The Rate of Plasticizer Uptake by Suspension PVC

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Synopsis

A microscopic technique employing image analysis was developed to measure the rate of swell of suspension PVC particles in both excess and finite amounts of plasticizer at temperatures below the crystalline melting point. The rates of plasticizer uptake derived from these swell measurements were found to be dependent upon the concentration of plasticizer and the rate of heating. A high value for the activation energy for plasticizer uptake was observed (60–100 kcal/mol) in agreement with earlier work. Each resin was also characterized by a total capacity for plasticizer (TC) which was found to be dependent on the resin type, the plasticizer type, and the maximum temperature achieved. An expression was derived for the rate of plasticizer uptake in a Brabender powder mix experiment. In this case the dry time is controlled by a single rate up to the maximum capacity for plasticizer of the resin (G_{max}). Values of G_{max} and TC were found to correlate on a one-to-one basis when measured at the same temperature. In all the cases investigated the rate of plasticizer uptake in the Brabender was found to correspond to a rate derived from image analysis swell at a plasticizer level of 0.25 cc/g. This behavior was in apparent contradiction to the concentration dependence generally observed and was demonstrated to be due to the large thermal gradients which exist in the Brabender powder mix head during the experiment. This work illustrates that Brabender powder mix times may have no relationship to dry times in a high speed mixer where heating is both even and higher temperatures are achieved.

INTRODUCTION

For a PVC resin to find a ready market acceptance in flexible applications it must be able to absorb plasticizer rapidly in a dry blending operation. Dry blending consists of the mixing of resin, compounding ingredients, and plasticizer under conditions which yield a free flowing (dry) powder.

Dry blending is generally carried out in a high-speed mixer such as a Henschel®, although occasionally a ribbon blender is employed. The basic procedure employed in dry blending consists of heating while mixing. The process is characterized by a *dry time* or powder mix time (PMT) which is the time between the addition of plasticizer and the transformation of the mix from a wet and lumpy mass to a free-flowing powder.

Traditionally a test employing a Brabender torque rheometer such as ASTM (D2396)[1] has been employed to measure the ability of a resin to take up plasticizer in a dry blending operation. However, the results of such testing are not reported in terms of the rate of plasticizer uptake.

It is the purpose of this communication to demonstrate how a rate of plasticizer uptake can be derived from a Brabender torque rheometer measurement and to compare these rates with those derived from quantitative measurement of PVC particle swell during plasticizer uptake.

Measurements of the swell of individual PVC particles in excess plasticizer were first reported by Bargellini in 1964.[2] This author obtained photomicrographs as a function of time as the PVC particles were heated in the presence

TABLE I
Properties of Resins Used in This Study

Sample identification code no.	Intrinsic viscosity	Porosity p_i (cc/g)	Particle size (μm)	Remarks
M-9	1.007	0.339	149	
M-11	1.031	0.443	274	Skinless resin with high plasticizer absorption ability
CA	1.12[a]	0.443	—	
M-2	0.992	0.261	148	
A	1.03[a]	0.243	189	
B	1.02[a]	0.270	179	
C	1.01[a]	0.349	179	
D	1.00[a]	0.540	184	
E	1.00[a]	0.266	192	
F	1.00[a]	0.235	198	
G	1.00	0.267	—	
H	1.00[a]	0.320	189	
I	1.00[a]	0.238	195	
J	1.00[a]	0.238	197	

[a] Estimated from polymerization temperature.

of excess plasticizer and reported the results in terms of the % area increase of the particle as a function of temperature. With the development of television image analysis equipment, such measurements can be very easily made. However, for real utility the data must be analyzed in such a way as to obtain a meaningful rate of plasticizer uptake.

MATERIALS

All plasticizers used in this study were commercial grade. The plasticizers employed were dioctyl phthalate (DOP), diisodecyl phthalate (DIDP), ditridecyl phthalate (DTDP), Vicoflex 7170, an epoxidized soya oil, and blend 6373.

This latter blend is similar to a formulation employed in a commercial wire coating operation.

The PVC resins employed in this study consisted of both commercial and experimental types. These are listed in Table I. The values of intrinsic viscosity, porosity, and particle size are typical of resins used commercially in dry blending operations.

The internal porosity (p_i) was measured by methods outlined previously,[3] and the particle size was determined by sonic sifter (ATM Inc.).

EXPERIMENTAL

Rate of Plasticizer Uptake by Rate of Swell Measurement

The basic assumption in any attempt to measure the rate of plasticizer uptake by a quantitative measurement of particle swell upon plasticization is that the volume of plasticizer and PVC in a plasticizer-swollen PVC particle are additive. This assumption was checked by dilatometry and the shrinkage found to be about 0.01 cc/g when PVC particles were plasticized at 80°C. The dilatometers used

were capable of detecting changes in volume of about 0.0006 cc/g. Thus for the purposes of this study the volumes of plasticizer and PVC in plasticizer-swollen PVC particles can be considered as additive.

Consider a glassy particle of PVC of volume V_0 which swells in plasticizer to a volume V_f. The volume of plasticizer taken up is merely

$$V_f - V_0 = \text{vol uptake} \tag{1}$$

Dividing by the product of the density and the initial volume gives the take up in terms of volume of plasticizer/g resin:

$$\frac{V_f - V_0}{V_f \rho_{PVC}} = \left(\frac{V_f}{V_0} - 1\right)\frac{1}{\rho_{PVC}} = \frac{\text{vol uptake}}{\text{g resin}} \tag{2}$$

Equation (2) will hold for either a single glassy bead or for more than one. If the particle is porous and swells isotropically, then we can rewrite eq. (2) substituting for ρ_{PVC} the apparent particle density. This can be shown to be numerically equal to $(0.714 + p_i)^{-1}$, where p_i is the resin's internal porosity. In addition the volume of plasticizer contained initially in the unswollen particle must be added:

$$p_i + (V_f/V_0 - 1)(0.714 + p_i) = U \text{ (cc/g)} \tag{3}$$

Since volume is proportional to area to the 3/2 power, we can rewrite eq. (3):

$$p_i + [(A_f/A_0)^{3/2} - 1](0.714 + p_i) = U \text{ (cc/g)} \tag{4}$$

In practice the quantity $(A_t/A_0)^{3/2}$ is studied as a function of time by image analysis as the temperature is increased at a predetermined rate.

Image analysis experiments on the rate of swelling of suspension PVC resin in excess plasticizer were carried out using a Cambridge Imanco Model 720 Quantimet coupled to a Zeiss Universal microscope equipped with a Mettler F-P5 hotstage modified to permit the use of 2.5× Na 0.08 objective. The PVC resin under study was sprinkled on a microscope slide previously coated with a very thin ($\approx$10 μm) layer of epoxy, adhesive. After the epoxy had cured, a drop of plasticizer was placed on the resin particles and a rectangular cover slip was epoxy-sealed in place on three sides, the open end to extend out of the hot stage in order to allow plasticizer vapor to escape. The preparation was then placed in the preheated hot stage and allowed to reach equilibrium. The hot stage was then programmed to heat at the desired rate until the maximum temperature of the run was reached.

