Plasticizer Diffusion as the Rate-Determining Step in Dry Blending of Poly(vinyl Chloride)

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Synopsis

Differential thermal analysis has been used to examine the process of dry blending of plasticizer and PVC. The rate of transformation of the glass transition from that of the polymer initially in the cold mix to the glass transition of the blend (blend T_g) has been examined at various temperatures from room temperature to above the polymer T_g. The dependence on temperature of this rate of transformation of the observed T_g is similar to the temperature dependence of the diffusion of plasticizer into PVC. It is concluded that diffusion of plasticizer into polymer particles is the rate-determining step in the dry blending of PVC. It also appears that a single mechanism of diffusion is involved both below and above the glass transition of the polymer.

Introduction

In recent years the development of the use of extruders for processing PVC has been accompanied by the production by resin manufacturers of modified grades of PVC polymers. Since the process of dry blending of plasticizer and polymer has been widely adopted as the initial stage preceding the extruder, these grades of PVC polymer have been designated as "dry-blend" resins in contrast to previous calendering grades of resin. The dependence of this dry-blending process on the parameters of size, shape, and surface area of polymer particles was discussed in detail by Park[1] in 1957 and again by Carleton and Mischuk[2] in 1964. Both papers emphasize the importance of time and temperature in the procedure of dry blending. In a previous publication[3] the relation of the dry-blending process to the glass transition of the polymer has been discussed. Information obtained from differential thermal analysis (DTA) will be presented, indicating that diffusion of plasticizer into polymer particles is the time controlling variable in the process. Also, it will be shown that as a result of temperature increase during the dry blending the resulting dry blend prepared for the extruder has undergone a phase change which has not occurred in the cold mix prepared for charge to the Banbury or other mixers preceding the calender.

Since the initial measurements of Clash et al.,[4] it has been recognized that plasticized PVC has a glass transition lower than that of the original poly-

mer.   This glass transition of the plasticized product occurs at a unique temperature related to the amount of plasticizer in the blend just as the melting point temperature of an alloy is related to the alloy composition. It has not been as clearly recognized that in production of the dry blend of a PVC polymer and plasticizer that this change from the polymer T_g to the lower T_g of the plasticized blend is an essential characteristic in the nature of the dry blend particle, distinguishing it from the cold preblend type particle.   The efficiency with which this change has been produced uniformly through the dry blend defines its quality.*   In this paper the glass transition temperature of the dry blend is referred to as the blend T_g. Essentially the dry blend and the usual plasticized PVC are identical phase systems differing only in that the dry blend is a loose aggregate of plasticized particles, whereas plasticized PVC is generally obtained as a continuous film or extruded mass.

Butylbenzyl phthalate has been used as plasticizer in this evaluation. Comparable results have been observed with DOP plasticizer which differ only in the time factor due to the slower diffusion rate of DOP. Clash[4] reported small differences in the T_g of plasticized PVC associated with different plasticizers.   Kikkawa[5] reports the diffusion coefficients for several common plasticizers and Touchette et al.[6] observed the variation of fusion rates in the processing of PVC with many plasticizers.   All manufacturers of plasticizers supply information on the relative efficiencies of their plasticizers.

Preliminary Examination of the Glass Transition
(Dry Blend versus Calendering Type PVC Resins)

There is considerable difference in behavior during processing between extreme examples of dry blend PVC resins as developed for the extruder and some of the earlier calendering grade resins, although both are classified as general-purpose resins.   It seemed desirable to establish that these differences do not also involve a difference in character of the glass transition as well as the differences in particle geometry described by both Park and Carleton.   Park defines the dry blend type as lower in surface area and of greater absorptive quality correlated with larger discrete particles and higher bulk density.   His calendering grade is higher in surface area and smaller in particle size with low bulk density.   Three commercial polymers within each type and of differing molecular weight were selected. However, in present commercial usage there is no clear dividing line between these classes, both being designated as general-purpose resins, and an experienced processor can handle all but the extremes of either group in either the extruder or the calender.

* This same decrease in temperature level of the glass transition occurs in the preparation of PVC plastisols in which case the fineness of polymer particle confines it to a shorter time period.   In the plastisol, gelation occurs in the transition from a plasticizer–polymer mixture to a plasticized blend and includes the change from T_g of the polymer to the blend T_g in the same manner as discussed here for the dry blend.

