

Dryblending Behavior of Commercial Polyvinyl Chloride

L. T. CARLETON* and E. MISHUCK,* *Aerojet-General Corporation, Azusa, California, and General Tire and Rubber Company, Akron, Ohio*

Synopsis

Ease of processing suspension-polymerized polyvinyl chloride (PVC) is related to its ability to accept sufficient plasticizer, while remaining a dry, free-flowing powder. The successful incorporation of plasticizer, termed cold preblending or hot dryblending, depends upon basic physicochemical factors. Cold preblending corresponds to a purely geometrical filling of intraparticle pores and fissures, while hot dryblending depends additionally upon a time-dependent absorption. Quantitative laboratory tests for these two effects were developed and standardized. When applied to experimental and commercial lots of PVC and their fractions, the tests gave results which showed slight correlation with gross properties of the particles. However, intercorrelation between tests for cold preblending and hot dryblending was strong, indicating that the same factors may be responsible for both. The tests also provided good ratings of polymers for actual processing behavior. It is possible to control particle geometry via the process variables of suspension polymerization, and thence to regulate cold preblending behavior; the effects on hot dryblending are not as clear. Post-polymerization grinding markedly alters the PVC particle surfaces and can substantially improve hot dryblending capacity. Severe grinding is needed to change particle geometry enough for any large improvement of cold preblending.

INTRODUCTION

The ability to remain "dry" and free-flowing while assimilating plasticizer is an important criterion of acceptance for suspension-polymerized polyvinyl chloride (PVC).

The manufacture of flexible shapes and finished articles from PVC requires the incorporation of plasticizers, stabilizers, colorants, fillers, and lubricants. In order to provide a uniform distribution of these ingredients in the final forming operations, certain blending techniques are very advantageous. These are (1) hot dryblending to prepare a feed for extrusion and molding, and (2) cold preblending for calendering. (This paper uses a terminology in which the blending of polymer, plasticizer, and other ingredients without heat is called preblending, and blending with heat applied is dryblending.) Both techniques enable the individual polymer particles completely to accept plasticizer (amounting to 20-100 parts) while keeping their identity, remaining dry, and flowing freely. Manufacturers have

* Present address: Space-General Corporation, El Monte, California.

developed separate grades of suspension-polymerized polyvinyl chloride designed especially for hot dryblending and for preblending. The simplifying advantages of these techniques over wet methods of compounding are impressive.

Polymers manufactured for cold preblending and hot dryblending differ in their general requirements. Experience has shown that the former depends on adsorption and the latter on absorption. (In the latter case, the plasticizer is frequently said to be "locked into" the particles.)

Park¹ attributed effective adsorption to a large surface area, resulting from a large number of relatively fine particles. On the other hand, absorptive polymers for dryblending have lower specific surface, but a higher bulk density, giving greater efficiency in charging. The differences noted on comparison of two series of adsorptive and absorptive polymers are summarized in Table I.

TABLE I

Polymer	Specific area, cm. ² /g.	Average particle diameter, μ	Bulk density, g./cm. ³
Adsorptive, for preblended calendering	306-742	48-94	0.28-0.42
Absorptive, for dryblend extrusion or molding	156-207	92-131	0.37-0.52

A manufacturer states² that dryblended particles must be coarse, for proper feed action to the extruder. They must also be of uniform size, to insure even distribution of plasticizer among particles. In an extreme case, uneven distribution may lead to unplasticized particles, called fish eyes, in the finished material.

A number of empirical tests or tests simulating use conditions are employed in the industry to indicate dryblending and preblending performance. The plasticizer used is normally, though not invariably, dioctyl phthalate (DOP). These include plasticizer take up (PTU) tests, performed by titrating dry polymer powder with plasticizer, blotting tests for removable wet plasticizer,³ and trial runs in the Banbury mixer or other mixing machinery. The Braebender Plastometer is superseding the Banbury mixer at present.

In contrast to these commercial tests, a basic kinetic study of the interaction of hot PVC and DOP was performed by Dannis.⁴ Rate curves for the swelling of PVC particles were determined at several temperatures by observations of the change of dielectric constant. Diffusion rates have also been determined by measuring changes in refractive index⁵ and infrared absorption⁶ as plasticizer was absorbed or removed.

When considered for use in product improvement studies the various empirical tests suffer from their dependence on so many arbitrary factors. On the other hand, the kinetic swelling experiments which have been

performed are experimentally too complicated for control work, and also disregard important effects of particle geometry and surface condition.

This paper develops a coherent explanation of dryblending and preblending, in terms of basic factors of the polymer particles and interactions between particles and plasticizer. Simple tests are proposed to provide quantitative measures of dryblending and preblending. As far as the availability of data permits, the tests are applied to evaluations of commercial and research polymers.

PHYSICAL CHEMICAL INTERPRETATION OF DRYBLENDING PROPERTIES

Basic Postulates

The present section introduces two basic postulates, covering the nature of cold preblending and hot dryblending, respectively. These postulates form the basis of simple laboratory tests which may be used to evaluate the dryblending and preblending performance of any PVC with dioctyl phthalate or other plasticizers.

First, the mechanism of cold preblending is postulated to be the filling by plasticizer of accessible, intraparticle pores, capillaries, and fissures. The act of filling occurs substantially on contact, or at least is completed during a small fraction of the blending cycle, so that there is no time dependence thereafter. The filling is irreversible, in that plasticizer is held tenaciously on the particles by capillary attraction or surface forces. It cannot be removed by the mechanical processes of agitation during the blending process, by draining, or by the suction or centrifugation of controlled laboratory tests. Being dependent only on particle geometry, cold preblending is independent of chemical or interaction factors. There is no absorption or swelling in the cold system.

On the other hand, hot dryblending, though containing a geometrical component, results principally from the absorption of plasticizers into polymer particles at elevated temperatures. This absorption is time-dependent, following a regular kinetic relationship.

Total Accessible Volumes

When fluid plasticizer is added to a cold mass of powdered PVC, the intraparticle amount retained in cold preblending is only a part of the amount needed to fill the total accessible volume. An additional component results from the fact that the particles are collected together, creating interparticle spaces to be filled. The volume fraction of all accessible voids is defined by

$$1 - \nu = \rho_a / \rho \quad (1)$$

in which ρ_a is bulk density of polymer powder (in grams per cubic centimeter), ρ is "true density" of the powder as measured by liquid displacement, and ν is volume fraction of accessible voids in the polymer powder.

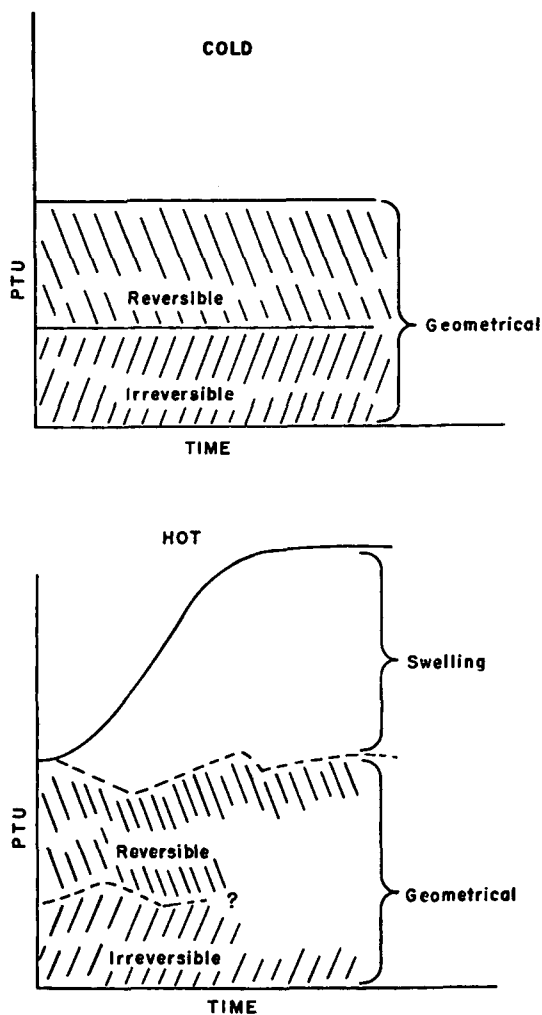


Fig. 1. Components of plasticizer take up (PTU).

Rearrangement gives the total accessible volume (in cubic centimeters per gram of polymer) as follows:

$$(1/\rho_a) - (1/\rho) = (1/\rho) \nu/(1 - \nu) \quad (2)$$

For dioctyl phthalate plasticizer, of 0.986 g./cm.³ density at 25°C., the number of grams of plasticizer taken up per 100 g. of polymer is

$$\text{PTU} = 98.6 [(1/\rho_a) - (1/\rho)] = (98.6/\rho) \nu/(1 - \nu) \quad (3)$$

(If PTU is measured at a different temperature, the appropriate density must be substituted.) Thus far this equation, which expresses an ideal condition without reference to experimental methods, is simply a "material balance" on void space.