The preparation was viewed in bright field and the image analyzer set to measure total area. The output from the Quantimet was fed directly to a Hewlett-Packard 9810 calculator interfaced to a 9862A Hewlett-Packard plotter. Plots of $(A_t/A_0)^{3/2}$ vs. time [where A_t = total field area at time t and A_0 = total initial field area] were thus obtained directly during the course of the experiment.

Plasticizer uptake in dry blending operations is carried out using finite quantities of plasticizer.

The swelling behavior of PVC particles in a finite amount of plasticizer was investigated by the following techniques.

A known quantity of resin and plasticizer were thoroughly mixed together on a metal plate using a spatula. A melting point capillary was then dropped into

the mixture and filled to a depth of ≈6 mm. The end of the tube containing the resin is pressed against the finger and a *microbolus* is formed by compressing the resin in the capillary by means of a close fitting piston. All but about 2 mm of the *microbolus* is extruded from the melting point capillary by means of the piston, and the end of the remaining *microbolus* is carefully squared against a smooth metal surface.

The ≈2 mm section remaining in the capillary is extruded on to a cover slip previously positioned in the hotstage. Plots of swell volume $[(A_f/A_0)^{3/2}]$ vs. time are then obtained as before. It has been found that a microbolus formed in the above manner will swell isotropically during the plasticizer uptake process. Curves *identical* in shape to those of particles swollen in excess plasticizer were obtained.

As a check of the microbolus swell method, the pores of resin samples were filled with DOP and the excess removed by centrifugation by a technique described previously.[3]

Resin samples so filled with DOP were spread on a microscope slide, and the rate of swelling of these samples was found to be comparable with the rates derived from microbolus swell measurements at similar concentrations.

In Figure 1 we see typical swell curves of the type observed when PVC particles are swollen in excess plasticizer. Note that there is a linear region which characterizes the rate of plasticizer uptake and a plateau which characterizes the maximum uptake of plasticizer by the resin (TC). Similar shaped curves have been obtained by Wingrave using a gravemetric technique.[4] The plateau is consistent with the well-accepted view that PVC contains unsolvated crystalline regions which act as crosslinks and allow the PVC to accept large amounts of plasticizer and still exhibit a rubbery behavior over a wide temperature range.[5–8] The rate of plasticizer uptake (R_p) *by the particle* is given by

$$R_p = \frac{\Delta(A_t/A_0)^{3/2}}{\Delta t} (0.714 + p_i) \text{ (cc plasticizer uptake)} \cdot (\text{g resin})^{-1} \cdot \text{s}^{-1} \quad (5)$$
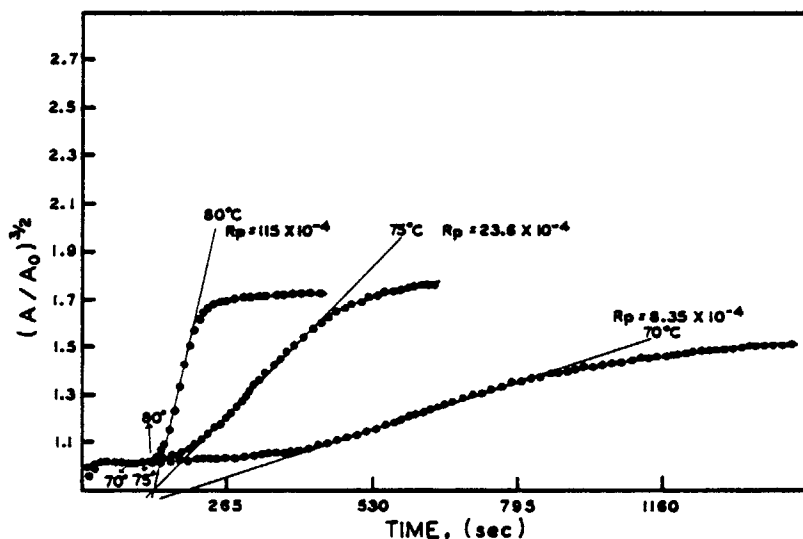

Fig. 1. Plots of volume swell, (A/A_0) 3/2 vs. time obtained on sample M-11 in excess DOP. Sample heated at 10°C/min from 60°C to T_{max} and then held.
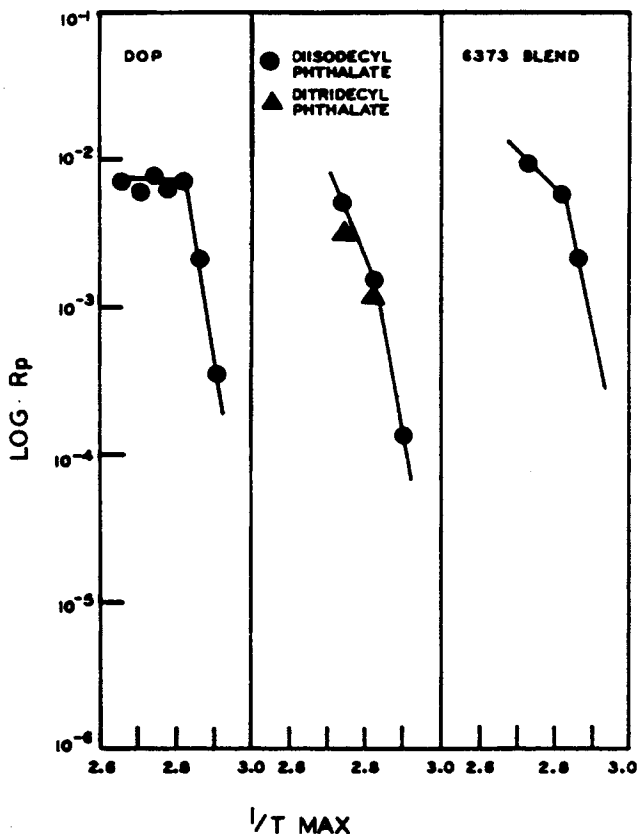
Fig. 2. $1/T_{max} \times 10^{-3}$ (°K)$^{-1}$ vs. log of the rate of plasticizer uptake in excess plasticizer (R_p) (cc, g^{-1}, s^{-1}), 3°C/min to T_{max}, sample M-11.

While the total capacity for plasticizer (TC) is obtained from the final swell $[(A_f/A_0)^{3/2} - 1]$.

$$TC = [(A_f/A_0)^{3/2} - 1] (0.714 + p_i) + p_i \qquad (6)$$

The rate of uptake of plasticizer by the PVC polymer omitting that in the pore structure is given by

$$R = \left[\frac{\Delta(A_t/A_0)^{3/2}}{\Delta t}\right] (0.714) \qquad (7)$$

One of the features of the rate of plasticizer uptake is its strong dependence on temperature. Note that in Figure 1. The rate of plasticizer uptake drops nearly 14 times in going from a maximum temperature (T_{max}) of 80°C to one of 70°C. In Figure 2 a plot of log R_p vs. $1/T$ are presented for M-11 samples heated at 3°C/min from 60°C to T_{max}. The values of $1/T$ plotted in Figure 3 are calculated from the values of T_{max}.