TABLE I

DTA Determination of Glass Transition Temperature of PVC Blends
(Dry Blend versus Calendering Type Commercial PVC Polymers)

T_g for plasticized blends, °C.

| Polymer type	T_g polymer, °C.	20 phr plasticizer				30 phr plasticizer				50 phr plasticizer			
		Cold mix		Heated mix		Cold mix		Heated mix		Cold mix		Heated mix	
		Initial	Rerun	Initial	Rerun	Initial	Rerun	Initial	Rerun	Initial	Rerun	Initial	Rerun
Dry blend													
Exon 965	74	72	20	25	26	73	7	6	8	74	−21	−17	−15
Escambia 3185	78	70	26	26	25	72	16	11	12	72	−19	−23	−21
Escambia 2250	81	73	28	30	30	74	20	16	16	76	−20	−22	−19
Calendering													
Exon 945	79	73	28	32	30	74	6	8	10	74	−15	−22	−16
Exon 924	79	79	27	31	25	76	21	6	8	82	−19	−21	−18
Geon 101	83	76	28	26	32	75	20	18	15	76	−16	−18	−22
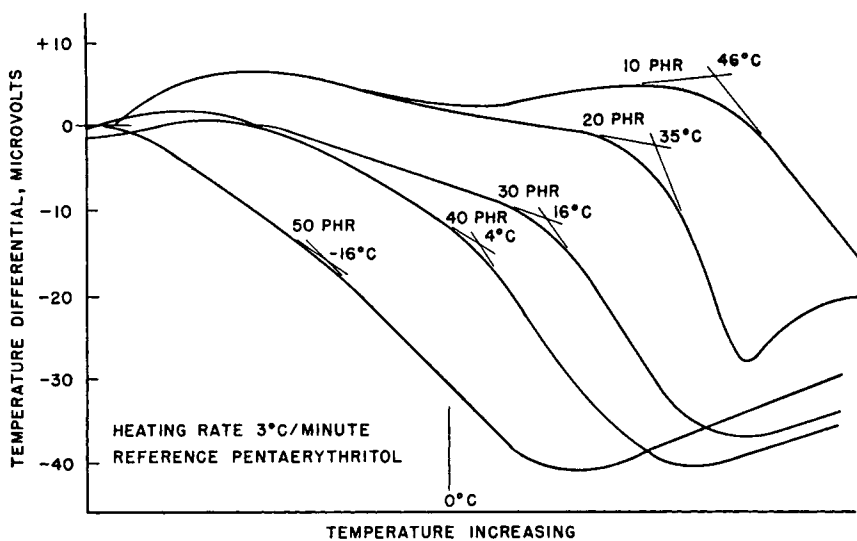
Fig. 1.   Effect of plasticizer level on determination of blend T_g.   DTA evaluation for
PVC polymer Geon 101 EP.

Blends of each polymer were prepared by mixing in the low-speed bowl-
type mixer at room temperature (cold mix) and by dry blend procedure
in the high-speed Henschel mixer with heating to above 100°C. (heated
mix).   Blends at 20, 30, and 50 phr plasticizer were prepared.   The results
are presented in Table I.   In each case the initial glass temperature was
determined, and without removal from the cell after reaching a temperature
of 120°C. the whole was rapidly chilled to −50°C. and the DTA curve
rerun to obtain the blend T_g.

In all cases, irrespective of polymer type, the cold mix has a high T_g
and the heated mix has the lower blend T_g during the initial DTA run.
Both show the blend T_g on the rerun.   There is then no behavioral dif-
ference between the two classes of polymers with respect to reduction of
glass transition temperature during plasticization.   During the usual
heating in production of a dry blend the glass transition of the mixture is
changed, but this is not an exclusive peculiarity of the dry blend polymer.

The relation of the temperature of the blend T_g to the ratio of plasticizer
to polymer is also clearly evident in the data of Table I.   Furthermore, the
determination of the blend T_g by DTA becomes increasingly less precise
as the amount of plasticizer is increased (Fig. 1).   This is not a new obser-
vation.   The same decrease in sharpness of the glass transition and other
physical property changes was observed with other methods of measurement
of plasticized PVC blends.[7-11]

Experimental Procedure

Three of the blends prepared in December 1963 for the previous study[3]
and stored at room temperature were re-examined after 16–18 months.

TABLE II
Effect of Aging on Glass Transition of Plasticized PVC Blend

Polymer	Plasticizer, phr	Preparation temp., °C.	Physical appearance		Glass transition temperature T_g, °C.			
					Freshly prepared		After storage (18 months)	
			When prepared	After storage	Initial	Rerun	Initial	Rerun
Opalon 610	20	100	Dry	Same	27		31	26
Opalon 610	20	25	Soft, will compact	Same	69	15	72	17
Exon 487	10	25	Gummy	Dry	53	24	68	34

The results obtained are shown in Table II. There was no appreciable change in the molecular state of these blends so far as the DTA evaluation showed. The blend heated to 100°C.,that is, above the glass transition of the polymer, continues to have the low T_g of 20–30°C. expected for a 20 phr plasticized blend of PVC. The two blends prepared at room temperature continue to show after 18 months essentially the T_g of this PVC polymer and only after heating *in situ* do the reruns show the reduced blend T_g. Thus, either it is necessary to heat the mixture above the T_g of the polymer to transform to a true dry blend or the rate of diffusion of plasticizer is remarkably slow at room temperature.