Irreversible Component of Cold PTU

The irreversible filling of intraparticle pores accounts for one portion of the total volume filled by plasticizer and cold preblending is related to this component. By difference, the reversible component represents the filling of the interparticle voids, and does not exist in isolated, individual particles. The corresponding division of PTU into irreversible and reversible components is illustrated in Figure 1. There is no general expression corresponding to eq. (3) for the value of the irreversible component, which depends upon the surface porosity of individual particles, and must be determined experimentally for each lot of polymer.

Hot Dryblending

Hot dryblending is also expressible in terms of PTU, when the meaning of the term is extended to include the amount of plasticizer absorbed at a high temperature.

If plasticizer is absorbed, then PTU will increase with time during the absorption process. The rate of PTU increase is postulated to be that of a simplified model which has the following properties: (1) the rate of swelling is equated to the increase of PTU, i.e., $d\text{PTU}/dt$ (ignoring the geometrical changes in PTU induced by swelling), (2) each microscopic unit of polymer within each PVC particle is either swelled or not swelled. (This assumption was also employed by Dannis.⁴) Thus if the final PTU at equilibrium swelling is PTU_F and the instantaneous value at time t is PTU , the concentration of unswelled PVC at time t is proportional to $\text{PTU}_F - \text{PTU}$,³ the free plasticizer concentration is always constant, at the value available at the PTU end point. The steady addition of new plasticizer through the course of the test assures this.

Considering the rate of interaction of unswelled polymer and free plasticizer to be proportional to their concentrations, and representing combined constant terms by k , then

$$d(\text{PTU})/dt = k (\text{PTU}_F - \text{PTU}) \quad (4)$$

Integration between PTU_0 and PTU_F , the initial and final values of PTU gives

$$\log \frac{\text{PTU}_F - \text{PTU}_0}{\text{PTU}_F - \text{PTU}} = \log \frac{1}{1-p} = \frac{k}{2.303} t \quad (5)$$

in which $p = (\text{PTU} - \text{PTU}_0)/(\text{PTU}_F - \text{PTU}_0)$ is the reaction of unconsumed PTU. This is the familiar integrated expression for a first-order reaction. These equations predict that, past the period of inhibition or retardation, the plot of $\log [1/(1-p)]$ versus t should be a straight line. This plot also has the great advantage of adjusting all curves to a common origin, for comparison. Equation (5) may also be derived by treating the diffusion of plasticizer under a concentration gradient extending inward from the surface of each (spherical) particle.

The interrelations of hot PTU and the components of cold PTU are illustrated in Figure 1. Hot PTU is depicted as a sum of effects due to swelling and to the geometrical filling of accessible voids. The geometrical effect should correspond to cold PTU at zero time; thereafter it may change somewhat because of the distortion of particles in swelling. The geometrical PTU is in turn divided into reversible and irreversible portions, and this division may also change with time in an unknown fashion, or may become meaningless.

DEVELOPMENT OF LABORATORY TESTS

In order to test the postulated mechanisms for cold preblending and hot dryblending, it is necessary to provide reliable methods for measuring the quantities in the relationships developed above. These are bulk density and true density of PVC particles, plasticizer takeup, the irreversible component of PTU, and PTU at different times at a high temperature.

Density Tests

A reproducible true particle density was found to be measurable by displacement of liquid in a pycnometer. For the present purposes, bulk density must be measured under conditions which compare with those of the actual mixing of polymer particles and plasticizer. This requirement precludes the use of ASTM standard method D1182-51T, or other procedures depending upon the free settling of powder. A more suitable method in which the PVC powder is vibrated to a constant volume was developed.

The density of consolidated or molded PVC, ρ_c , is also of interest for certain correlations, and was determined to be consistently 1.40 g./cm.³, in agreement with the literature value.

Cold PTU by Spatula Method

A PTU test already in use in the vinyl plastics industry was adopted.² This test depends upon mixing plasticizer into the PVC with a spatula, and noting the end point at which the mix is barely fluid. It is described in Appendix I. Typical values for PTU range roughly from 75 to more than 150 g. DOP/100 g. polymer, for different commercial grades of PVC.

Check of Equation for Ideal PTU

If plasticizer takeup is to be used as a basic tool for investigation, it is necessary to establish its reliability at the outset. The measured PTU must be shown to correspond to the ideal PTU of eq. (3), corresponding to the plasticizer needed to fill all accessible voids. Values of measured PTU (after determining vibrated bulk density, for consistency), ρ , ρ_a , and ρ_c were determined for several fractionated and unfractionated lots of PVC, as well as for three different sizes of glass beads and for a commercial lot of polyvinyl alcohol. [The measurement of ρ_c permitted the closed

voids within polymer particles to be calculated, as additional information. Thus, per cent closed voids = $100(1 - \rho/\rho_c)$.] Of the PVC's, one lot of experimental polymer A (Lot 21) and one composite of commercial and experimental lots were fractionated by screening; and both the original specimens and the fractions, ranging from $-48 + 60$ to $-250 + 270$ sieve sizes, were tested. The results for all materials are given in Table II.

Values of experimental PTU are plotted against $(1/\rho_a - 1/\rho)$ in Figure 2, with the straight line representing the ideal PTU. The agreement between measured and ideal PTU is good in all cases. Thus the theoretically derived equation applies generally to measured PTU, regardless of variations in chemical composition of the particles, particle size distribution, surface area, particle shape, surface roughness and absolute density. The measured PTU is shown to be a fundamental property of the polymer. (In later tabulations, the experimental PTU's do not agree as closely with the theoretical value, because they were determined on unvibrated polymers.)

Centrifuge Test for Irreversible Cold PTU

It should be possible by some simple test to remove the plasticizer between particles, i.e., the reversible component, and leave behind the plas-

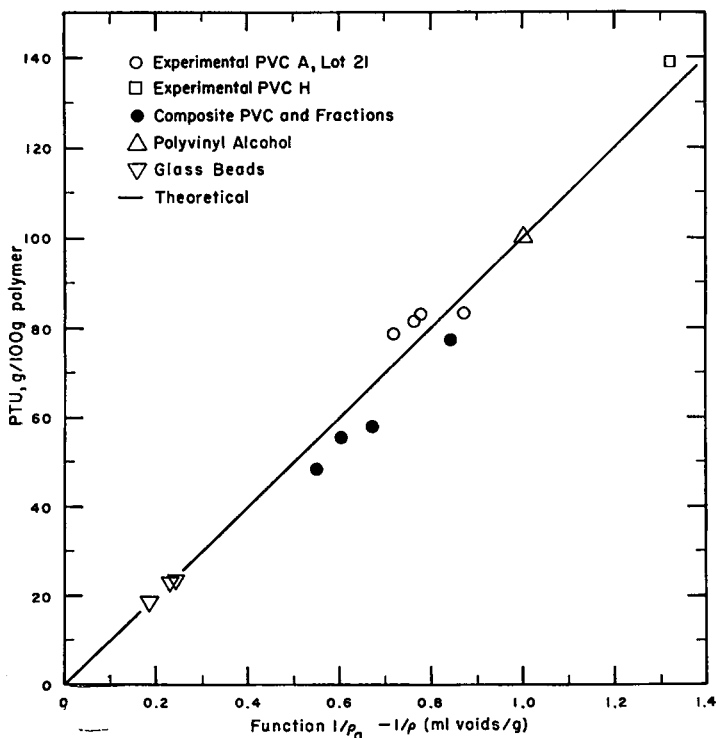


Fig. 2. Theoretical and experimental PTU.