The breaks in the plots of $1/T$ vs. R_p in Figure 2 at about 80°C should not be interpreted as indicative of a change in mechanism, but rather an indication that the swelling process is completed before T_{max} is reached. In Figure 3 we see
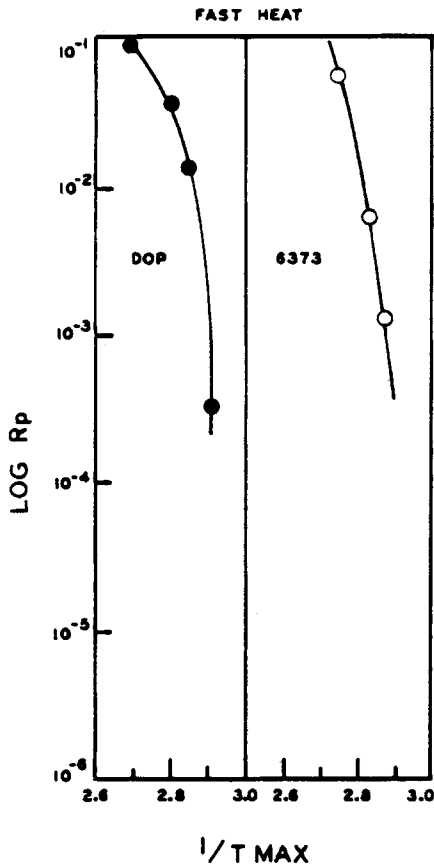
Fig. 3. $1/T_{max} \times 10^{-3}$ (°K)$^{-1}$ vs. the log of the rate of plasticizer uptake in excess plasticizer (R_p) (cc, g^{-1}, s^{-1}), fast heat to T_{max}.

similar $1/T$ vs. log R_p plots for M-11 in excess DOP and blend 6373 with the temperature in the hot stage being raised to T_{max} as rapidly as possible. The heat-up profile for the Mettler hotstage run in this "fast up" mode is given in Figure 4. Although the rate from 60°C is now dependent upon the T_{max} value, the heat rates, however, are greater than 30°C/min in most cases, and the $1/T$ vs. log R_p plots in Figure 3 show less curvature. Thus we would expect that $1/T$ vs. log R_p curves to be linear if it was possible to come up to temperature instantaneously. The activation energy values estimated from Figures 2 and 3 are very high with values of from 59–105 Kcal/mol °K. This corresponds to a better than a 10-fold increase in rate for each 10°C temperature rise. This degree of temperature sensitivity is on the same order of magnitude as observed by Dannis over 30 years ago.[9]

Dannis employed a dilatometric technique whose success in the light of this work appears to depend upon the presence of a large fraction of particles whose pericellular membrane was very complete.[10] It is suspected that the large volume decrease 0.074 cc/g observed by Dannis was the result of the presence of particles whose porosity was unaccessible to cold plasticizer. Essentially plasticization of the skin was the quantity being measured since a system volume decrease would be observed when the plasticizer entered the previously unaccessible porosity.
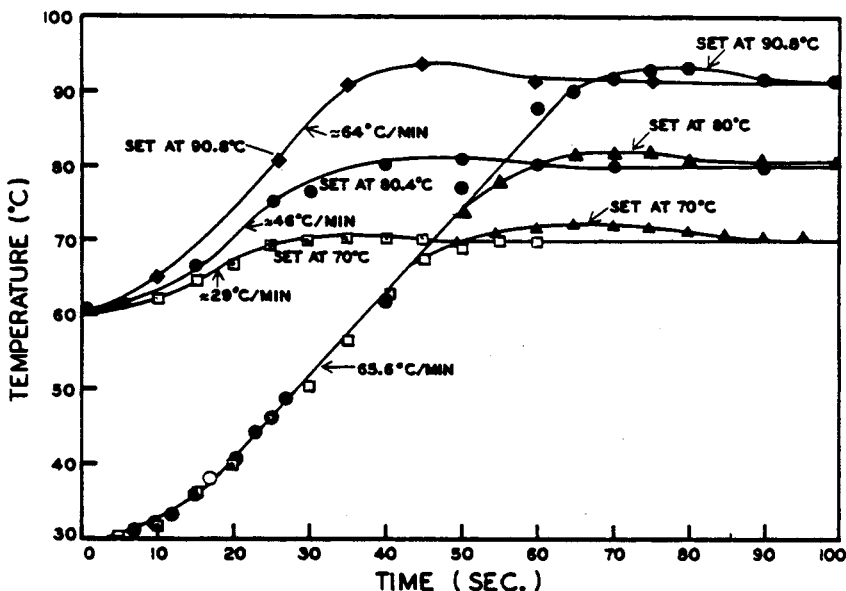
Fig. 4. Heat up characteristics of modified mettler FP-5 hot stage used in this work when stage is heated in "fast up" mode of operation.

In Figure 5 we see $\ln R_p$ vs. $1/T$ plots for a 103EP sample, M-9, run at plasticizer levels of 0.4 and 0.6 cc/g, respectively. Also presented is a plot for M-11 for DOP at a plasticizer level (G) of 0.5 cc/g. These experiments were run by the microbolus swell technique outlined previously. Note that the same general trend of strong temperature dependence of R_p is also exhibited in these samples. The activation energy data from Figures 2, 3, and 5 is given in Table II.

Examination of Figure 1 will reveal that plasticizer uptake curves exhibit an induction period. In experiments where the time devoted to temperature programming is longer than the induction period, a temperature at which rapid plasticizer uptake occurs can be defined.[11] In light of the high activation energy for plasticizer uptake, such behavior would be expected since the response of the image analyzer to volume change is linear with a lower limit of detectability of changes in V/V_0 of about 0.005 and thus low rates of plasticizer uptake which occur over short time priods will not be detected. In a temperature-programmed run, plasticizer uptake will appear to "start" at a temperature which is in fact the temperature where the logrithmicly increasing rate of plasticizer uptake starts to give readily detectable increases of V/V_0. However, the induction periods longer than the temperature programming period are observed for samples plasticized at T_{max} of 70°C (see Fig. 1).

This suggests that plasticizer uptake is carried out in two steps—an initial solvation of the surface followed by a rapid swell. At temperatures below 70°C the surface solvation effect may become sufficiently slow as to appreciably delay the onset of swell.

At rapid rates of heating ($\approx 65°C$/min) plasticizer uptake generally begins once T_{max} is reached. Giving an induction time of 20–30 s this, again suggests that plasticizer uptake is a two-step process.

