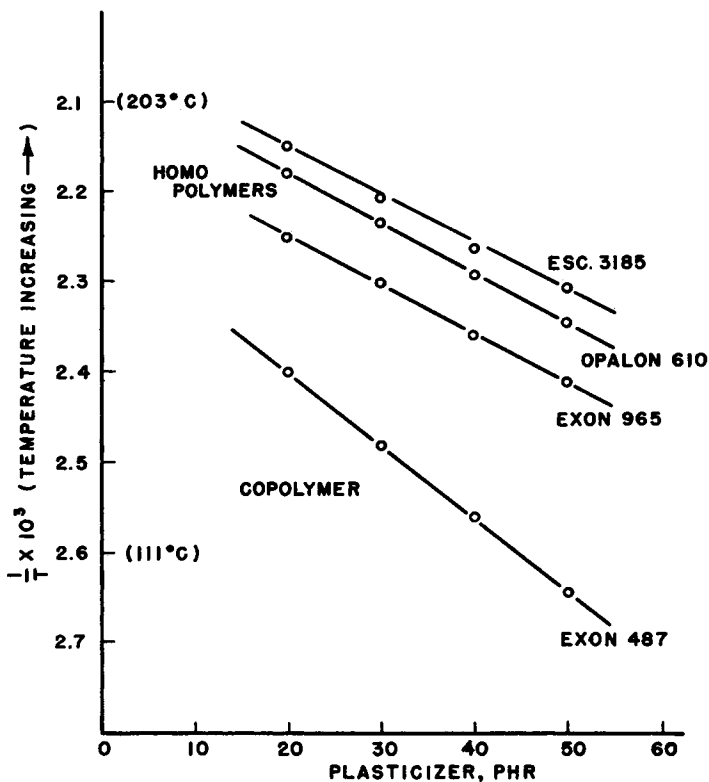$$[\eta] = 2.4 \times 10^{-4}\bar{M}_n{}^{0.77}$$

Fig. 7. Comparison of PVC polymers at temperature of equal ease of processing at 1000 m.-g. torque.

was used for the calculation of number-average molecular weight and the equation of Mead and Fuoss[5]

$$[\eta] = 1.12 \times 10^{-5} \bar{M}_w$$

for calculation of weight-average molecular weight.

Melt viscosity as indicated by the meter-gram torque values measured in the Plasti-Corder correlate well with solution viscosity and therefore with calculated molecular weights for this wide range of commercial poly(vinyl chloride) polymers, as shown in Figure 8. A group of five experimental co-polymers, each with 13% acetate content but differing in molecular weight, also give the same approximately linear relationship between solution viscosity and melt viscosity on the basis of data at the lower temperature of 140°C. These values are shown as the broken line in Figure 8. The correlation is poorer for the high viscosity homopolymers, and the copoly-mers with appreciable amounts of acetate are definitely lower in melt vis-cosity. For example, the two homopolymers, Exon 965 and Escambia 3185 have intrinsic viscosities (0.50 and 0.72) essentially equal to those of the copolymers Exon 487 and VYNS (0.50 and 0.74); however, the melt vis-
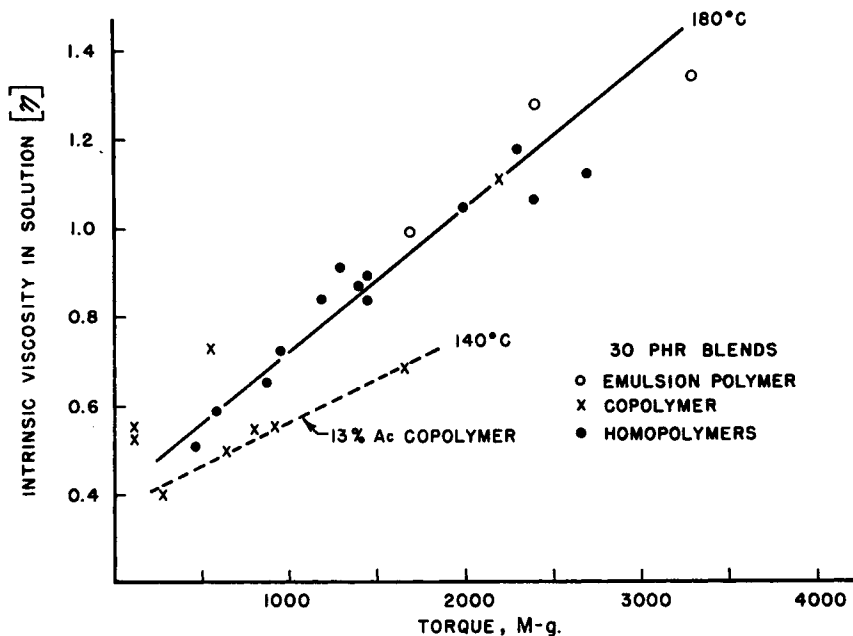
Fig. 8. Correlation of melt viscosity of commercial PVC polymers (30 phr blends) with solution viscosity.

cosities as torque values in the Plasti-Corder are 490 and 960, respectively, for the homopolymers but much lower (100 and 560) for the copolymers. This, of course, is in agreement with experience and the usual statement that the acetate unit in the copolymer acts as an internal plasticizer, but in a manner that is not reflected in the specific viscosity measurement.