TABLE II
Summary of PTU Parameters

Material	Mesh size	Average diameter d , μ	$1/d$	ρ_p , g./cm. ³	ρ , g./cm. ³	v , %	Closed voids, %	PTU	
								Experimental (vibrated)	Calculated ^a
Glass beads	-325	36	0.0278	1.63	2.60	37.3	—	22	23
	-230 +270	59 (53-62) ^b	0.0169	1.615	2.60	37.9	—	22	23
	-120 +140	115 (105-125)	0.00870	1.73	2.60	33.4	—	19	20
Experimental PVC A lot 21,		83.8	0.0119	0.65	1.30	50.0	7.8	81	76
Fractions:	0.60 μ	30	0.0333	0.60	(1.30)	53.9	7.8	89	89
	"-200 waste"	67 (60-74)	0.0149	0.68	1.33	48.9	5.7	79	71
	-200 +230	68	0.0147	0.65	(1.30)	50.0	7.8	—	76
	-170 +200	81 (74-88)	0.0123	0.64	(1.30)	50.8	7.8	—	78
	-150 +170	97 (88-105)	0.0103	0.65	(1.30)	50.0	7.8	—	76
	-100 +150	127 (105-149)	0.00787	0.64	1.28	50.0	9.2	82	77
	-80 +100	163 (149-177)	0.00613	0.61	1.30	53.1	7.8	83	86
		—	—	0.69	1.30	47.0	7.8	58	67

PVC Composite

Fractions:

-325	22 (0-44)	0.0454	—	—	—	—	—	—	—
-70 +325	49 (44-63)	0.0204	—	—	—	—	—	—	—
-250 +270	58 (53-62)	0.0172	0.71	1.38	48.6	2.1	—	—	68
-200 +250	68 (62-74)	0.0147	0.78	1.37	43.0	2.8	49	—	54
-150 +200	90 (74-105)	0.0111	—	—	—	—	—	—	—
-100 +150	127 (105-149)	0.00787	0.73	1.31	44.3	7.1	56	—	60
-80 +100	153 (149-177)	0.00654	ca. 0.68	1.26	46.0	10.6	—	—	67
-65 +80	194 (177-210)	0.00515	0.60	1.22	50.9	13.5	78	—	84
-60 +65	230 (210-250)	0.00435	—	—	—	—	—	—	—
-48 +60	274 (250-297)	0.00365	0.51	1.16	56.0	17.7	—	—	109
Pilot plant PVC J	—	—	0.475	1.27	62.6	9.9	139	—	130
Polyvinyl alcohol	—	—	0.55	1.33	—	—	100	—	105

^a $PTU = 98.6[(1/\rho_e) - (1/\rho)] = (98.6/\rho) \nu / (1 - \nu)$.

^b Values in parentheses are dimensions of sieve openings.

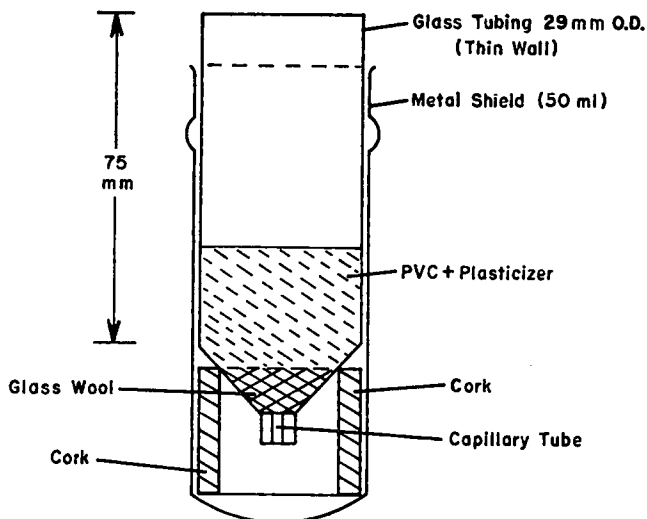


Fig. 3. Centrifuge tube and shield for measuring irreversible PTU.

ticizer within pores on individual particles, the irreversible component of cold PTU. A successful test must be simple, accurate, reproducible, and invariant to small changes in conditions.

Following unsuccessful trials of suction on a filter crucible, a centrifuge technique was successfully developed for removing excess DOP. The centrifuge can exert forces on the order of 100 G. to drive all excess liquid out of the polymer contained in a filtering tube, and force is applied regardless of whether or not the liquid forms a seal. It was found that a suitable sample holder could be prepared by drawing down a glass tube and sealing on a short length of capillary tubing. The entrance to the capillary section is filled with a small pad of glass wool, and PVC and plasticizer are mixed inside the tube (Fig. 3). The tube and its contents are then centrifuged to constant weight. (An International clinical centrifuge, No. 400 Series, equipped with four 50-ml. metal shields is used.) At practical speeds the time required to attain equilibrium is usually about one hour.

A simple experiment with glass beads and excess plasticizer sufficed to prove that the centrifuge drives out all interparticle plasticizer. After 38 min. only 2 and 1 PTU units, in duplicate runs, remained behind.

An analysis of variance showed no significant effect for DOP/PVC ratio in the charge (all ratios being large enough to provide initial filling of all voids), or for centrifuge speeds from 900 to 1700 rpm. The effect of tube size was found to be slightly significant. In any case the differences noted are small in comparison with the differences among polymers, and are apparently random in sign.

Comparison of average results from the centrifuge (29-mm. tubes) and suction methods shows very close agreement between methods for polymers A and B (Table III). The difference between methods for polymer P

are of the order of 20 PTU units retained and suggest that the suction treatment may not be severe enough to remove all the reversible DOP from blotter-type polymers.

TABLE III

	DOP Retained, PTU Units	
	Centrifuge	Suction
Experimental PVC, Type A	20	21
Commercial PVC, Type B	32	32
Commercial blotter PVC, Type P	68	87

On the basis of the results described above, the centrifuge method with 29-mm. centrifuge tubes was adopted as standard. Centrifuged speeds of 1300 rpm and a 200/100 ratio of DOP to PVC were chosen. Complete directions for performing this test are given in Appendix II.

One further experiment was performed to demonstrate the additive nature of the test with a mixture of different polymers.

All test results support the evidence that this method indicates a fundamental physical property of a polymer, the irreversible component of cold PTU, which must be reliably measurable before proceeding with a study of cold preblending differences.

Hot PTU Test

It was recognized early that a high temperature coefficient of PTU is important for hot dryblending performance.² Furthermore, PTU was seen to become time-dependent at high temperatures. At constant temperatures from 167 to 200°C., values of PTU determined at successive intervals increased rapidly at first, and then tended to level off. At higher temperatures, a further rise toward complete solubility was noted. It is desirable to retain a form of PTU test for hot dryblending behavior, both for consistency with the cold PTU tests and also to benefit from the simplicity of the techniques. After some experimentation, a method was adopted in which 5.00 g. of polymer is held in a 1/2-pt. metal can immersed in a constant temperature oil bath, and DOP is added from a heated buret and mixed in with a spatula. As in the cold PTU test, the end point is the condition at which the mix is barely fluid. An isothermal PTU-time curve is determined from a series of alternating steps: (1) titrating to a PTU end-point, and (2) allowing the titrant to soak into (swell) the PVC.

This method was completely standardized in a series of experiments with an experimental PVC Type A, lot 98, with the oil bath set at 185°F. The variables studied were time intervals between titration end points, and initial temperature conditions (hot or cold) of polymer and plasticizer. Experience showed that the least time in which the first end point could be attained, under the prescribed conditions of the test, was about 3 min. With hot (i.e., preheated) PVC and hot DOP, there is a steady upward dis-

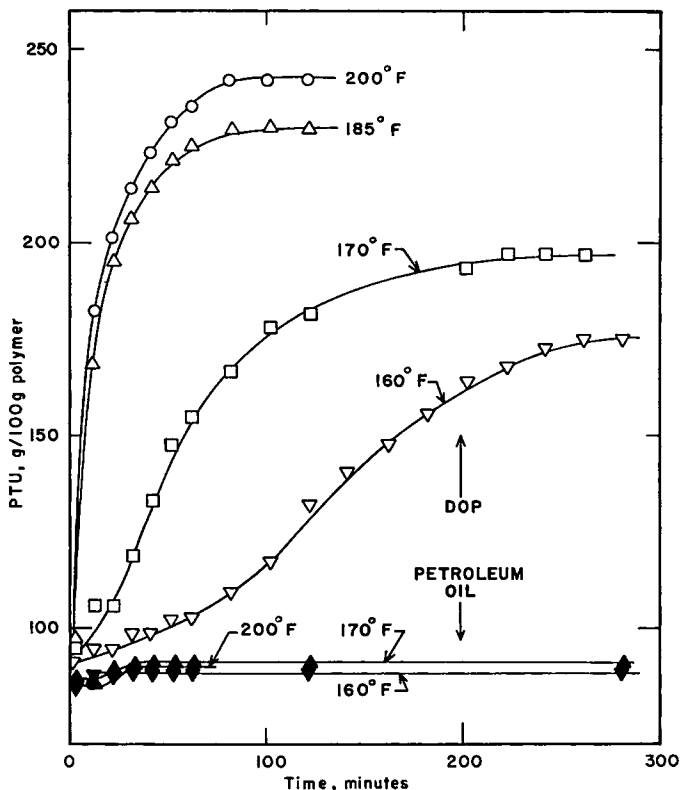


Fig. 4. Typical hot PTU isotherms (polymer A, lot 100).

placement of the curves as the time intervals are shortened between remaining end points from 40 to 10 min. Presumably, a curve for the simplified condition in which DOP is always maintained at the PTU end point level, corresponding to infinitely small time intervals between additions, would lie somewhat higher. However, the condition of 10-min. titration intervals offers the closest practical approach.