The rate of plasticizer uptake was found to be dependent upon the concentration of plasticizer with faster rates generally observed at high concentrations of plasticizer.
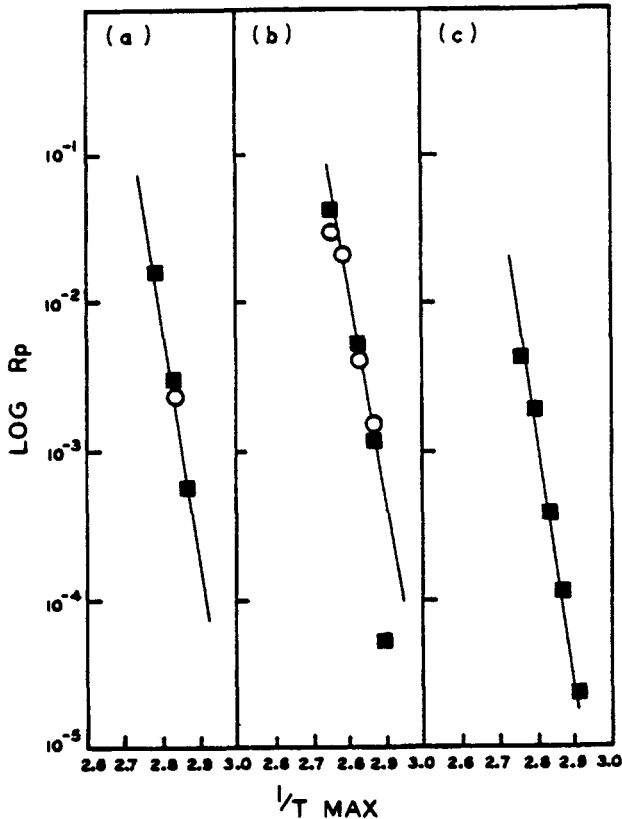
Fig. 5. $1/T_{max} \times 10^{-3}$ (°K)$^{-1}$ vs. the log of the rate of plasticizer uptake T_{max} (R_p) (cc, g^{-1}, s^{-1}) for: (a) M-9, $G = 0.396$; (b) M-9, $G = 0.597$; (c) M-11, $G = 0.493$ all for blend 6373 plasticizer; (■) trial 1; (○) trial 2.

In Figure 6 is shown a plot of R_p vs. G with R_p measured at 1°C, 3°C, and 10°C/min from 30°C to 100°C. Note that at the 3°C/min and 10°C/min rate of heating, the rate of plasticizer uptake goes through a maximum at a plasticizer level of 0.6–0.7cc/g.

Although the rate of plasticizer uptake is highly temperature-dependent, this

TABLE II
Summary of Activation Energy Data

Resin	Plasticizer	G^a (cc/g)	EA (kcal/mol °K)	Range (°C)	Rate of heating
M-9	6373 blend	0.396	−77.5	85–75	Fast
M-9	6373 blend	0.597	−66.0	70–90	Fast
M-9	6373 blend	Excess	−66.3	90–75	Fast
M-11	DOP	0.493	−78.4	70–90	Fast
M-11	DOP	Excess	−105.6	70–100	Fast
M-11	6373 blend	Excess	−61.9	75–90	Fast
M-11	DTDP	Excess	−91.5	85–100	Fast
M-11	DOP	Excess	−75.4	70–80	3°C/min

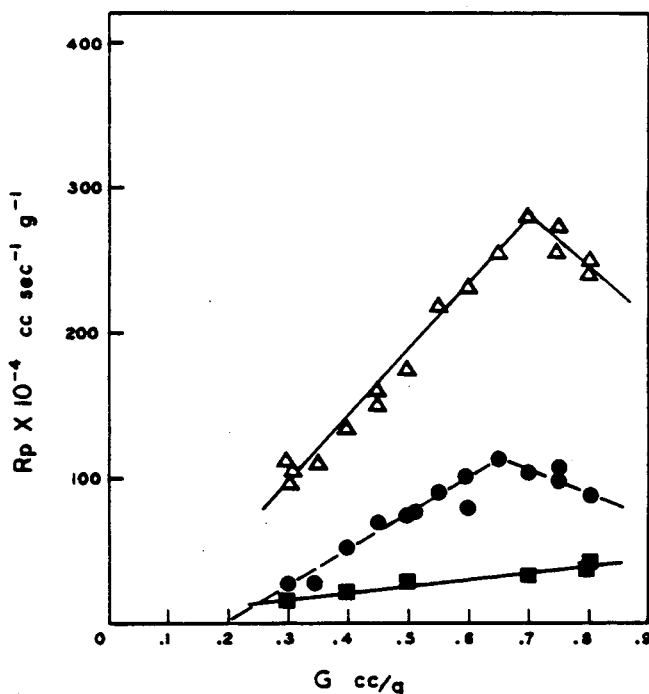^{a} G = concentration of plasticizer.

Fig. 6. Rate of plasticizer uptake (R_p) vs. concentration of plasticizer (G) for sample M-2 at ($\triangle$) 10°C/min, ($\bullet$) 3°C/min, ($\blacksquare$) 1°C/min sample heated from 30°C to 100°C and held.

is not the case for the total capacity for plasticizer or TC as calculated from eq. (6).   In Table III we see a comparison of TC values determined at different rates of heating and maximum temperatures.   Note that TC is nearly independent of heating rate.   For the samples in Table III and DIDP plasticizer, TC was found to increase about 0.009 cc/g for each degree of temperature rise.

TABLE III
Effect of Maximum Temperature (T_{max}) on Total Capacity for Plasticizer (TC) for Diisodecyl Phthalate

Resin	Heating rate to T_{max} from 30°C	T_{max} (°C)	p_i (cc/g)	TC (cc/g)
A	10°C/min	80	0.243	0.63
A	10°C/min	85	0.243	0.645
A	10°C/min	90	0.243	0.721
A	10°C/min	100	0.243	0.760
B	10°C/min	80	0.270	0.82
B	Fast up	80	0.270	0.82
B	10°C/min	90	0.270	0.887
B	Fast up	90	0.270	0.86
B	10°C/min	100	0.270	1.03
B	Fast up	100	0.270	0.89
C	10°C/min	80	0.349	1.09
C	10°C/min	90	0.349	1.20
C	10°C/min	100	0.349	1.23

Characterization of Plasticizer Uptake by the Brabender Torque Rheometer

The procedure used in this investigation was similar to that described in ASTM procedure (DD2396)-36,[1] entitled "Powder Mix Test of Poly(Vinyl Chloride) Resins Using a Torque Rheometer." As in the ASTM procedure a Brabender torque rheometer equipped with a 650-mL sigm mixer with a 1.5-1 rotor ratio was employed. The rheometer was run at 63 rpm and the head temperatures set at 88 ± 1°C. The apparatus is shown in Figure 7. 200 g of the resin under test mixed with 50.0 g of compound ingredients consisting of a mixture of:

clay 10 g	dibasic lead phthalate 6.0 g
basic lead carbonate 14 g	water ground whiting 20.0 g