Effect of Stabilizers and Other Additives

Almost all additives to a poly(vinyl chloride) formula affect the processing in some manner, and this can be measured in the Plasti-Corder evaluation, as shown in the data of Table III with a copolymer resin and butyl benzyl phthalate plasticizer. Among the stabilizers, barium-cadmium laurate adds a small plasticizing effect equal to one-third that of an equal amount of plasticizer but has no apparent effect on the temperature of fusion. Pentaerythritol is essentially inert. Both stearic acid and a liquid organic phosphite stabilizer are equal to the plasticizer in reducing melt viscosity. However, the lubricant action of stearic acid is indicated by a small increase in fusion temperature. The epoxy soya oil has good plasticizing action and considerable lubricant effect. The alternate plasticizer DOP has equal plasticizing efficiency but increases the fusion temperature. Addition of a filler such as finely ground limestone increases the initial fusion temperature and the relative melt viscosity as shown in Figure 9.

TABLE III
Effect of Additives on Mixing Torque
(Relative Melt Viscosity)

Additive	Amount added, phr	Initial fusion temperature, °C.	Torque at 121°C., m.-g.	Torque decrease, % of effect of 10 phr plasticizer
Control[a]	—	56	1460	—
Plasticizer	10	57	800	100
Ba-Cd laurate[b]	2.5	57	1450	1.5
Ba-Cd laurate	5.0	57	1350	17
Ba-Cd laurate	7.5	55	1280	27
Organic phosphite[c]	5	53	1040	64
Ba-Cd caprate[d]	5	63	1400	9
Pentaerythritol	5	60	1525	−10[e]
CZ-45[f]	5	57	1500	−6[e]
Organo-tin[g]	5	53	1200	40
Stearic acid	5	58	1075	59
Epoxy soya oil[h]	10	64	970	75
Polyester[i]	10	61	1100	55
Polyglycol phthalate[j]	10	53	1040	64
Acrylate[k]	10	46	1700	−36[e]
DOP	—	69	1450	1.5

[a] Control is blend Exon 487 polymer with 30 phr plasticizer.
[b] Stabilizer 613A, Nopco Chemical Company.
[c] Ferro 904, Ferro Chemical Corporation.
[d] A-5, Ferro Chemical Corporation.
[e] Increase.
[f] Advastab CZ-45, Carlisle Chemical Works, Inc.
[g] Q275, Argus Chemical Corporation.
[h] G-62, Rohm & Haas Company.
[i] G-25, Rohm & Haas Company.
[j] Armstrong Cork Company.
[k] K-120, Rohm & Haas Company.

Irregularities in the Plasti-Corder Curves and the Dry Blending Phenomenon

In the evaluation of processing of poly(vinyl chloride) polymers by use of the Plasti-Corder, certain irregularities were observed in the initial or low temperature portion of the charts as in Figure 1. Unsuccessful efforts were made to correlate these irregularities with various physical factors, such as surface area, size and shape of polymer particles, bulk density, or even differences in method of polymerization. Surface adsorption of plasticizer followed by absorption into the particle provides a partial explanation. just as it has been used in the past to explain the mechanism of dry blending. However, physical absorption is a slow process and did not satisfactorily fit the evidences for a specific temperature at which this increase in torque occurred. It was postulated that the glass transition of the polymer, a

phase change occurring at a definite temperature for each polymer, might be involved. It was reasoned that when the polymer in the bowl of the mixer expanded as it does at the glass transition temperature that an increase in torque occurred and that with plasticizer present, in the case of the copolymers, fusion also occurred immediately and the two phenomena overlapped. In order to separate the physical adsorption of the plasticizer from the glass transition and the latter from the fusion temperature, a homopolymer (Exon 965) was selected for experimental illustration.