Tests of the influence of temperature of polymer (PVC) and plasticizer (DOP) before mixing showed that cold DOP gives values of PTU well below those of a truly isothermal experiment, while the initial state of the PVC has no significance. Therefore, heated DOP and PVC and 10-min. titration intervals (after the first titration) were adopted as standard conditions and used in all further investigations. From a statistical analysis of replicate runs, the standard deviation of PTU in this test is 4.8 units; it does not change significantly with time.

Isotherms for another PVC (Type A, lot 100) at 160–200°F. clearly illustrate the postulated components of PTU, as shown in Figure 4. The isotherms for DOP plasticizer show typical features of absorption, including a short initial rise, followed by an asymptotic leveling off to a final value. The curves for mineral oil at different temperatures, ranging from 84 to

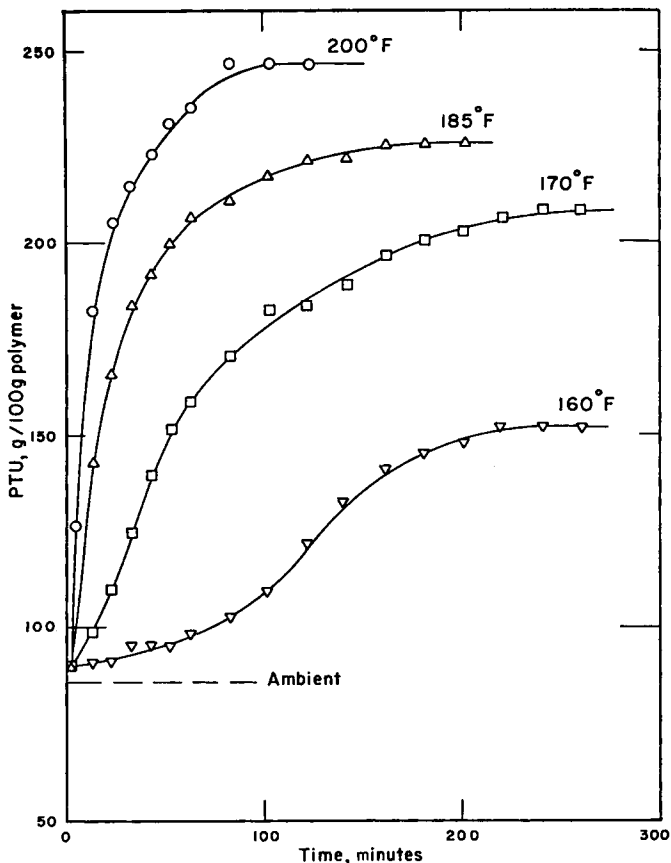


Fig. 5. Typical hot PTU isotherm (polymer A, lot 98).

91, are essentially constant and equal to the cold PTU with DOP (90). Mineral oil and DOP differ chemically, and differ in that DOP is absorbed by PVC and mineral oil is not. For these reasons, the observed constant PTU must represent a nonabsorptive (i.e., geometrical) effect. As additional evidence, (1) neither cold PTU nor hot PTU with mineral oil changes with time, and (2) the extrapolated, zero-time hot PTU (for DOP), PTU_0 , has the same value. In brief,

$$\text{Geometrical PTU} = \text{cold PTU} = \text{hot mineral-oil PTU} = PTU_0$$

Figure 5 shows hot PTU isotherms for Type A, lot 98 PVC at four temperatures. Figure 6 shows the derived plot of $\log [1/(1-p)]$ versus time. Each line contains an extended straight portion, in agreement with eq. (5).

It is concluded that the hot PTU test approaches an absolute experiment in the kinetics of absorption, in that: (a) no mineral oil is taken up at the high temperature, and therefore, PTU_0 , the geometrical contribution to

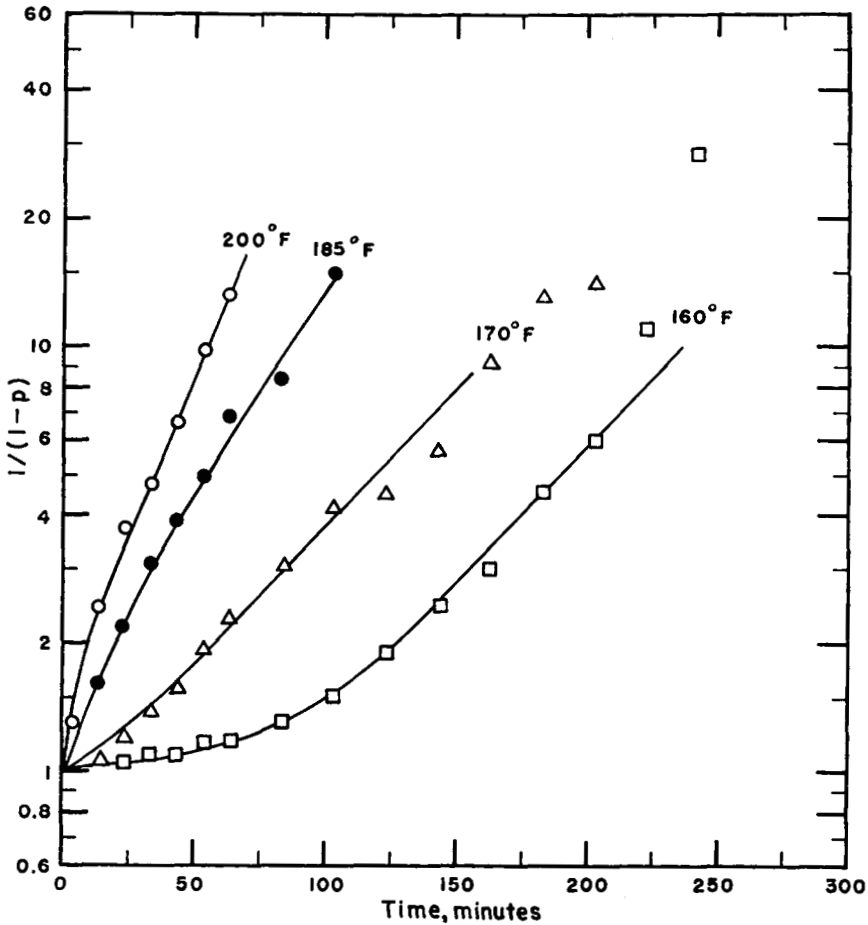


Fig. 6. Reciprocal of fractional unconsumed PTU vs. time for polymer A, lot 98.

PTU, is practically unaffected by temperature *per se*; (b) following a short induction period, the plot of $\log [1/(1-p)]$ versus t is substantially linear; (c) the rate and extent of hot PTU increases with temperature; (d) data on other specimens of PVC (tabulated later) show that $PTU_F - PTU_0$ is roughly constant for all, indicating the attainment of thermodynamic equilibrium; (e) the induction period denotes initial resistance of the skin of the particles to penetration by plasticizers.

The following sections will show that the test also distinguishes good and poor dryblending polymers.

TESTING OF TYPICAL POLYVINYL CHLORIDES

Physicochemical Properties

An intercomparison of important physicochemical properties of commercial and experimental PVC's and their fractions supports the evidence for

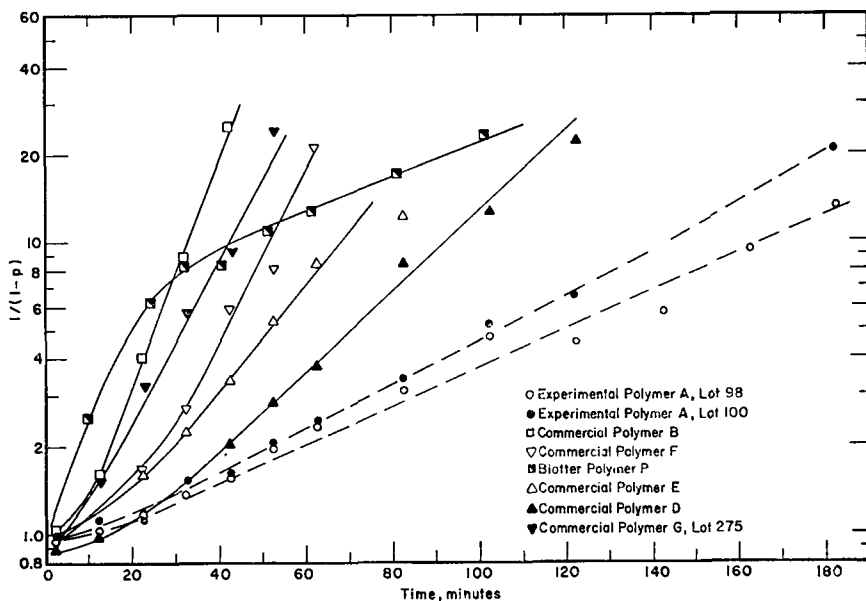


Fig. 7. Reciprocal of fractional unconsumed PTU vs. time for PVC at 170°F.

using cold and hot PTU as measures of preblending and dryblending performance.