For the detailed time study, blends of PVC polymer with 20 phr plasticizer butylbenzyl phthalate and 5 phr Ba-Cd laurate stabilizer were prepared at room temperature by mixing in a bowl-type mixer at relatively low speed with no temperature increase. Commercial polymers were used: Opalon (Monsanto Chemical Company), Exon (Firestone Plastics Company), Escambia (Escambia Chemical Company), Geon (B. F. Goodrich Chemical Company), the plasticizer was butylbenzyl phthalate, Santicizer 160 (Monsanto Chemical Company). Portions of this blend in glass bottles were placed in controlled temperature ovens. Samples were removed at successive time intervals and a differential thermal analysis (DTA) made in the equipment used in the previous publications[3] and similar to that described by Keavney and Eberlin.[12] In the present studies, pentaerythritol has been used as the reference material, since it has proved to be closely similar to granular PVC polymer in heat conductivity and specific heat change and has the advantage over the more usual isophthalic acid, that it does not absorb moisture from the atmosphere. In all of the present studies the equipment has been cooled below freezing and usually to −30°C. prior to each measured DTA curve. This is necessary in order to obtain a flat or regular baseline before the transition temperature of the plasticized blends.

The rate of temperature increase was 2.8°C./min. throughout this study. The oven temperatures selected were 25, 46, 49, 60, 70, 82, and 100°C., extending from room temperature to above the glass transition temperature of the polymer.

DTA Curve of Glass Transition in Plasticized PVC

The differential thermal analysis is not an equilibrium procedure; temperature of the environment is being increased at a regular rate. However, with calibrated equipment, quantitative results beyond the requirements of the present glass transition measurements are possible.[13,14] Typical curves are shown in Figure 2. The potential energy differences of the two thermocouples (sample versus reference) in microvolts is plotted against time or increasing temperature as shown. The upper curve illustrates the normal glass transition (T_g) for granular PVC polymer, in this case 82°C. for Opalon 630. The glass transition is endothermic and requires time for completion. The DTA curve of a 20 phr blend of butylbenzyl phthalate
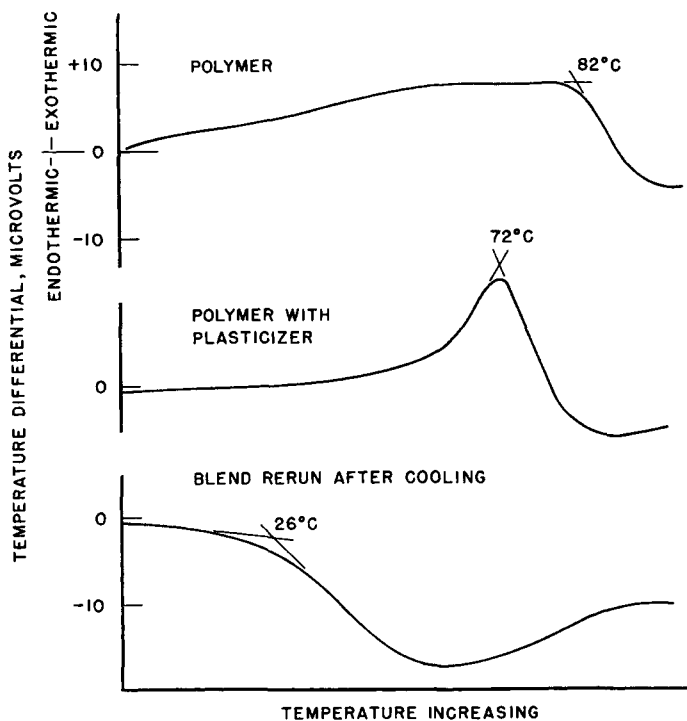
Fig. 2. Characteristic DTA curves for PVC polymer (Opalon 630) with and without 20 phr butylbenzyl phthalate plasticizer.

plasticizer with the same PVC mixed at room temperature immediately prior to the analysis is shown in the middle curve.   There is an exothermic drift followed by the glass transition endotherm at 73°C., about 10°C. lower than that of the polymer alone.   Such a minor shift in the polymer T_g immediately on mixing has been observed for many PVC blends and will be discussed.   If the heating of this plasticized blend in the DTA equipment is stopped at 120°C., the entire unit quickly cooled with Dry Ice to -30°C., and the DTA repeated, the lower curve in Figure 2 is obtained.   The glass transition endotherm appears at 26°C. and is less sharp.   Note that there is now no evidence of an endotherm in the 72–82°C. range of the T_g of this polymer alone.