In experiment 170 (Fig. 10) with the charge of dry resin and plasticizer added directly to the mixing chamber of the Plasti-Corder and heated at the relatively slow heating rate adopted for this entire investigation, an initial
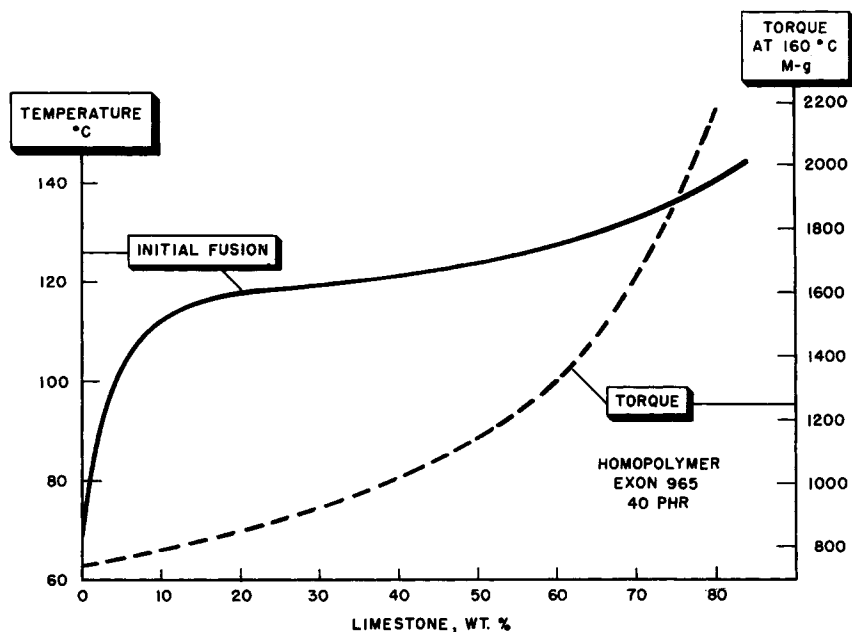

Fig. 9. Effect of limestone filler on the processing of PVC homopolymer (Exon 965, 40 phr blend) in the Plasti-Corder.

low peak in torque occurred at 76°C.; the mix then became dry with a drop in torque until fusion occurred at about 128°C. In a premixed batch (experiment 169) which had aged 19 days at room temperature, the torque increased much more rapidly from room temperature, showing slight irregularity about 60–80°C. with rapid increase of torque and immediate fusion at this low temperature.

In experiment 177 a dry blend was prepared, that is, a portion of premixed batch 169 was placed in a sigma blade mixer and heated above 80°C., held there for 30 min. and cooled. This is an exaggerated dry blending technique. The product is a dry powder, having an initial low torque in the Plasti-Corder at room temperature decreasing to a negligible value and
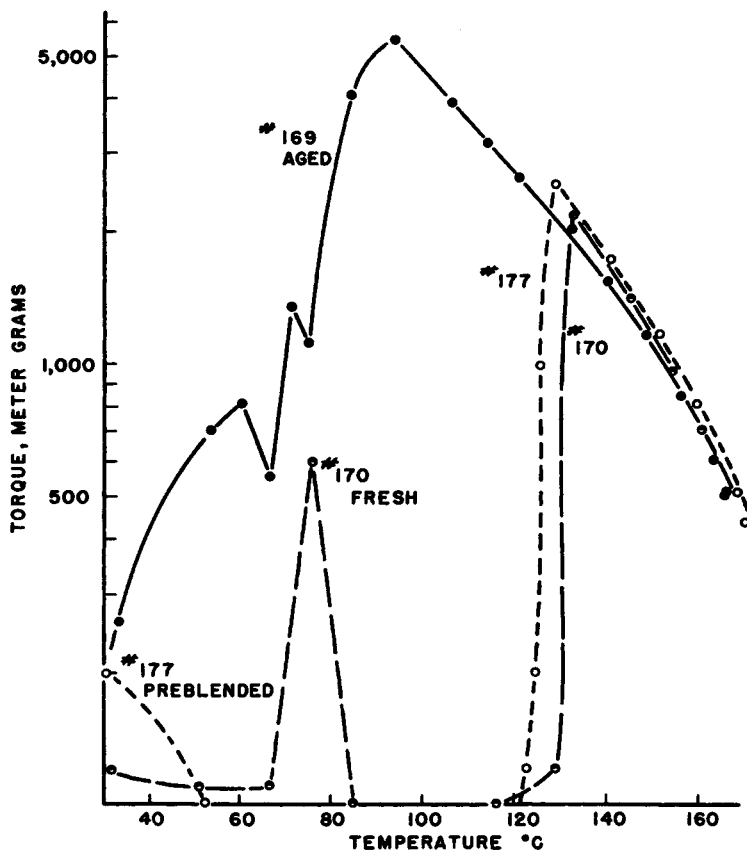
Fig. 10. Correlation of dry blending procedure with irregularity in processing in the
Plasti-Corder of Exon 965 (butyl benzyl phthalate plasticizer).

remaining a dry blend as with experiment 170 until fusion occurred at
126°C.

It was predicted that 76°C. should approximate the glass transition of
Exon 965 polymer and that of the blend should be about room temperature.
Both predictions were confirmed by differential thermal analysis (DTA)
studies which will be described in detail.

It is now suggested that the process of dry blending consists of heating a
mixture of polymer and plasticizer to and above the glass transition tem-
perature of the polymer under conditions free from pressure or any approach
to the fusion temperature. It is also assumed that the plasticizer molecu-
larly penetrates the polymer to form a stable and completely uniform blend.
In the case of the fresh blend of homopolymer with plasticizer (experiment
170), the polymer fusion temperature is enough above the glass transition
temperature that the expansion and complete absorption of plasticizer
occurs without fusion. Apparently in contrast in experiment 169 during
the aging period the excess of plasticizer on the outside of each particle has

already penetrated the polymer, but not uniformly, and the overplasticized surfaces fuse at a lower temperature in the Plasti-Corder.