Table IV summarizes the properties of commercial polymers from several manufacturers, and experimental polymer A. (Not all are representative of current manufacture, because some have been superseded.) The group includes typical examples of both good and poor dryblending and preblending behavior. Table V gives properties of fractions of commercial and experimental polymers, separated both according to particle size, by screening, and according to density, by sedimentation. Vibrated bulk densities and true densities are determined for these polymers and their fractions, and corresponding values for accessible voids and closed voids were calculated from these. For an indication of relative molecular weights, values of the intrinsic viscosity in tetrahydrofuran solution were determined on the various fractions and the parent polymers. Both hot and cold PTU tests were performed, and the tables summarize values of cold PTU (designated PTU_0), irreversible cold PTU by centrifuge, final hot PTU (PTU_F), and the half-life of hot PTU ($t_{0.50}$) at 170°F. (For brevity, only results for this temperature are shown, although some polymers were also tested at 160 and 185°F.)

Many resulting plots of $\log [1/(1-p)]$ versus time (Fig. 7), show well-defined straight portions, in agreement with eq. (5). Initial periods of induction or retardation appear at both 170 and 160°F. This behavior is believed to be due to surface resistance to penetration, or "shell effects" in the polymer. Blotter polymer P, with its spongy, irregular surface, is unique because it exhibits an initial period of acceleration instead of induc-

tion, followed by a slower absorption at values of $1/(1-p)$ above 7. This may be interpreted as a high surface receptivity, and microscopic observation confirms the extremely spongy appearance of the surface. (A later section shows that the induction period is also absent in a sample of polymer A whose surface has been torn apart by lengthy grinding.)

Activation energies calculated from the straight-line portions of each plot ranged from 5,000 to 50,000 kcal. For many polymers, the activation energy underwent a change of value in the region 160–185°F., indicating some change in the mechanism of absorption.

Correlation with Parameters of Cold PTU

It is reasonable to test variations of cold PTU both with surface (or particle size) and true density, as properties of particles which might be expected to influence PTU. Fractionation by screening and sedimentation provides natural series of values of both properties. As a simple estimate of the surface area of irregular particles, the following expression, which holds exactly for certain regular shapes, may be used:

$$\text{Specific surface} = 6/\rho = d$$

where d is the particle diameter. Considering all series of screen fractions in Table V and also in Table II, there is no consistent variation of PTU with surface or with diameter, within series. Likewise, there is no variation for the glass beads, from 36 to 115 μ diameter. Exceptionally, certain series show somewhat increased values of PTU at large or small particle sizes. These are attributed to: (a) large particles formed from irregular clustering of small, regular particles, with consequent increases of void space, and (b) the "spreading effect" in many fine powders ($d < 30 \mu$), attributed to electrostatic repulsion.

There are no consistent trends of PTU with ρ or with the derived quantities ν and closed voids. Similarly, PTU appears unrelated to intrinsic viscosity (which does not in any case show a large spread of values within series).

It is concluded that eq. (3) expresses the only general relation of PTU to other physicochemical properties.

Although Table IV suggests that the occurrence of closed voids might correlate with irreversible cold PTU in commercial polymers, this indication is not confirmed by Table V. Otherwise, irreversible cold PTU does not correlate, either with total cold PTU or with other physicochemical properties of the polymer alone. There does appear to be some correlation with hot PTU, as discussed in the following paragraphs.

Correlation of Hot PTU

The behavior of hot PTU with respect to the factors of particle size and shape and density appears to parallel that of irreversible cold PTU.

However, closer examination of some cases shows not so much a true lack of correlation as a conflict of factors which are not adequately described by

TABLE IV
Basic Properties of Commercial and Experimental PVC

Polymer	Bulk density (vibrated)		Compressed density	Interstitial volume	Closed voids, %	Experimental cold PTU (DOP)	
	ρ_v , g./cm. ³	True density ρ , g./cm. ³				v , %	Original ^a
Experimental A, lot 98	0.67	1.30	1.40	48.5	7.1	86	17
Experimental A, lot 100	0.66	1.29	1.40	48.9	7.9	90	19
Commercial D	0.70	1.19	1.40	41.2	15.0	75	22
Commercial E	0.67	1.20	1.40	44.1	14.3	84	27
Commercial F	0.68	1.24	1.40	45.2	11.4	78	26
Commercial G	0.62	1.15	(1.40)	46.1	17.8	87	33
Commercial B	0.64	1.16	1.40	44.9	17.1	91	32
Commercial Blotter P	0.40	1.19	(1.40)	66.4	15.0	178	68

^a Not determined on vibrated specimens. These values are not expected to agree with (lower) calculated values.

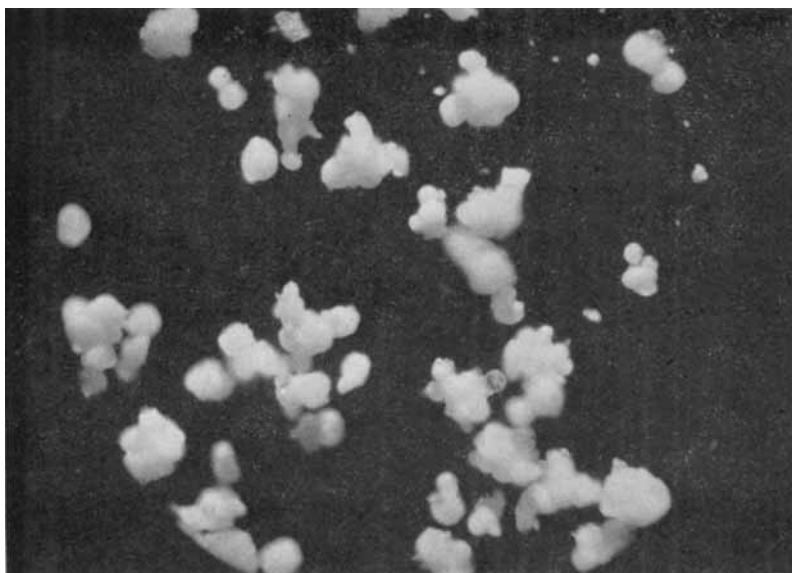
TABLE V. Properties of Production and Experimental PVC and Their Fractions

Polymer	Method of separation	Fraction	Fract- tion of total, %	Density, g./cm. ³		Voids, % Ac- ces- sible Closed	In- trinsic vis- cosity [η], dl./g.	Irrev. cold		PTU parameters at		$t_{0.50}$, min.	
				True	Bulk			PTU	PTU ₀	PTU _F	PTU ₀		
Experimental A, lot 177	Screening	Total	100	1.29	0.65	51	0.69	20	83	179	96	70	
		-60 +80	8	1.33	0.60	55	0.69	20	91	194	103	42	
		-100 +150	26	1.32	0.66	50	—	19	83	194	111	80	
		-170 +200	3	1.34	0.70	48	—	19	—	—	—	—	—
		-250 +325	1	—	—	—	0.69	20	—	—	—	—	—
	Sedimentation	1.29-	13	1.34	0.72	46	—	20	71	145	74	104	
		1.26-1.29	38	1.30	0.63	52	—	17	87	183	96	94	
		1.24-1.26	22	1.31	0.62	53	—	21	91	194	103	61	
		1.22-1.24	14	1.26	0.63	50	—	20	91	190	99	61	
		1.10-1.22	12	1.28	0.61	52	—	—	91	202	111	55	
Experimental A, lot 30-307	Screening	Total	100	1.32	0.74	44	0.65	20	71	130	59	90	
		-60 +80	23	1.37	0.72	47	0.63	13	71	122	51	123	
		-100 +150	27	1.38	0.74	46	0.63	13	75	118	43	114	
		-170 +200	7	1.36	0.74	46	0.64	15	79	145	66	103	
		-200 +250	3	—	—	—	—	—	79	156	77	120	
	-250	5	1.37	—	—	—	2	—	—	—	—	—	
	Screening	Total	100	1.28	0.44	66	0.65	49	154	262	108	22	
		+32	17	1.29	0.43	67	—	44	83	206	123	26	
		-32 +48	4	1.31	—	—	0.67	—	—	—	—	—	
		-200 +250	8	—	—	—	—	—	138	255	117	21	
-250 +325		20	1.31	0.47	65	0.60	50	138	259	121	23		