Experimental Results

At each oven temperature a series of DTA curves was obtained after successively longer time intervals, as shown in Figure 3, for a blend of Opalon 630 with 20 phr plasticizer heated at 60°C.   The residual peak for the unplasticized polymer fraction appears in all early curves, becoming successively lower until it disappears after more than 1 day at 60°C.   At the same time a second, lower-temperature endotherm appears at 3 hr. and in each sampling thereafter, stabilizing for this 20 phr blend at about
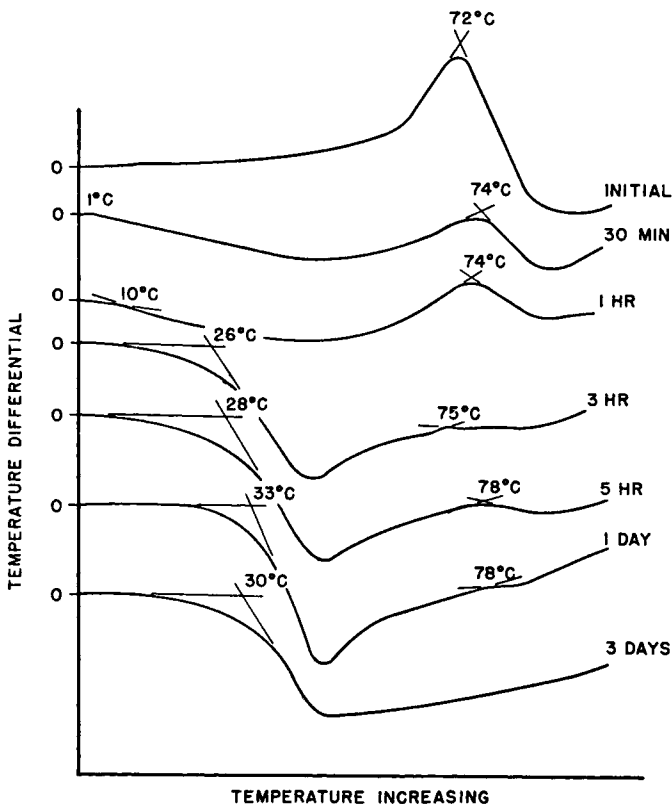
Fig. 3.   Time factor in development of blend T_g for mixture of PVC (Opalon 630) with 20 phr plasticizer at 60°C.

30°C.   Similar data, but for the lower oven soaking temperature of 46°C. are presented in Figure 4.   Here, whereas at the 60°C. heating temperature the residual polymer transition had disappeared after 3 days, at the 46°C. heating temperature for the same time period a considerable 73°C. peak and endotherm remain.   This endotherm decreases with additional time, but even at $6\frac{1}{2}$ months a small residual peak is present.   Again, a second, lower-temperature endotherm appears at 6°C. after 1 month, 22°C. after 3 months and 29°C. after $6\frac{1}{2}$ months.   The complete data at all six soaking temperatures are given in Table III.   At 70°C. the residual endotherm of the polymer disappears after one hour, decreasing regularly from a maximum of 11 μv. for the 5-min. sample (Table III).   At this temperature the lower temperature or blend endotherm appears after 15 min.   At 82 and 100°C. the polymer endotherm is negligible at 10 min. and disappears completely after 30 min.

Three additional PVC polymers were examined with the data summarized in Table IV.   The section of the table which lists the T_g of the polymer endotherm is omitted for sake of brevity, since its value is unchanging and

TABLE III
Time Factor in Elimination of Polymer T_g and Development of Blend T_g
(Blend PVC Opalon 630 with 20 phr Plasticizer)

Time	T_g of polymer endotherm, °C.						Height of polymer endotherm, μv.						T_g of blend endotherm, °C.					
	ST = 100°C[a]	ST = 82°C	ST = 70°C	ST = 60°C	ST = 49°C	ST = 46°C	ST = 100°C	ST = 82°C	ST = 70°C	ST = 60°C	ST = 49°C	ST = 46°C	ST = 100°C	ST = 82°C	ST = 70°C	ST = 60°C	ST = 49°C	ST = 46°C
5 min.	79	75	73				1	3	11				29	28	—			
10 min.		80	74					1	6					33	—			
15 min.	86	86	76				1	1	5				34	32	28			
20 min.			76						3						29			
30 min.	—	—	78	74					3	6			34	32	32	1		
45 min.	—	—	81						1				36	33	34			
1 hr.	—	—	—	74						4			35	35	30	—		
3 hr.	—		—	75						1			36		32	26		
5 hr.		—	—	78	74	72				1	10	15		34	34	28	—	
1 day				78	76	72				1	5	13			37	33	4	
3 days				—	76	73					1	11			30	30	14	
1 week					75	74					1	5					19	
1 month					74	74					1	3					22	6
3 months					72	74					2	3					32	22
6.5 months					76	73					1	3					34	29

[a] ST = soaking temperature.