This response to operating in the neighborhood of the glass transition temperature is further illustrated with the experience with highly plasticized blends of this low molecular weight homopolymer, Exon 965.

Whereas the polymers considered in Figures 1 and 2 gave very regular changes in processing as the amount of plasticizer was increased, this was not true with Exon 965. As shown in Table IV at the normal heating rate with 10, 20, and 30 phr of plasticizer the increase in temperature at fusion occurred at successively lower temperatures in a regular manner. However, 40 and 50 phr blends fused much lower, near the glass transition temperature 74°C. By increasing the heating rate, the fusion temperature of the 30 phr blend was lowered, and by decreasing the heating rate both 30 and 40 phr blends became dry blends and required higher temperatures for fusion.

TABLE IV
Fusion Temperatures of Plasticizer Blends of Low Molecular Weight Homopolymer Exon 965 in the Plasti-Corder

	Initial fusion temperature, °C.		
Plasticizer, phr	Normal heating rate (140°C. in. 60 min.)	Fast heating rate (150°C. in 30 min.)	Slow heating rate (130°C. in 90 min.)
10	148		
20	138		
30	127	78	140
40	68	72	120
50	72	78	

II. EVALUATION BY DIFFERENTIAL THERMAL ANALYSIS

The use of differential thermal analysis (DTA) procedures in the evaluation of high polymers is well described by Ke.[6]

A typical first-order transition is shown in Figure 11, the melting of NH_4SCN, which was used to check the calibration of the equipment. In the same figure but on a different scale the second-order transition of Exon 924, a medium molecular weight poly(vinyl chloride) homopolymer, is also shown. The differences in the two curves both in shape and order of magnitude are typical. The heating rate was 2.5°C./min., and $1/2$-in. cells were used with isophthalic acid as the reference.

Experimental Equipment and Procedure

The equipment is similar to that described by several authors, for example, Keavney and Eberlin.[7] However, during the course of this investigation we used four widely different cell sizes, from the $1/2$-in. cells in large aluminum blocks similar to those used by Keavney holding 1-2 g. of sample

to the small cells used in first-order transition studies which have a capacity of 30 mg. of sample. As in the studies with the Plasti-Corder, samples were dry powders in the case of the raw polymer or fresh mixtures with plasticizer.

A variety of commercial poly(vinyl chloride) polymers were examined and the glass transition temperatures T_g are listed in Table V. The range of transition temperatures is not great. In the homopolymers the transition temperature ranged from 83°C. for high molecular weight Geon 101 E.P. to
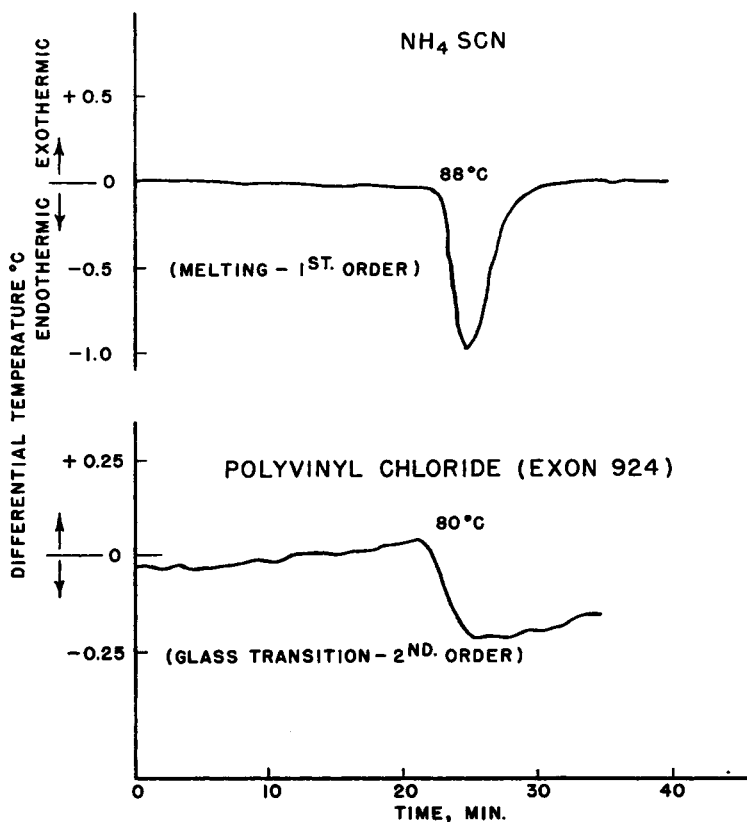

Fig. 11. Comparison of DTA curves of melting point and glass transition; 0.3 g. NH₄-SCN, 1.24 g. Exon 924.

74°C. for Exon 965, a polymer of less than half the molecular weight. The acetate copolymers of equal viscosity (molecular weight) have a characteristically lower glass transition temperature. The values obtained are in agreement with those reported in the literature, except for the early determinations by the volume expansion procedure reported for VYNW and VYNS copolymers.