These were placed in the preheated mixing head and allowed to stir for 5 min. After the preheat period, the plasticizer was added to the resin via the distribution funnel placed in position over the head of the Brabender as described in the ASTM procedure.
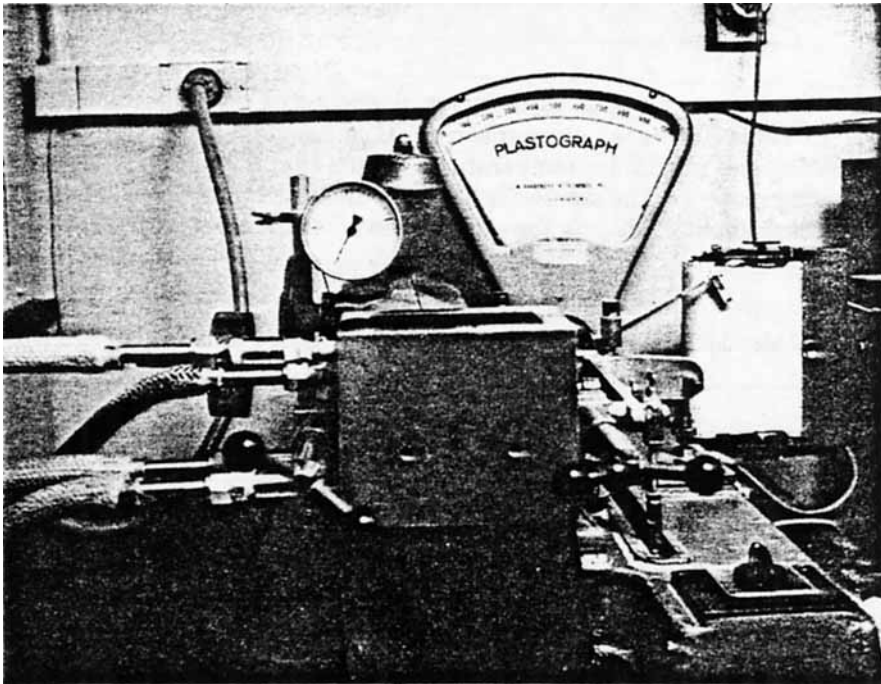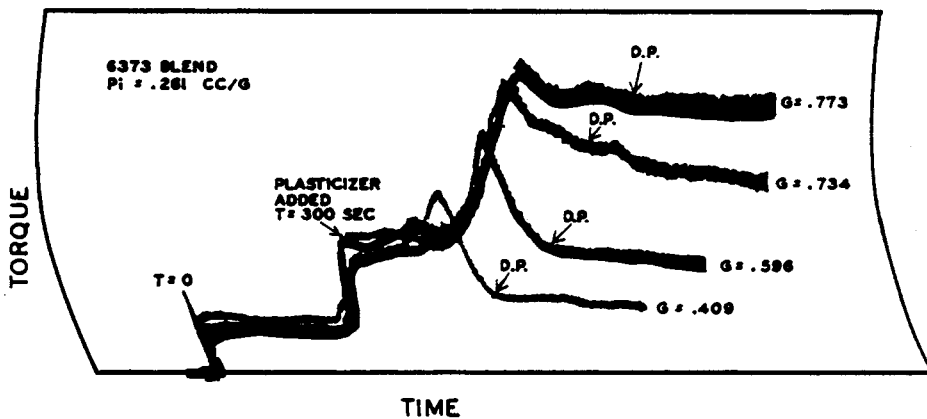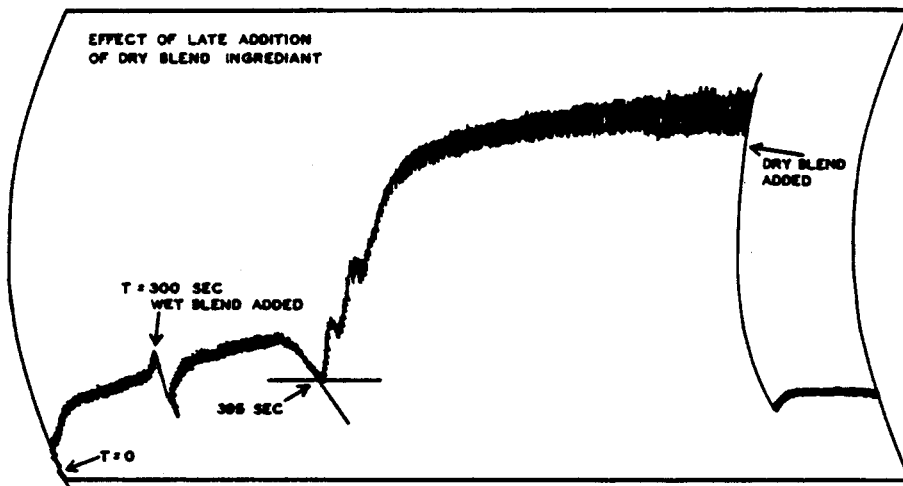

(a)

Fig. 7. Brabender torque rheometer equipped with sigma blade mixing head: (a) entire instrument showing torque readout, (b) interior of mixing head. (c) Brabender torque vs. time curves for sample M-2 and blend 6373 (DP indicates the visual dry point). (d) Brabender torque vs. time curve for late addition of dry compounding ingredients.
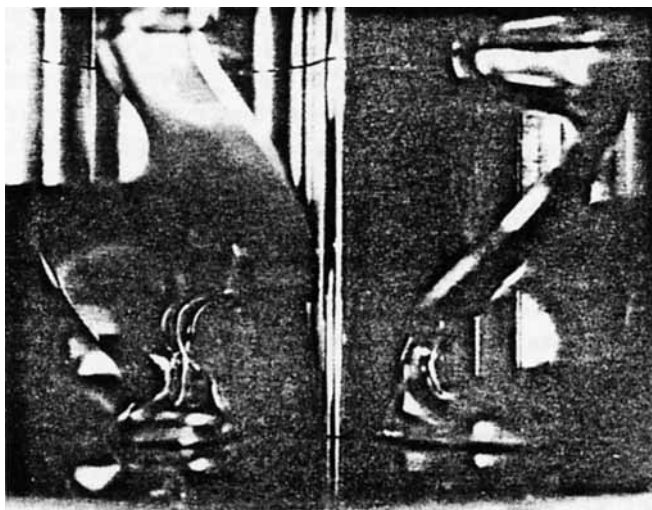
(b)

(c)

(d)

Fig. 7. (*Continued from previous page.*)

Such a procedure will yield a torque vs. time curve whose shape depends on the resin, plasticizer type, and level of plasticizer employed. Typical curves for a single resin using different levels of plasticizer are shown in Figure 7(c). In the case of the lower levels of plasticizer the *dry time* or the time of transition between a wet lumpy mix to a dry free-flowing powder is signaled by a drop in torque. At the higher plasticizer levels, a visual indicator of the dry point must be used.

The time between the addition of the plasticizer and the dry point is the *dry time* of the resin and is the traditional indicator of the ability of a resin to absorb plasticizer.

In Figure 7(d) we see a Brabender torque vs. time curve in which the compounding ingredients (clays, whiting, etc.) have been omitted. Note that the torque continues to rise after a slight dip at the "dry point." This behavior is not surprising as hot plasticized PVC is "sticky." If we add the compounding ingredients to the mix while in this condition the torque instantly drops [see Fig. 7(d)]. Thus, the compounding ingredients act as *powder flow agents* to produce a free-flowing powder.