TABLE IV

Time Factor in Elimination of Polymer T_g and Development of Blend T_g

Blend	Time	Height of polymer endotherm, μv.							T_g of blend endotherm						
		ST[a] = 100°C	ST = 82°C	ST = 70°C	ST = 60°C	ST = 49°C	ST = 46°C	ST = 25°C	ST = 100°C	ST = 82°C	ST = 70°C	ST = 60°C	ST = 49°C	ST = 46°C	ST = 25°C
Blend PVC Geon 101 with 20 phr plasticizer	1 hr.	—	—	—	8				36	35	35	13			—
	2 hr.	—	—						33	36					
	3 hr.		—		2	16	20				37	32	—		
	5 hr.		—	—	1	17	16			33	37	35	—	—	
	1 day					10					37	36		—	
	2 days			—							38				
	3 days				—	5	15					37	5	—	—
	1 week				—	2	14	18				38	20	—	—
	1 month				—	1	4					37	31	2	—
	3 months				—	2	4	20				36	33	15	—
	11 months							23							—
Blend PVC Exon 965 with 20 phr plasticizer	1 hr.	—	—				11		30	27	21	25			—
	5 hr.	—	—				8		29	32	27	28			—
	1 day				1	3				32	31	24	−2	−7	
	3 days				—	2	4					26	5	−5	
	5 days				—	2	4					29	9	3	
	1 week				1	2	3					29	16	9	
	1 month				1	1	2	14				28	25	20	
	3 months				1	1	2						28		
	7 months				1	1		15					26		
Blend PVC Escambia 3185 with 20 phr plasticizer	1 hr.	—	—	1	8				34	34	26	4			—
	2 hr.	—	—						32	32					—
	3 hr.			—	2	10					29	18			
	5 hr.			—	1	9	17			34	33	22	—	—	

	Height of polymer endotherm, μv.							T_g of blend endotherm, °C.						
	ST = 100°C	ST = 82°C	ST = 70°C	ST = 60°C	ST = 49°C	ST = 46°C	ST = 25°C	ST = 100°C	ST = 82°C	ST = 70°C	ST = 60°C	ST = 49°C	ST = 46°C	ST = 25°C
1 day	—	—	—	—	11	4	—			35	33	32	4	—
2 days					7	2					35	34	5	-1
3 days					6	1					35	34	21	2
1 week					1	1					34	34	24	2
1 month					3	1	2				34	34	33	21
3 months					2		2					35	34	26

a ST = soaking temperature.

TABLE V

Time Factor in Elimination of Polymer T_g and Development of Blend T_g (Blend Copolymer Exon 487 with 20 phr Plasticizer)

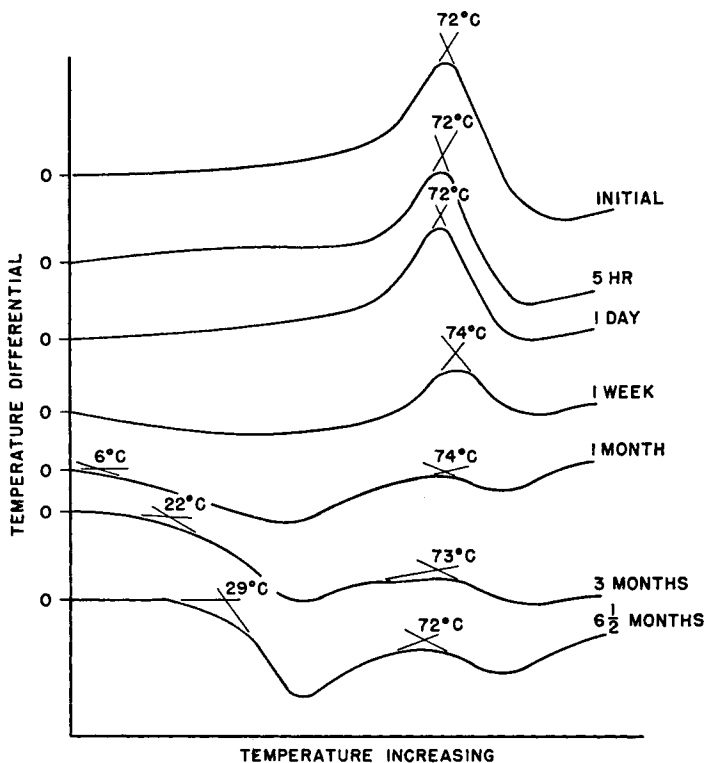|	Height of polymer endotherm, μv.							T_g of blend endotherm, °C.						
	ST = 100°C,a	ST = 82°C	ST = 70°C	ST = 60°C	ST = 49°C	ST = 46°C	ST = 25°C	ST = 100°C	ST = 82°C	ST = 70°C	ST = 60°C	ST = 49°C	ST = 46°C	ST = 25°C
1 hr.	—	—	2	9				27	20	11	4			
2 hr.		—							24					
3 hr.					10							4		
5 hr.			—	4					29	25	13			
1 day			—	1	7	7				30	23	14	9	
2 days				1	5	7					26	17	14	
5 days				—							30			
1 week					4	5						20	18	
3 weeks					2							28		
1 month					2	5	12					26	24	—
3 months					1	3	12					30	28	-1
7 months					1	2						32	29	

a ST = soaking temperature.