A few of these resins were fused and press-molded into films; the glass transition temperatures were determined by the torsion pendulum procedure[9] and the results listed in Table V. Except for the higher molecular

TABLE V
Glass Transition Temperature of Commercial Poly(vinyl Chloride) Polymers

Polymers	Molecular wt. (estimated from $[\eta]$)	T_g, °C. Present study		Literature values			
		DTA	Torsion pendulum[a]	DTA	Torsion	Volume expansion	Specific heat
Suspension PVC							
Geon 101EP	58,700	83					
Escambia 2250	53,900	81	90				
VC-32C	44,300	80					
PVC-40	43,400	79					
Escambia 2200	41,700	78	79				
Opalon 630	40,300	78					
Exon 924	40,300	79					
Escambia 3185	36,000	78					
Opalon 610	32,700	76					
Exon 965	25,100	74	74				
Emulsion PVC							
Geon 121	64,000	74					
Marvinol VR-10		80		81[b]			
Marvinol VR-53		78					
PVC type not specified					86[d]	82[c]	79[e]
Suspension copolymers							
Exon 487 (13% Ac)	24,800	66					
Solution copolymers							
VYNW (3% Ac)	55,000	79				61[f]	
VYNS (10% Ac)	36,800	74				59[f]	
VYNH (13% Ac)	26,800	65	69				
VYFS (13% Ac)	27,400	68					

[a] Torsion pendulum values determined in Armstrong Cork Company Laboratory by J. L. Work.
[b] Data of Keavney and Eberlin.[7]
[c] Data of Nielsen.[9]
[d] Data of Wood.[10]
[e] Data of Alford and Dole.[11]
[f] Data of Clash and Rynkiewicz.[8]

weight polymer Escambia 2250, these T_g values are the same as those determined with the DTA procedure.

Effect of Plasticizer

Blends of butyl benzyl phthalate plasticizer with poly(vinyl chloride) polymers effectively lower the glass transition temperature as shown in Figure 12 for three levels of plasticizer with poly(vinyl chloride) homopolymer (Opalon 610). This series was run in a small DTA cell, $1/4$ in. in diameter, with the use of a 0.22-g. sample. The resulting endotherm is smaller than with larger sample sizes. The glass transition of the polymer alone is
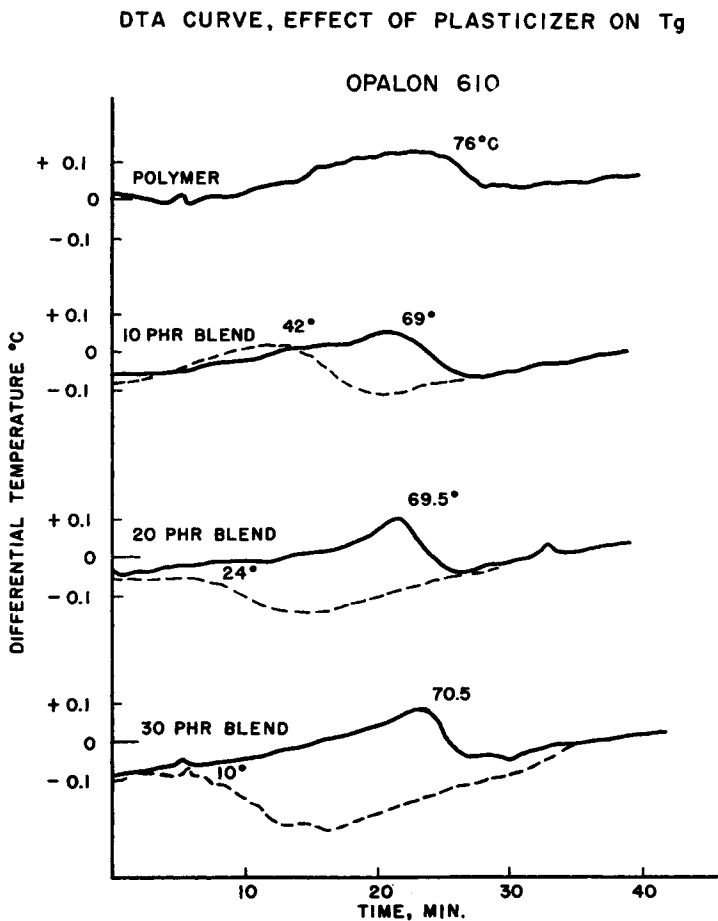
DTA CURVE, EFFECT OF PLASTICIZER ON Tg

OPALON 610

Fig. 12. DTA curves showing reduction of glass transition temperature T_g of Opalon 610 by plasticizer: (———) initial run, fresh mix of polymer and plasticizer; (—) rerun. Small DTA cell, $^1/_4$-in. diameter, 0.22-g. sample.