In Figure 8 we see typical plots of dry time versus the level of plasticizer employed [G (cc/g)] in the test. Note that these curves show a region where the dry time increases linearly with plasticizer level bounded by (1) a lower level of plasticizer concentration where the dry time drops very rapidly and (2) an upper
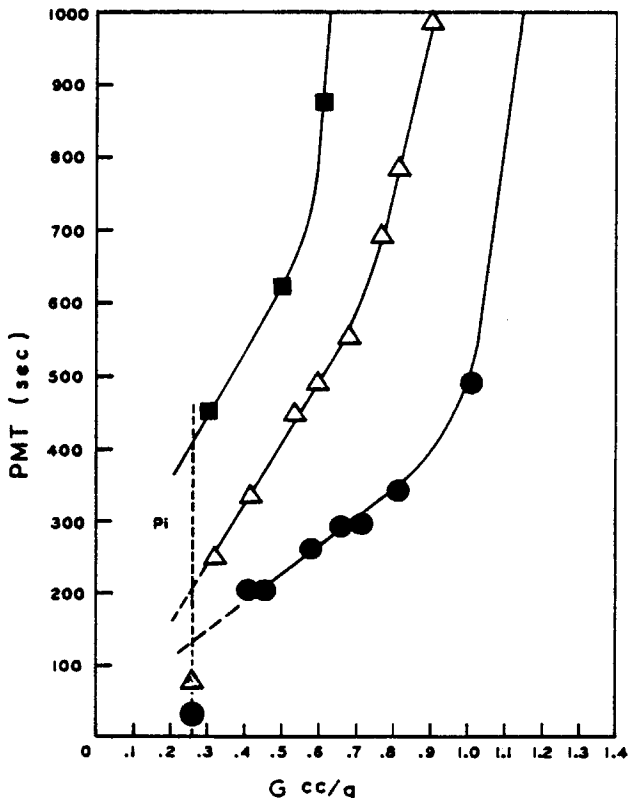

Fig. 8. Brabender powder mix time (PMT) vs. plasticizer level (*G*) x-blend 6373: (O) DOP, (□) DTDP for sample M-2.

level where the dry time goes to infinity. The lower plasticizer level was found to be identical with the resin's internal porosity while the upper concentration level will be shown to be identical with the TC values as determined by image analysis.

These observation suggested that a rate of plasticizer uptake up to G_{max} could be derived from dry time vs. plasticizer level data using the following expression:

$$\text{dry time (s)} = \frac{G - p_i}{R_0} + k_0 \tag{8}$$

where G = level of plasticizer (cc/g resin), p_i = internal porosity (cc/g), R_0 = rate of plasticizer uptake, and k_0 = const.

As would be expected from Figure 8, plots of G-p_i vs. dry time were found to be linear (see Fig. 14), and, for a given plasticizer, k_0 was found to be a constant which was nearly independent of the resin being tested. In Table IV we see a tabulation of k_0 values obtained on the Brabender torque rheometer used in this study.

The observation that plasticizer uptake in the Brabender can be described by a single rate is surprising in light of the concentration dependence of the rate of plasticizer uptake noted earlier in the image-analysis swell experiment.

It was suspected that k_0 represented the time required for the PVC—plasticizer mix to become heated to a temperature where diffusion of plasticizer into the PVC is "rapid." As was discussed previously, the onset of swell or plasticizer uptake has been found to be initiated at very specific temperatures under conditions of extended temperature programming. Thus the temperature of the mix in the Brabender at k_0 s should correlate with the temperature of the onset of swell as determined by image analysis.

To verify this hypothesis, the temperature profile of the mixing powder in the Brabender was determined by infrared thermometry using a Barns "thermal master." Image analysis swell experiments in excess plasticizer were then carried out using the same thermal profile as was observed in the Brabender after the addition of the plasticizer. The thermal profile obtained from the Brabender and the matching hotstage program is given in Figure 9.

Inspection of Table IV will reveal excellent agreement between the observed temperature of the onset of swell and the temperature at k_0 (s) in the Brabender, thus confirming our hypothesis that k_0 is the time required for the mix to become hot enough for "rapid" plasticizer uptake to occur.

TABLE IV
Value of k_0 Found in This Study, Temperature at k_0, and Temperature of Onset of Swell as Measured by Image Analysis

Plasticizer	k_0 (s)	% deviation at 90% confidence	Temperatures at k_0 in Brabender (°C)	Temperature of onset of swell in image analyzer (°C)
Blend 6373	186.6	15	82	81
DTDP	422	9	86.5	86
DOP	143	5	80	80
DIDP	253	7.8	84.2	83.8
Vicoflex 7170	236.6	11	—	—

BARNS IR "THERMAL MASTER"
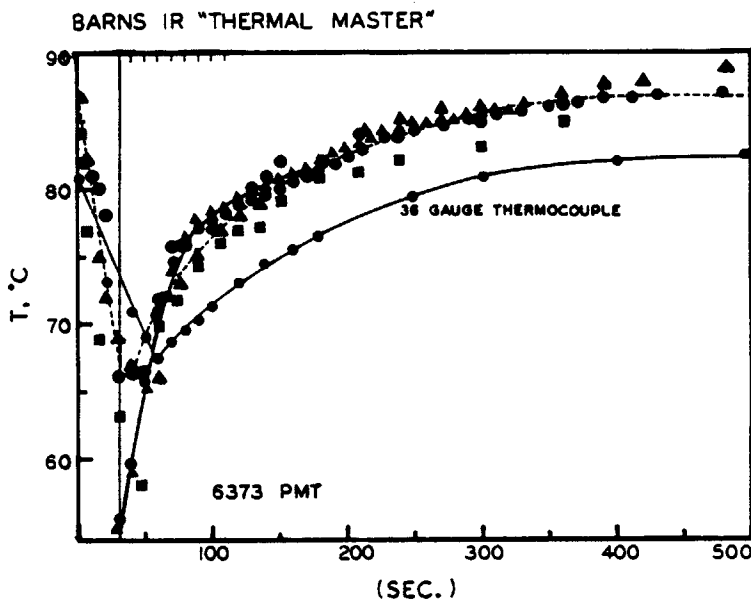
Fig. 9. Temperature profile of the Brabender powder mix experiment as measured by IR thermometry ($\bullet$, $\blacktriangle$, $\blacksquare$) and degree of match obtained using the F-P5 hot-stage (O, $\triangle$, $\square$): (O) run 1; ($\triangle$) run 2. A heating profile of the Brabender powder mix experiment using a thermocouple is also included. Hot stage schedule (°C): fast up (55–70); 10°C/min (70–76); 3°C/min (76–84); 1°C/min (84–86.5); 0.2°C/min (86.5–88).

It should be noted that in all cases the temperature at k_0 is less than the set temperature of the Brabender record (88°C). Since the temperature is still increasing after k_0 s have elapsed, the concept of a "temperature" at which plasticizer uptake becomes "rapid" is valid.