Fig. 4. Time factor in development of blend T_g in mixture of PVC (Opalon 630) with 20 phr plasticizer at 46°C.

its presence is indicated by a value for the height of the endotherm in microvolts. Geon 101 represents a high molecular weight finely powdered general-purpose PVC. Exon 965 was selected as a low molecular weight PVC with coarser aggregate type particles. Escambia 3185 was selected as an average molecular weight PVC typical of the dry blending type. In all the PVC polymer–plasticizer blends two changes are evident in the DTA curves: the height of the polymer T_g endotherm decreases and disappears as the temperature of the blend T_g increases and reaches a maximum.

The initial study referred to in Table II included the PVC copolymer Exon 487. A detailed time–temperature study of 20 phr plasticizer blends

TABLE VI
Temperature Dependence of Rate of Change in Glass Temperature
(Blend Exon 487 with 20 phr Plasticizer)

Temperature, °C.	Time to develop blend T_g
100	1 hr.
82	5 hr.
70	1 day
60	5 days
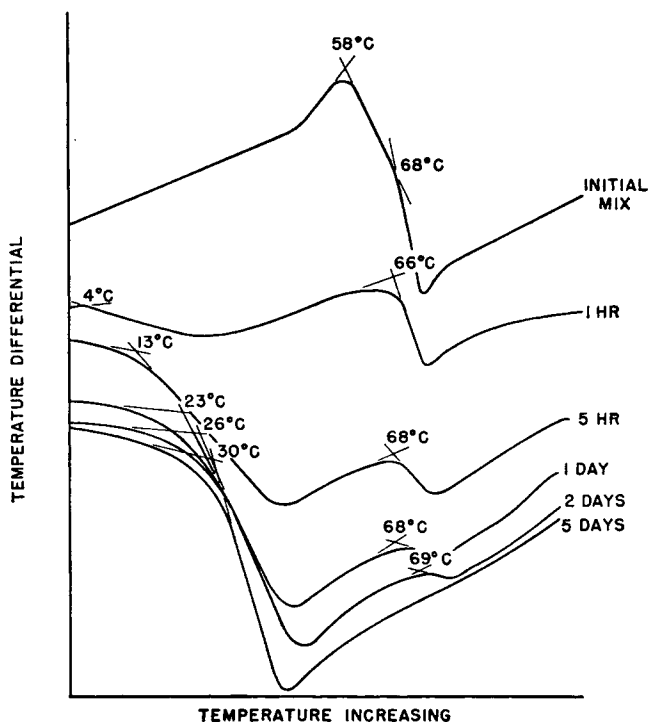
Fig. 5. Time factor in development of blend T_g in mixture of PVC copolymer (Exon 487) with 20 phr plasticizer at 60°C.

of this copolymer has also been completed and the DTA curves after various time periods in an oven at 60°C. are shown in Figure 5.   This granular copolymer without plasticizer has a T_g of 69°C.   The data for seven soaking temperatures are presented in Table V and are entirely similar to the results previously obtained with the homopolymers.   These data were examined on the assumption that diffusion of plasticizer into the solid particles of polymer is the time-controlling step in the elimination from the DTA curve of the inflection due to the polymer T_g and the appearance of an inflection at a lower temperature due to the blend T_g (Table VI).   When these time data are plotted as the log of time against the reciprocal of temperature ($\log t$ versus $1/T$) a straight line is obtained (Fig. 6).   Three values coincide with the straight line and only that at 100°C. fails to agree. The selection of 1 hr. for the short time sample was arbitrary, and apparently measurements should have been made at shorter time periods to obtain the true limiting diffusion time at this temperature.   Furthermore, extrapolation of the straight line to room temperature (25°C.) gives a diffusion time of 4 yr., 30 weeks.   This explains the information obtained with the original room temperature blends (Table II) in which no apparent diffusion appeared to have occurred in 16–18 months.   The rate of diffusion of plasticizer is indeed extremely slow at room temperature.   These