76°C., upper curve. For the blends the dry polymer was mixed with plasticizer at room temperature in an open bowl type food mixer (Sunbeam Mixmaster) in order to obtain a reasonably uniform blend of plasticizer and resin, but free from the intense shear of the Henschel type blender. The initial DTA measurement of the fresh blend is shown as a solid line in the figure and in each case the glass transition is close to that of the raw polymer. Apparently the amount of immediate plasticization is low.

Immediately after each initial run, which was carried to at least 120°C., the entire unit was chilled rapidly with Dry Ice and the DTA curve was redetermined. These curves are shown as broken lines in Figure 12. The glass transition is now at a lower temperature proportional to the amount of plasticizer in the blend. This lower T_g is a true physical constant of the blend and is constant after indefinite storage, after fusion, and after proc-

TABLE VI
Reduction of the Glass Transition Temperature by Plasticizer

Polymer	Polymer T_g, °C.	T_g of blend, °C.		
		10 phr	20 phr	30 phr
Homopolymers				
Geon 101EP	83	42	31	11
Escambia 2250	81	48	34	13
Escambia 3185	78	45	21	7
Opalon 630	80	42	26	10
Opalon 610	76	42	24	10
Exon 965	74	37	22	9
Geon 121	74	37	22	13
Copolymers				
Exon 487	66	33	18	6
VYNW	79	47	28	13
VYNS	74	38	31	13
VYHH	65	39	22	9

essing into film or finished product, as long as no additional compounding occurs. Several polymers were examined in a similar manner, and the results are presented in Table VI. As might be expected from the narrow range of the T_g values for the polymers listed in Table V, at any specific plasticizer level the glass transitions of the blends are very similar.

As predicted from consideration of the Plasti-Corder data shown in Figure 10, the glass transition T_g of Exon 965 is 74°C. and that of the 30 phr blend at 9°C. is well below room temperature. Clash and Rynkiewicz[8] and Nielsen[9] present data on this lowering of T_g by the presence of plasticizer in fused polymer blends as measured by other procedures.

Effect of Stabilizer

In the past, stabilizers have generally been treated as inert so far as plasticizing action or effects on the physical constants are concerned. The

TABLE VII
Effect of Stabilizer on the Glass Transition Temperature

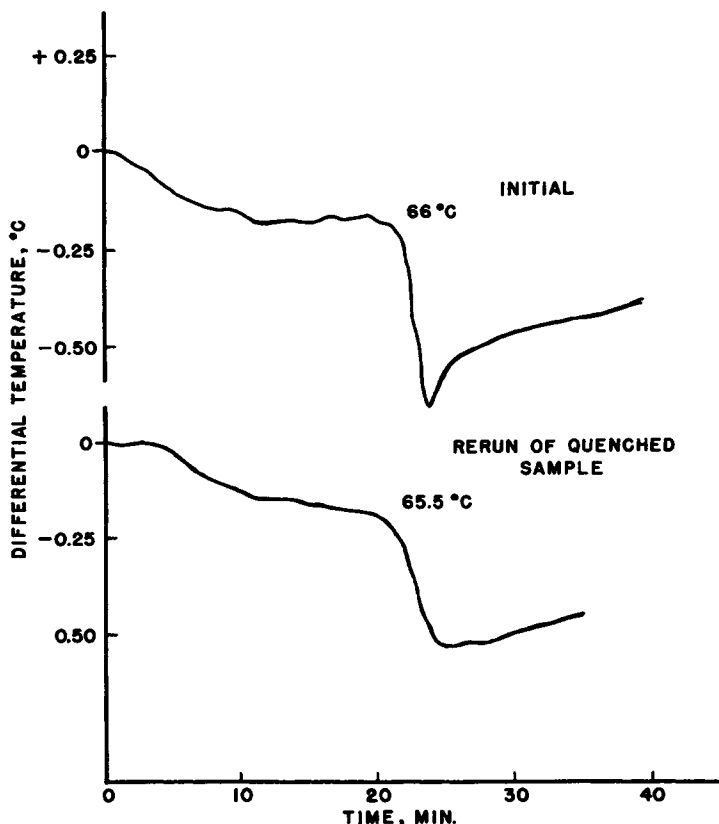| Polymer	Polymer T_g, °C.	T_g of blends at 5 phr stabilizer, °C.			
		Ba-Cd laurate	Organic phosphite	Organotin	Inorganic lead
Homopolymers					
Exon 965	74	74	53	59	75
Opalon 630	80	76	60	70	
Escambia 2250	81	83	64	68	84
Geon 101	83	83	74	73	
Copolymers					
VYHH (13% Ac)	65	65	52	62	69
Exon 487 (13% Ac)	66	64	53	51	
VYNW (3% Ac)	79	78	63	67	

Fig. 13. DTA curve showing T_g of PVC–vinyl acetate copolymer (Exon 487). Cell $^3/_8$-in. diameter, 0.45 g. sample.

evaluation of processing in the Plasti-Corder has indicated that stabilizers differ in their activity. Their effect on the glass transition temperature has been determined and several results are given in Table VII for seven different poly(vinyl chloride) polymers or copolymers. These are dry blends of stabilizer and resin which have been heated above 100°C. and then rerun in the DTA procedure. A barium-cadmium laurate stabilizer has no effect. At 5 phr both the organic phosphite and the organotin stabilizer act as plasticizing agents and lower the glass transition temperature by 10–20°C.