As was mentioned previously, eq. (7) was found to hold up to a maximum level of plasticizer above which the resin refused to dry. This maximum level G_{max} was found to be identical with the total capacity (TC) as defined by eq. (6) when measured under similar thermal conditions as found in the Brabender. In Table V are listed values of G_{max} and TC for several different resin–plasticizer com-

TABLE V
A Comparison of Total Capacity as Defined by Eq. (6) and G_{max} Values Observed in a Brabender

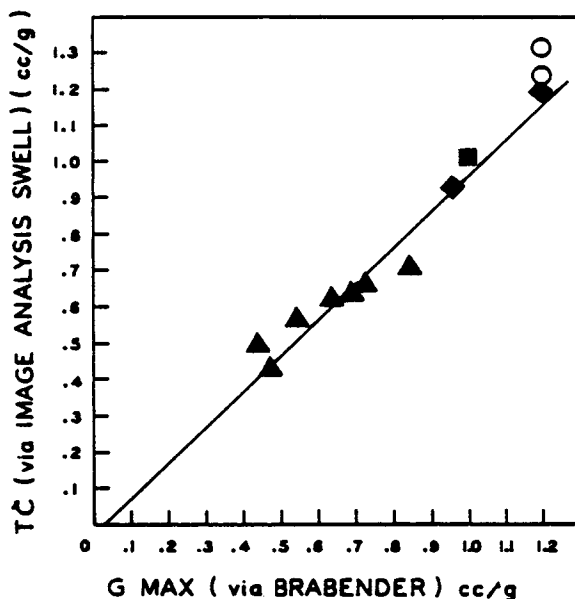| Resin	Plasticizer	G_{max} (cc/g)	TC (cc/g)
M-11	6373 blend	1.20	1.21
M-11	DOP	1.20	1.24
M-11	DIDP	1.00	1.04
M-11	DTDP	0.84	0.707
M-2	6373 blend	0.96	0.938
M-2	DOP	1.20	1.31
M-2	DIDP	0.82	1.01
M-2	DTDP	0.68	0.639
H	DTDP	0.720	0.66
E	DTDP	0.635	0.64
I	DTDP	0.544	0.58
F	DTDP	0.477	0.44
J	DTDP	0.440	0.49

Fig. 10. Total capacity for plasticizer for samples in Table IV as measured by image analysis swell (TC) vs. the maximum absorbed in a Brabender powder mix experiment (G_{max}) X-6373; (O) DOP; (□) DTDP; (▲) DTDP.

binations and these data are presented graphically in Figure 10. A least squares analysis yielded the following relationships:

$$TC = 1.063 \, G_{max} - 0.0374$$

$$\text{Std deviation} = 0.082, 93\% \text{ of variation explained} \tag{9}$$

Since plasticizer uptake is (1) highly temperature-dependent and (2) concentration-dependent, a series of microbolus swell experiments were conducted using the temperature profile in Figure 9 for comparison with the R_0 values obtained from Brabender powder mix experiments. Figure 11 shows such a plot for a single resin sample and in all cases investigated to date R_0 has been found to correspond to the rate at $G = 0.250$ cc/g despite levels of plasticizer employed in excess of this value in the Brabender powder mix experiment.

In Figure 12 we see a plot of 35 observed Brabender powder mix times vs. those predicted from eq. (7), using R_0 values of R_p at $G = 0.250$ obtained from plots of the type shown in Figure 11. In Figure 12 measured k values from Brabender PMT data were employed. A least squares analysis, of these data yielded the following:

$$PMT_{observed} = 1.01 \, PMT_{predicted} + 6.27$$

$$98\% \text{ variation explained} \tag{10}$$

If the average k values of Table IV are used,

$$PMT_{observed} = 1.02 \, PMT_{predicted} + 5.64$$

$$96\% \text{ variation explained} \tag{11}$$

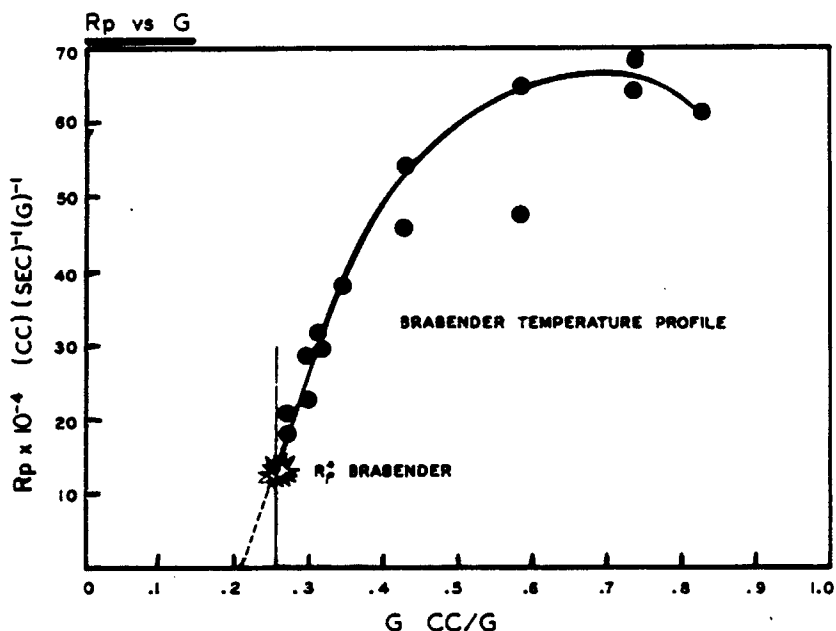Thus for all practical purposes a one-to-one correlation is obtained.

Fig. 11. Rate of plasticizer uptake (R_p) by image analysis swell (cc, s^{-1}, g^{-1}), vs. the level of plasticizer employed (G), cc/g for sample M-2 and 6373 blend using the temperature in Figure 9.

DISCUSSION

This work has established that plasticizer uptake by PVC is (1) concentration-dependent and (2) highly temperature-dependent. Furthermore, it has been demonstrated that the rate of plasticizer uptake in a Brabender powder mix experiment can be described by a single low rate which is independent of plasticizer concentration—a result which appeared contradictory to the general observation of the concentration dependence of the rate of plasticizer uptake.

Although the exact cause of this anomaly is not known, temperature gradients are known to be important. The temperature of the mixing powder in the Brabender powder mix head is far from even after plasticizer is added; infrared thermometry and thermal imaging experiments have revealed that differences of at least 5°C and perhaps 10°C exist in the mix well past the dry point. Thermal imaging was accomplished using an Inframetric® 525 thermal imaging system whose output was recorded on a portable 0.5 in. VTR (Sanyo Inc.). Selected portions of the tapes were time base corrected and transferred to 2 in. quad (Ampex Inc.) through a video quantizer (Colorado Video). The quantizer was adjusted so as to assign to distinct color isotherms covering the entire 50°C range normally employed in these studies. The colorized tapes wee then transferred to 16 mm film for ease in handling and analysis. Study of these films revealed the presence of temperature gradients as large as 5–10°C. In Figure 13 we see single line scans obtained from the thermal imaging system in the line scan mode. These show temperature variations of greater than 5°C even past the dry point. However, inspection of the colorized thermal images suggest differences as large as 10°C may sometimes be present. Since plasticizer uptake has a high activation energy, this 5–10°C temperature differences can mean as much as a 5–10 times variation in the rate of plasticizer uptake within the mix.