results correlate well with similar calculations of the direct diffusion rates
measured by Grotz,[15] in which he obtained even slower diffusion rates for
the initial phase of diffusion of DOP plasticizer into the higher molecular
weight PVC polymer which he used.   In our laboratory J. T. Bergen[16]
has made a supporting calculation using the time periods from the data of
Table III with Opalon 630 polymer.   Assuming spherical particles and
that Fick's equation with constant diffusion coefficient D is followed
throughout this step of development of the blend T_g and using Grotz's
value for D, he has calculated the average diameter of particle.   The value
he obtained is 150 μ, which compares favorably with the manufacturer's
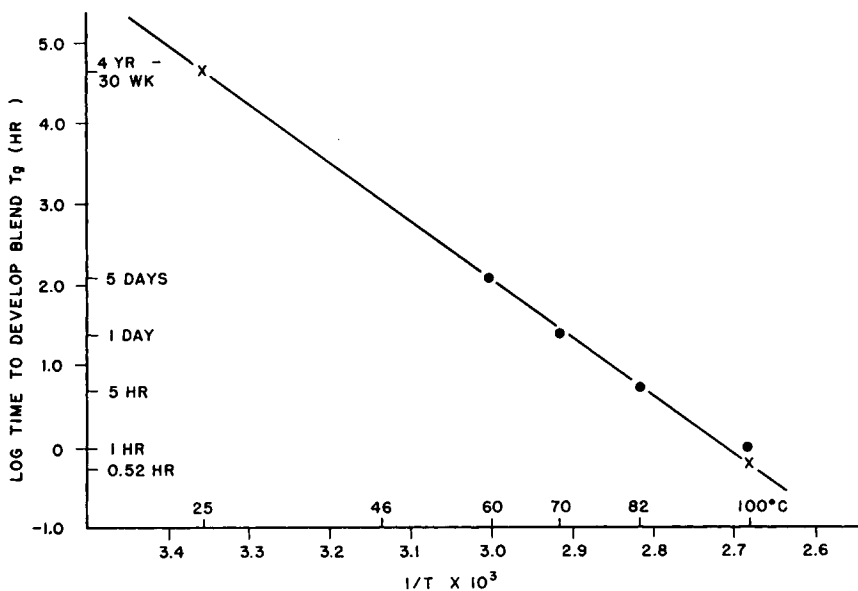
Fig. 6.   Temperature dependence of time required to develop blend T_g in mixture of
PVC copolymer (Exon 487) with 20 phr plasticizer.

value of particle size range (75–400 μ) for this commercial polymer.   In
view of the facts that there is a wide distribution of particle size and per-
haps shape, that only 20 phr plasticizer was available, and that the larger
particles are those which are last to be completely plasticized, this is indeed
very good agreement.

Temperatures above the glass temperature of the PVC polymer were
included in this study in the hope of determining whether the process of
diffusion is continuous through the glass transition and it appears that it is.
The fact that the data of Figure 6, plot of log t versus $1/T$, are linear, be-
tween 60 and 82°C. for the copolymer with a glass transition of 69°C. is
certainly indicative of a single type of mechanism.

Discussion

Commercial PVC in the solid state at room temperature is considered to be a mixture of polymer molecules of widely varying chain lengths with the chains randomly intermingled, including possibly an irregular amount of coiled chains. When heated at the glass transition temperature (T_g) the polymer chain backbone (including coiled areas) relaxes, as is evidenced by an observed increase in volume. This abrupt change in volume was one of the early methods of determination of T_g.[4] An increase in volume is also observed in the dry blending procedure of adding plasticizer to polymer, and is often referred to as the "fluff point temperature" or "dry point temperature."

When plasticizer is mixed with granular particles of many sizes it first becomes mechanically dispersed over the surface of the particle. At room temperature, diffusion into the particle is extremely slow. However, the very fine particles and surface layers of larger particles are associated with an excess of plasticizer which creates the gummy and compacting property of the cold preblending product discussed by Carleton and Mishuck. Thus, in the present experiments at each oven temperature the first blend T_g observed is low (Fig. 4). This temperature is the blend T_g of a much higher ratio of plasticizer and polymer than that of the composition as a whole. Only with time, and as diffusion proceeds to equilibrium, does the blend T_g reach the T_g of the composition containing 20 phr plasticizer. The dry blend differs from the cold blend in that heating during its preparation increases the rate of diffusion of plasticizer into the polymer particle. Thus, dry blending when properly done results in the elimination of an inflection at the glass transition of the polymer and the production of a uniformly plasticized PVC which has a lower and unique blend T_g, and, of course, with the attendant easier and more uniform processing quality.

In the initial stage within the DTA cell, as the temperature increases the rate of diffusion naturally increases. However, at 2.8°C./min. the glass temperature of the polymer is approached before diffusion can be complete within the larger particles. The plasticizer on the surface diffuses between the polymer chains permitting relaxation (swelling) at the surface first, and then completely through more and more of the fine particles. Presumably then, this surface swelling produces a closer packing between polymer particles and increased mobility of the polymer chains which then result in a greater heat conduction rate to the thermocouple within this sample cell as compared to the thermocouple in the reference cell. The result registers as an exothermic trace on the chart (Figure 2, middle curve). Very quickly, however, the bulk of the polymer approaches the glass transition temperature, and the energy absorption in this physical change produces an endothermic trace on the chart. It is interesting that this inflection temperature of the endotherm is generally less than the T_g of the polymer and drifts upward as diffusion continues at each temperature (Fig. 3 and Table III). This may represent a rough averaging due to variable particle size and amount of available plasticizer. However, it

could be an indication that the center portion of the larger particles consist of higher molecular weight fractions formed during the initial stage of polymerization.