Evidence for Crystallinity in Poly(vinyl Chloride)

Not all DTA curves of the glass transitions are simple. Many are intermediate in shape between the theoretical curves for first- and second-order transitions. Figure 13 illustrates this type as obtained with Exon 487, an acetate copolymer of relatively low molecular weight. The DTA curve for the initial heating of a dry polymer is shown in the upper part of the chart. A large endotherm equal to 0.50°C. temperature difference was obtained at a glass transition temperature of 66°C., over a time interval of 1.5 min. and

at a heating rate of 2.7°C./min.   After the temperature reached 120°C., which is well above the glass transition temperature, the sample was quenched by rapidly cooling the closed aluminum block with Dry Ice, and the DTA curve was rerun at the same heating rate with results as shown in the lower curve.   This curve is the typical second-order DTA curve described in the literature.   There is no extra "tail" as in the initial curve. The glass transition temperature is unchanged.   The temperature difference of the endotherm is less (0.35°C. in a 3-min. time interval).

In the early publication by Keavney[7] on the application of DTA to the determination of the glass transition of polymers, the illustrations include these same types of DTA curves with no discussion of the difference.   We have been able to produce either type at will with several polymer or polymer–plasticizer blends.   The normal curve is always obtained with samples which have been quick-chilled and is believed to represent the amorphous polymer.   The curve with "tail" is obtained after slow cooling or annealing at the glass transition temperature and is believed to represent a mixture containing a small amount of "crystallinity" or regular ordering of segments of the long polymer molecules.   That the amount of crystallinity is small is indicated by failure to obtain any x-ray pattern for these samples.   A detailed analysis of this phenomenon is planned for later publication.

DTA and the Dry Blending Phenomenon

The effect of dry blending of plasticizer with polymer, as it affects the glass transition temperature, is shown in Figure 14 for the homopolymer Opalon 610.   For the moment, we disregard the shape differences of the curves since those minor differences have been related to the crystallinity phenomenon.   The DTA curve for the polymer alone is shown in the upper curve.   The glass transition temperature is 77.5°C. and is essentially unchanged in the repeat run after cooling.   The results with a fresh room temperature mix with 10 phr of butyl benzyl phthalate plasticizer are shown in the middle set of curves.   In the initial determination (solid line) the T_g is lowered only a small amount below that of the unplasticized polymer. After heating to above 100°C. and quick chilling, the T_g is much lower (42°C.) and with the second repeat after slow cooling the T_g is 46°C.

Finally a similar 10 phr blend with plasticizer was dry-blended in an open mixer to above 100°C., which is below the fusion temperature of the blend. The DTA curves for this dry blend are shown in the lower section of Figure 14.   The initial run resulted in a T_g at 50.5°C. and reruns after quick chilling and slow cooling are essentially the same.

These results correlate with the information presented concerning irregularities found in processing fresh, aged, and dry blends of the Exon 965 polymer in the Plasti-Corder.   Mixtures of plasticizer and polymer remain essentially mixtures over storage periods up to three months at room temperature, whereas heated blends (dry or fused) have a definite and lower T_g proportional to the amount of plasticizer used.

Similar results were obtained with all the homopolymers and copolymers examined. Fusion of the plasticized blends on the mill, in the extruder, and in the laboratory press resulted in similar lowering of the glass transition temperatures. Space does not permit presentation of these results. A long time (years) investigation of the storage effects on T_g as measured by DTA for PVC polymers is in progress.

Finally, as previously discussed, the same "tail" which has been considered to be evidence for crystallinity appears on certain of these DTA
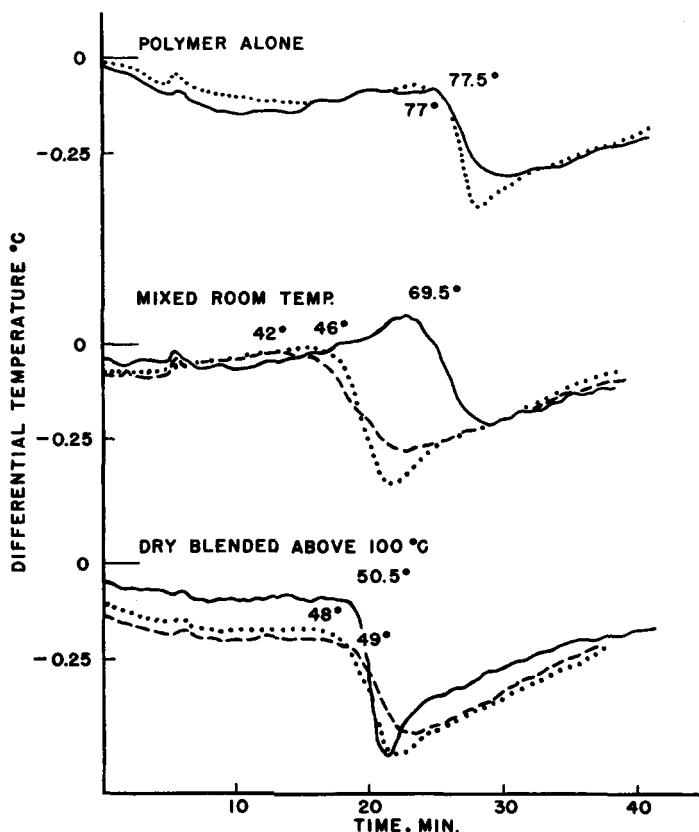