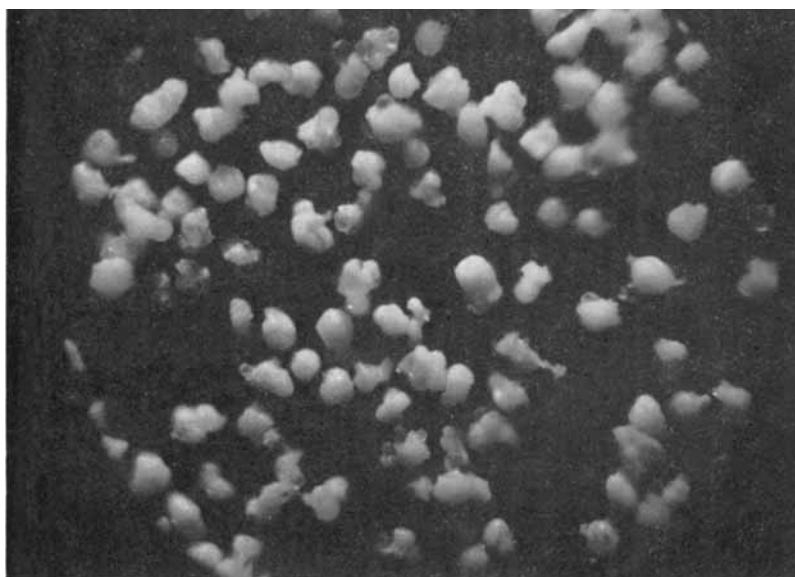
Experimental H,
lot 30-220

Screening	Total	100	1.32	0.33	75	6	—	71	217	308	91	16
	-60 +80	21	1.35	0.32	76	4	—	70	245	278	133	30
Sedimentation	-100 +150	15	1.37	0.38	72	2	—	64	181	281	100	15
	-170 +200	4	1.39	0.44	68	1	—	55	150	243	93	27
	-250	4	1.29	0.48	63	8	—	50	130	225	95	22
	1.36	13	1.37	0.33	76	2	—	74	221	327	106	23
	1.35-1.36	37	1.31	0.34	74	6	—	77	213	331	118	36
	1.34-1.35	19	1.31	0.34	74	6	—	74	209	308	99	21
Commercial G, lot 42	1.31-1.34	7	1.30	—	—	7	—	76	205	331	126	32
	1.25-1.31	8	1.21	0.35	71	14	—	70	181	299	118	39
	-1.25	6	1.07	0.34	68	24	—	62	158	289	131	36
	Total	100	1.29	0.67	48	8	—	32	87	202	115	36
Screening	-60 +80	27	1.31	0.61	53	6	—	32	79	194	115	27
	-110 +150	17	1.36	0.63	54	3	—	33	87	198	111	22
Sedimentation	1.125	27	1.34	0.65	52	4	—	30	79	183	104	38
	1.10-1.125	11	1.33	0.65	51	5	—	31	83	198	115	38
	1.06-1.10	35	1.25	0.64	49	11	—	33	83	189	106	36
	1.03-1.06	14	1.23	0.62	50	12	—	35	83	202	119	39
Commercial G, lot 30-289	-1.03	11	—	—	—	—	—	37	87	202	115	38
	Total	100	1.30	0.54	58	7	—	45	83	206	123	37
	1.295-	25	1.37	0.52	62	2	—	51	122	240	118	37
	1.27-1.295	20	1.37	0.48	65	2	—	49	91	232	141	48
Sedimentation	1.215-1.27	21	1.33	0.49	63	5	—	44	67 ^a	168	99	34
	1.15-1.215	22	1.20	0.48	60	14	—	51	51 ^a	149	98	47
	-1.15	13	1.16	0.45	61	17	—	32	39 ^a	122	83	48

^a Approximate.



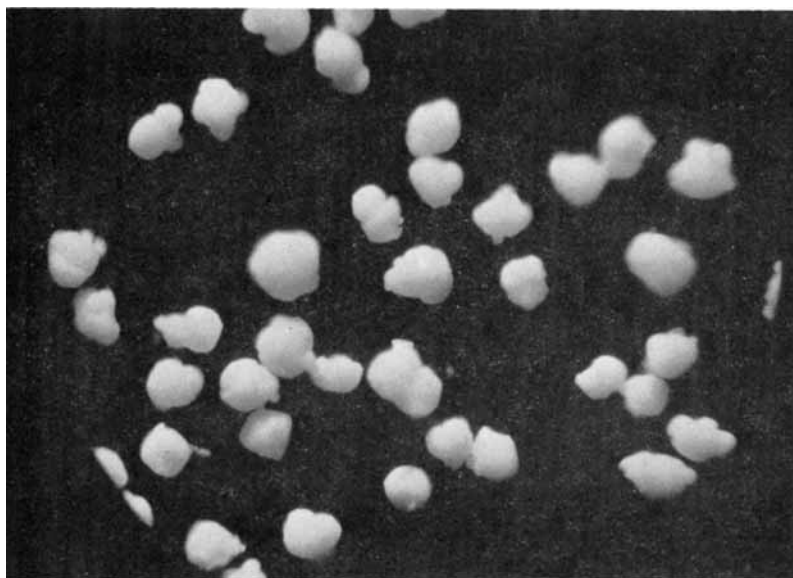
(a)



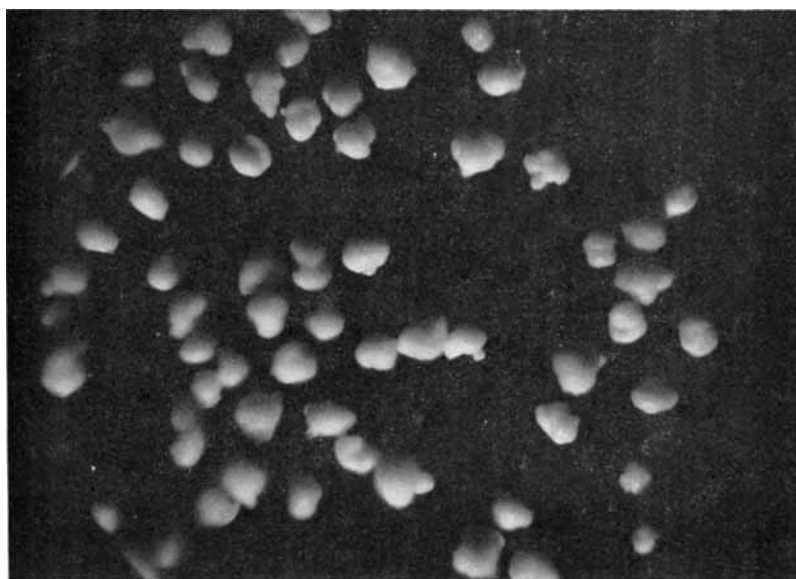
(b)

Fig. 8. Photomicrographs of polymer A sieve fractions: (a) - 65 +80; (b) -150 +20.

simple tests. An example is the irregular variation of hot PTU behavior in different series of screen fractions. Normally, in the absence of complicating factors, fine particles would be expected to swell more quickly than coarse ones because swelling rates vary directly with surface area for similar surfaces. The figures in Table VI show fractions of commercial



(a)



(b)

Fig. 9. Photomicrographs of polymer B sieve fractions: (a) $-65 + 80$; (b) $-150 + 200$.

polymer B to exhibit normal trends, and fractions of polymer A lot 100 to behave abnormally.

The most reasonable explanation for the anomalous behavior of polymer A is that the surfaces of the coarse of fine fractions are different. Certainly their shapes are different, as shown by the photomicrographs of Figure 8.

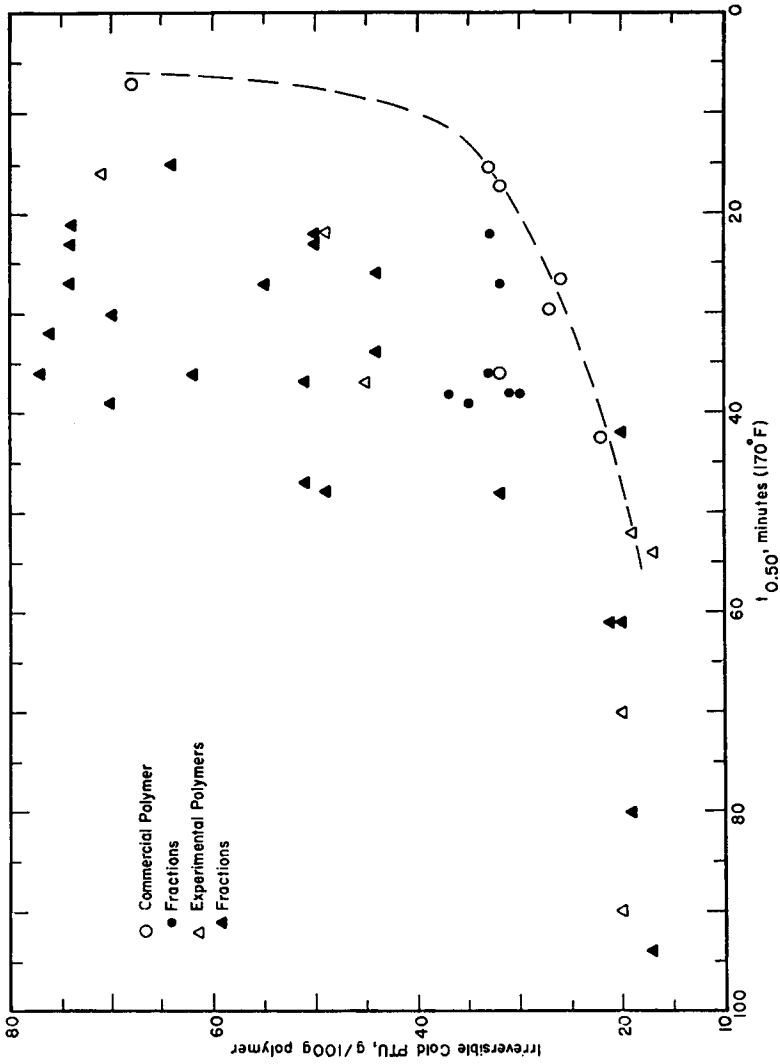


Fig. 10. Relation of cold preblending and hot dryblending.