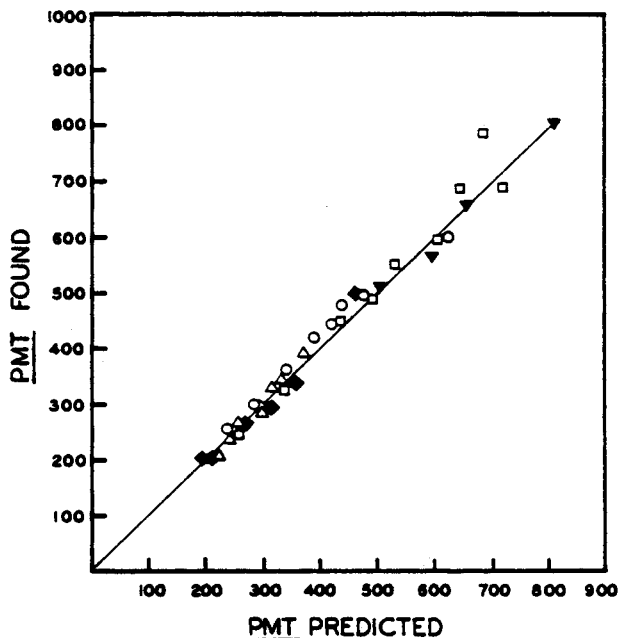It has been shown that the pore structures of most commercial resins quickly

Fig. 12. Powder mixture (PMT) as measured in the Brabender plastograph vs. that calculated from Figure 8, using values of R_0 derived from image analysis; R_p at $G = 0.250$ cc/g. K observed values were those actually measured from plots of G-p_i vs. PMT for the samples employed. ($\square$) M-2 6373 blend; (O) M-9 6373 blend; ($\triangle$) M-11 6373 blend; ($\diamond$) M-2 DOP; ($\triangledown$) M-9 ditridecyl phthalate.
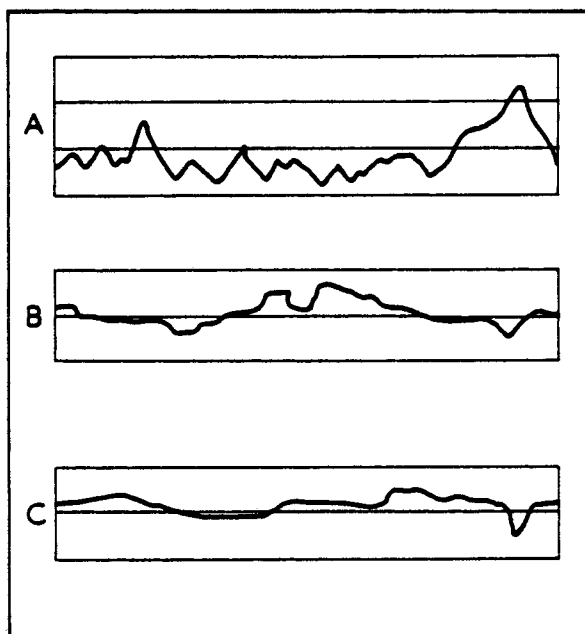

Fig. 13. Typical single line scans showing the temperature distribution in the center 2/3 of the Brabender mixing chamber (long direction across the rotor): (A) just after plasticizer addition; (B) just before dry point; (C) just after dry point. *Note:* Each division represents 5°C; each line scan takes 1/60 s.
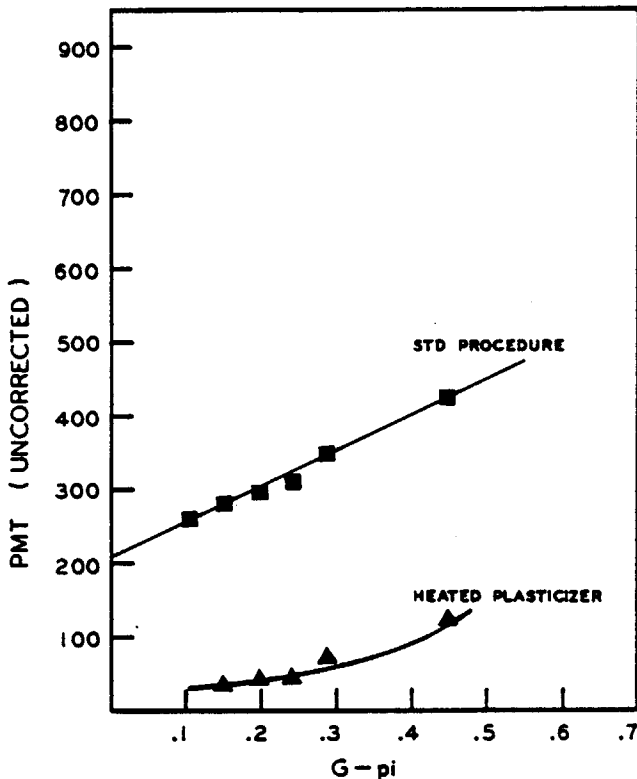
Fig. 14. Brabender dry time (PMT) vs. G-p_i for sample CA and blend 6373: (■) standard procedure; (▲) isothermol experiment at 86°C.

fills with plasticizer, and indeed eq. (7) implies that the dry time is controlled by the diffusion of $(G$-$p_i)$ cc. of plasticizer into the PVC.

It may be that the hot particles quickly take up all the plasticizer in their immediate vicinity, leaving the cooler particles to absorb the remainder at a low rate. It should also be noted that slow rates of heating result in less concentration dependence of the rate (see Fig. 6).

The importance of temperature fluctuation in the observed powder mix behavior in the Brabender can be easily demonstrated by running isothermal powder mix experiments. It has been found that by heating the plasticizer to 100°C before addition results in essentially no drop in temperature of the mix from a value of 86°C obtained in the resin preheat period.

In Figure 14 we see a comparison of isothermal vs. normal powder mix behavior. On the basis of plasticizer swell studies carried out at rapid rates, we would expect K_0 to assume some low value on the order of 5–20 s. In addition the G-p_i vs. time plot is altered to a nonlinear form. Such nonlinear behavior is indicative of a rate of plasticizer uptake which is a function of plasticizer concentration. Some resins exhibit a dry time which is constant over a wide range of G values when run in an isothermal powder mix experiment. This behavior would also give rates which are concentration-dependent.

This work illustrates the importance of even heating in a commercial dry blending operation if short cycle times are to be achieved. Indeed the short cycle times observed in high speed mixer such as the Henschel can be ascribed to the

conditions of both even heating of the mix and higher temperatures which are achieved in these machines.

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