Fig. 14. DTA evaluation of mixing vs. dry blending for Opalon 610 with 10 phr plasticizer: (——) initial run; (—) rerun after quench chill; (···) rerun after slow cool.

curves for Opalon 610 and blends shown in Figure 14. In each case quick chilling produces an amorphous type curve, and slow cooling, the tail. It appears then from these curves that the raw polymer, Opalon 610, as received, is essentially amorphous whereas the copolymer, Exon 487 as received, is partially crystalline. Presumably, the amorphous or crystalline nature of the raw polymer depends on whether slow or rapid cooling through the glass transition temperature occurs in the last step in manufacture of commercial polymers.

III. DISCUSSION

Thermoplastic polymers, of which poly(vinyl chloride) is typical, have certain physical properties in common. At high temperature they are viscoelastic liquids, at intermediate temperatures they have rubberlike properties, and at lower temperatures they are brittle or glasslike solids. The temperature at which the polymer changes from the glass to rubber state is known as the glass transition temperature. As shown in the data of Table V, the glass transition temperatures of commercial poly(vinyl chloride) homopolymers and copolymers are above room temperature. However, the addition of plasticizers lowers the glass transition temperature below room temperature (Table VI). Thus, in normal use conditions poly(vinyl chloride) compositions are in their tough rubbery physical state. It appears reasonable to conclude that the practical usefulness of products manufactured from poly(vinyl chloride) polymers correlate with the temperature range of this glass transition, and that working properties during manufacture correlate with the ease by which PVC compositions are changed to viscoelastic liquids by heating.

There is a high degree of correlation between the intrinsic viscosity number determined for poly(vinyl chloride) polymers as measured in dilute solutions and the melt viscosities of high temperature melts of plasticized blends of these polymers as determined in the Plasti-Corder. This is a very useful result. It confirms the general custom of classifying PVC polymers by their specific viscosities from solution.

IV. CONCLUSIONS

The data from evaluation of the processing of a large number of commercial poly(vinyl chloride) polymers and copolymers with the Brabender Plasti-Corder and from differential thermal analysis are completely consistent. The physical property of the glass transition of poly(vinyl chloride) polymers and copolymers and their plasticized blends is an important factor in the behavior of these polymers on processing either in mixing equipment or in dry blending procedures. Melt viscosities determined as Plasti-Corder readings for plasticized blends are proportional to the molecular weights of the polymers as calculated from specific viscosities. However, the acetate content of the copolymer reduces the melt viscosity and glass transition temperature, as the comonomer acts as an internal plasticizer although it does not affect the measurement of solution viscosity from which molecular weight is calculated.

In the measurement of the glass transition temperature by differential thermal analysis there is a difference between annealed and quickly cooled samples which it is suggested is evidence for a small amount of crystallinity in both homopolymer and copolymer and in their plasticized blends.

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Résumé

Seize polymères de chlorure de polyvinyle commerciaux ainsi que des copolymères d'acétate de polyvinyle ont été étudiés afin d'établir des corrélations entre les processus de fabrication caractéristiques et les propriétés physiques mesurables. La transformation a été évaluée à l'aide du Plasti-Corder de Brabender. La température de transition vitreuse et le procédé de "mélange à sec" ont été examinés par analyse thermique différentielle. Les polymères contiennent des matériaux de poids moléculaire bas et élevé et sont le résultat de méthodes de polymérisation en suspension, en émulsion et en solution. Les effets dus à la quantité de plastifiant, de stabilisateur et d'autres additifs ont été mesurés et discutés.

Zusammenfassung

Sechzehn handelsübliche Polyvinylchloridpolymere und Acetatcopolymere wurden in Bezug auf Korrelationen zwischen der Verteilungscharakteristik und messbaren physikalischen Eigenschaften untersucht. Die Verteilungcharakteristik wurde mit dem Brabender Plasticorder ermittelt. Die Glasumwandlungstemperatur und das "Trockenmisch"-Verfahren wurden durch Differentialthermoanalyse überprüft. Es wurden hoch- und niedermolekulare Polymere untersucht, die nach Suspensions-, Emulsions- und Lösungspolymerisationsmethoden erhalten worden waren. Die Einflüsse der Weichmachermenge, von Stabilisatoren und anderen Zusätzen wurden gemessen und werden diskutiert.