The $-65 +80$ fraction consists almost entirely of clusters. In the $-150 +200$ fraction, about half of the particles are clustered and half are of a roughly spherical shape. In contrast, particles of coarse and fine polymer B, as shown in Figure 9, appear to have the same roughly spherical shape. The shape difference in A is confirmed by the slightly higher reversible cold PTU of the coarse fraction.

The data show no clear-cut effect of molecular weight and its distribution on hot PTU; more refined experiments are needed to separate this factor from many other influences.

When the polymers and fractions of Tables IV and V are rated for speed

TABLE VI

Polymer	Screen fraction	$t_{0.50}$, min.	PTU ₀	Irreversible cold PTU
A, lot 100	Original	53	90	19
	Coarse ($-65 +80$ mesh)	47	87	18
	Fine ($-150 +200$)	72	83	18
B	Original	16	91	32
	Coarse ($-65 +80$)	16	91	—
	Fine ($-150 +200$)	11	91	—

of hot PTU and for irreversible cold PTU, there is an unmistakable correlation, in spite of much scatter. This is shown on Figure 10, in which irreversible cold PTU is plotted against $t_{0.50}$, the half-life of PTU at 170°F ., for all original polymers and fractions. This implies that a good hot dryblending polymer is thus a good cold preblending polymer. Therefore, some factors which promote hot dryblending performance should also improve cold preblending.

Microscopic Observation

In order to determine any visible differences in commercial PVC's which correlate with differences in PTU test results, all polymers tested were examined under the microscope. The ratings, according to either hot PTU or irreversible cold PTU, had no consistent relation to particle shape or size, or to the number of observable bubbles. However, there is a trend in appearance of surface ranging from shiny for polymer A, the poorest dryblending and preblending polymer, to dull for P, the best. The particles of polymer P are exceptional in having an almost spongelike quality, and hence a very high surface area.

RELATION TO COMMERCIAL APPLICATIONS

Final verification of the concepts of hot dryblending and cold preblending must depend upon processing experience which is necessarily somewhat qualitative. However, some examples may be cited. The present

studies, for instance, were occasioned by the need to improve the dryblending and preblending quality of polymer A, an example of an unsatisfactory PVC for marketing. On the other hand, polymer P was known to be an efficient blotter because it was used in innumerable formulations to dry up the blend. This wide difference is reflected in differences of the parameters of hot and cold PTU. Between these extremes lie the other commercial polymers of Table IV, rated as shown in Table VII on the basis of dryblending behavior. The rating is seen to correlate well with $t_{0.50}$, and also with irreversible cold PTU. Results of the laboratory Banbury test are included for comparison; evidently this is not an especially sensitive or reliable criterion.

TABLE VII

Polymer	Rating	$t_{0.50}$, min.	Irreversible cold PTU	Banbury time, sec.	
				To blending	Total
Experimental A, lot 100	Poor dryblend	54	19	45	205
Commercial D	Poor dryblend	42.5	22	0	140
Commercial E	Satisfactory dryblend	29.5	27	10	140
Commercial F	Satisfactory dryblend	26.5	26	0	165
Commercial G, lot 275	Satisfactory dryblend	15.3	33	—	—
Commercial B	Satisfactory dryblend	17.3	32	0	160
Commercial P	Blotter	7	68	0	165

Another comparison between an outstanding blotter and cold preblending polymer (Q) and one which performs less well (R) gives the differences in properties listed in Table VIII.

TABLE VIII

Polymer	Bulk density, g./cm. ³		PTU ₀	Irreversible cold PTU	Particle size
	Normal	Vibrated			
Q	0.31	0.40	185	88	86% +230 -100
R	0.30	0.44	180	54	89% +230 -80

Evidently the critical difference is the higher irreversible cold PTU of polymer Q. Significantly, all blotter polymers on the market displayed the particle geometry needed for high adsorption. Thus, a survey of 13 commercial blotter polymers² showed the ranges of properties given in Table IX.

Although values of cold PTU are generally higher, and values of bulk density are generally lower in blotter polymers than in all-purpose polymers (as

TABLE IX

Cold PTU	Irreversible cold PTU	Bulk density, g./cm. ³ ^a
116-244	45-95	0.23-0.41

^a By ASTM D-1182-51; not vibrated.

would be expected), there is some overlap. What is uniquely characteristic is the very high values of irreversible cold PTU.

ROLE OF PROCESSING TECHNIQUES

Mechanisms of Control of PTU Parameters

Particle geometry acts through the agency of irreversible cold PTU to improve cold preblending. Geometry, which is understood to include all the factors of particle size, shape, and distribution, also controls density and porosity. Polymer particles may be prepared in many shapes, including clusters, sponges, impervious spheres, hollow spheres, and others, and in all ranges of size and size distribution. In these circumstances, there is no simple relation of good preblending behavior to bulk density, for example. The form of relation depends upon the type of particles, as the experiments reported earlier have confirmed.

To aid visualization, the basic mechanisms of geometrical (cold) changes in particles are listed in Table X. The possible effects of each of the variables cold PTU, its reversible and irreversible components, bulk density, true density, and volume per cent voids are also indicated. The mechanisms include the following processes entailing no change of gross particle outline: (1) closing over pores, (2) filling in pores and rounding shoulders, (3) opening previously closed voids. Others in which the external outline is changed are: (4) a uniform shrinking in on closed voids, (5) approach to the spherical shape, and (6) fracture, with exposure of internal voids. It is believed that these mechanisms (including the reverse of each), alone or in combination, may account for all possible changes in particle geometry.

The tabulated mechanisms may be considered to be either changes which take place in manufacture, or also comparisons of two separate polymers.

In manufacturing, an increase of irreversible cold PTU is seen to result from opening previously closed voids to make retentive pores, from breaking up particles to expose inner voids (increase in number of retentive pores), or from expansion of particles without changing the relative external shape (increase of capacity of existent pores). However, if a low bulk density is also desired the last-mentioned mechanism must be emphasized. The table also shows how attempts to improve preblending by a simple, indiscriminate increase of cold PTU may be misleading. If PTU is increased by simple clustering, for example (which may be considered the reverse of fracture), the irreversible component is actually decreased.

TABLE X
Basic Mechanisms of Change of Particle Geometry

Possible mechanism	Change in parameters ^a				
	Total PTU	PTU (irreversible)	PTU (reversible)	ρ_a	ν
1. Closing over pores; no change of gross outlines	(-)	(-)	0	0	(-)
2. Filling in pores and rounding shoulders; no change of gross outlines	0	(-)	+	0	0
3. Opening previously closed voids; no change in gross outlines					
(a) To make retentive pores ^b		+(a)	0(a)		+
(b) To make nonretentive cavities		0(b)	+(b)		0
(c) To make either					0
4. Uniform shrinking in on closed voids; no change in external shape	+	(-)	(-)	+	+
5. Change of gross outline to approach spherical shape	(-)	0	(-)	+	0
6. Fragmentation	+	+	+	(-)	+

^a Here + denotes an increase, - denotes a decrease, and 0 denotes no change.

^b 3a is the reverse of 1.

For hot PTU, the measure of hot dryblending quality, there is no clear relation to observable particle geometry. Undoubtedly, hot PTU is influenced by some of the same factors which control irreversible cold dryblending. However, further understanding of the chemical nature of the surface is needed, in terms of molecular-scale influences.

The sections which follow discuss particular methods of regulating the preblending quality by control of particle geometry in manufacture.

Recipe and Reactor Factors

In suspension polymerization, conditions within the reactor interact with chemical factors of the recipe to determine the particle geometry.