Conclusions

The differential thermal analysis procedure is useful in examination of the changes occurring during the blending of plasticizer and granular polymer. The dry blend product differs from the cold blend product in possessing a lower glass transition temperature which is specific and dependent only on the T_g of the original polymer and the ratio of plasticizer present. The rate-determining process in dry blending is the diffusion of plasticizer within the polymer particle which is shown by a downward shift of the glass transition temperature from that of the polymer to that of the blend with the change accelerating as the temperature of mixing is increased. This diffusion process has a high temperature coefficient between room temperature and the usual blending temperature of about 100°C. The variation with temperature of the time for completion of the phase change from polymer T_g to the blend T_g (plot of log t versus $1/T$) is linear and is considered to be evidence that the mechanism of diffusion of plasticizer into PVC is the same below and above the glass transition of the polymer.

References

1. R. A. Park, Bulletin, Firestone Plastics Company, Pottstown, Pa.; paper presented to the 7th Annual Symposium Technical Progress in Communications Wires and Cables, December 3, 1958; *Wire Products*, **34**, 1123 (1959).

2. L. T. Carleton and E. Mishuck, *J. Appl. Polymer Sci.*, **8**, 1221 (1964).

3. P. V. McKinney, *J. Appl. Polymer Sci.*, **9**, 3359 (1965).

4. R. F. Clash, Jr. and L. M. Rynkiewicz, *Ind. Eng. Chem.*, **36**, 279 (1944).

5. M. Kikkawa, *Kobunshi Kagaku*, **14**, 636 (1957).

6. N. W. Touchette, H. J. Seppala, and J. R. Darby, *Plastics Technol.*, **10**, 33 (July 1964).

7. J. M. Davies, R. F. Miller, and W. F. Busse, *J. Am. Chem. Soc.*, **63**, 361 (1941).

8. L. E. Nielsen, R. Buchdahl, and R. Levreault, *J. Appl. Phys.*, **21**, 607 (1950).

9. T. Gast, *Kunststoffe*, **43**, 15 (1953).

10. F. P. Reding, E. R. Walter, and F. J. Welch, *J. Polymer Sci.*, **56**, 225 (1962).

11. P. Heydeman and A. Zosel, *Acustica*, **12**, 360 (1962).

12. J. J. Keavney and E. C. Eberlin, *J. Appl. Polymer Sci.*, **3**, 47 (1960).

13. M. L. Dannis, *J. Appl. Polymer Sci.*, **7**, 231 (1963).

14. S. Strella, *J. Appl. Polymer Sci.*, **7**, 569 (1963).

15. L. C. Grotz, *J. Appl. Polymer Sci.*, **9**, 207 (1965).

16. J. T. Bergen, in *Rheology Theory and Application*, Vol. IV, F. R. Eirich, Ed., Academic Press, New York, 1967 (in press).

Résumé

L'analyse thermique différentielle a été utilisée pour examiner le processus de mélange à sec de plastifiants et de PVC. La vitesse de transformation de la transition vitreuse de celle du polymère initialement présent dans le mélange froid à la transition vitreuse du blend (T_g blend), a été examiné à différentes températures depuis la température de chambre jusque au-dessus de la température T_g. La dépendance de la température de cette vitesse de transformation de T_g observée est semblable à la dépendance thermique de la diffusion du plastifiant au sein du PVC. On en conlut que la diffusion du plastifiant au sein de particules polymériques est l'étape déterminante de vitesse dans le mélange à sec du PVC. Il semble ainsi qu'un seul mécanisme de diffusion soit inclu à la fois, endessous et au-dessus de la transition vitreuse du polymère.

Zusammenfassung

Der Prozess der Trockenmischung von Weichmacher und PVC wurde mittels Differentialthermoanalyse verfolgt. Die Geschwindigkeit der Überganges von der anfänglichen Glasumwandlung der Polymeren in der kalten Mischung zu der Glasumwandlung des Gemisches (Gemisch-T_g) wurde bei verschiedenen Temperaturen von der Raumtemperatur bis oberhalb von T_g des Polymeren gemessen. Die Temperaturabhängigkeit dieser Übergangsgeschwindigkeit des beobachteten T_g ist derjenigen der Diffusion von Weichmacher in PVC ähnlich. Es ergibt sich der Schluss, dass die Diffusion des Weichmachers in die Polymerteilchen der geschwindigkeitsbestimmende Schritt bei der Trockenmischung von PVC ist. Weiters scheint unterhalb und oberhalb der Glasumwandlungstemperatur des Polymeren ein einziger Diffusionsmechanismus beteiligt zu sein.