The conditions for stabilizing suspensions during agitation were demonstrated by Winslow and Matreyek,⁷ using mixtures of divinylbenzene and ethylvinyl benzene suspended in water and stabilized by polyvinyl alcohol. They showed how agitation, dispersants, viscosities, and interfacial tension cooperate to determine the ultimate size, distribution, and extent of agglomeration of polymer particles. The suspension represents a dynamic balance between droplets, formed by shearing of monomer which is then dispersed by surface tension, and aggregates formed by collision. Chemical stabilizers or protective colloids minimize the tendency to aggregation by forming protective films on the droplets. By a proper selection of recipe and operating factors, the authors produced extremely uniform spherical beads of polymer.

Similar mechanisms operate in the suspension polymerization of polyvinyl chloride. In addition, the final particle shape is influenced by the extremely high shrinkage of polymerization (about 35%) and by the volatility of unreacted monomer, which must find paths of escape.

A separation and evaluation of the effects of the many factors which operate here would be extremely difficult. In practice, the conditions for the production of particles of the desired geometry must be determined empirically. The record of some experiments may be cited. Early pilot plant preparations of PVC in a specific 300-gal. reactor, in which only the agitator speed and level of colloid were varied, showed the pattern of variation of average PTU with agitator speed and colloid level given in Table XI.

TABLE XI

Colloid level, parts/100 parts monomer	PTU			
	123 rpm	136 rpm	141 rpm	166 rpm
0.07	—	110	—	96
0.08	92	122	113	118
0.10	94	112	105	127
0.12	63	101	—	119
0.14	—	61	—	—
0.16	—	103	—	102
0.20	—	54	—	131
0.24	—	—	—	72

As the colloid concentration increased, at a given agitation intensity, the PTU value appeared to increase to a maximum, then decreased abruptly to a minimum. At this low point the product consisted of smooth, spherical, mostly translucent particles. The batches made at 136 rpm indicated that this minimum point is followed by a range of high PTU's where clusters of small spheres are produced, having low bulk densities. A further increase in colloid concentration gave low PTU's and smooth spheres again.

The chemical nature of the colloid used is also of extreme importance in determining particle geometry. It has also been established by extensive pilot plant investigations that many additional variables must be considered, including temperature, the composition, level and purity of other ingredients of the recipe, the order of addition of these ingredients, and other factors.

Partial Conversion and Recipe Changes

One simple, direct means of producing a polymer with very high takeup and retention of plasticizer is to stop the polymerization at low conversion, and quickly to blow down the reactor charge.^{2,8} For example, one series of pilot plant runs showed low conversions (<50%) to give polymers having extremely high values of PTU (~300 to 500) and of irreversible cold PTU (>100). Those relations are plotted in Figures 11 and 12. The abrupt change of irreversible cold PTU at about 50% conversion corresponds to a change in consistency of the reactor charge from a stable cream to a quick-breaking suspension. The particle size distribution also

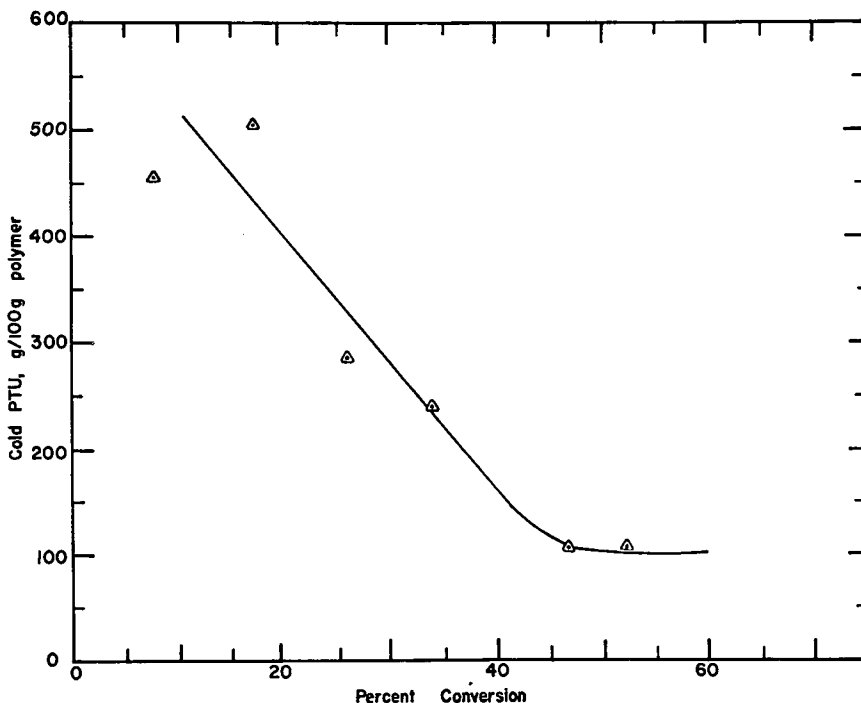


Fig. 11. Effect of conversion on total cold PTU.

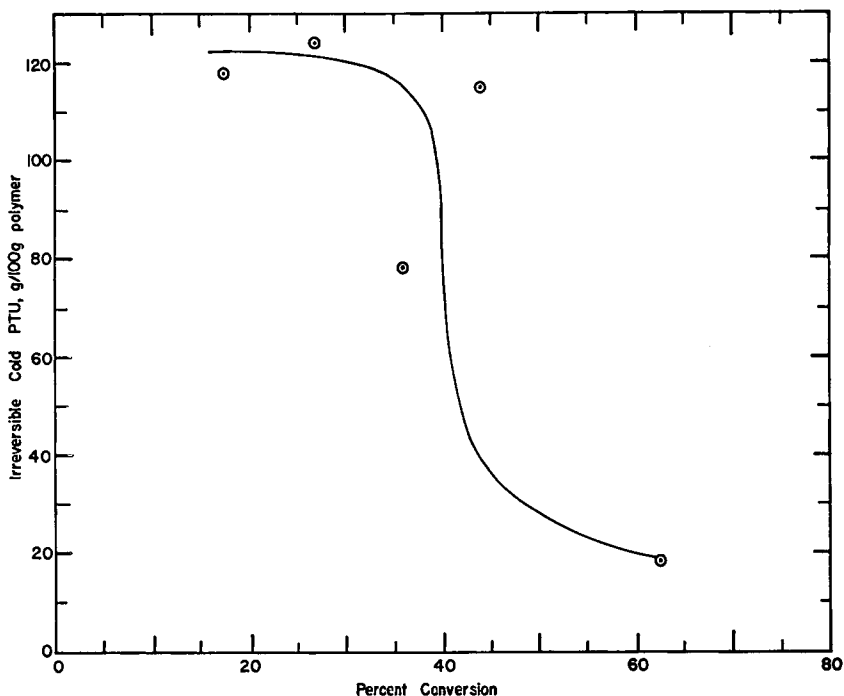


Fig. 12. Effect of conversion on irreversible cold PTU measured by centrifuge.

changed rather abruptly at the same time, in that the large particles produced at low conversion almost disappeared at high conversion. Bulk density increased steadily with conversion throughout the series.

Further studies confirmed that the extreme porosity of the low-conversion polymers was produced by monomer vapor pressure, being very sensitive to such variables as the final reactor temperature and pressure, and the blowdown pressure. It was also observed that low agitation speed during the run favors blotter properties.

Other striking modifications of the parameters of PTU may be made by chemical changes in the recipe. Blowing agents, latex seeds, chain-transfer agents, and other ingredients are effective in special ways. Evidently the development of a PVC to meet certain specifications must take account of an extremely large number of chemical factors and process variables and it is certain that most of these interact heavily.

Grinding

Grinding alters the surface, size, and configuration of particles. In grinding commercial polymer A, there may be further complication due to the change in character of particles of the original polymer with size (Fig. 8). A systematic separation of all these effects would require many experiments. Only a few preliminary experiments have been performed, but they show striking results.

First a quantity of polymer A, lot 100, was ground for six days in a ball mill. The final product was discolored, and appeared ragged under the

TABLE XII

Polymer	Particle size	$t_{0.50}$, min.	Irreversible cold PTU
Unground	-150 +200	72	18
Ground	-150 +200	1	56

microscope. The feel of the original PVC was gritty; that of the ground product was soft, like face powder. The Sharples Micromerograph indicated an appreciable shift in mean particle size with grinding, although sharp maxima occurred at 80μ in the curves for both the unground and ground samples. Evidently the original aggregates have a strong tendency to break up into particles of 80μ diameter, even from the shock of dispersion in the Micromerograph, with the number of particles reduced to this size depending on the degree and extent of attrition.

The hot dryblending behavior of the polymer, measured by the PTU test at 170°F ., was improved enormously by grinding. This is shown by the value of 4 min. for $t_{0.50}$, which is even lower than that of blotter polymer P (7 min.). The irreversible cold PTU was changed from 19 to 48. In order to distinguish the influence of grinding from effects of particle diameter or surface area, both unground and ground polymer of the same particle size range were compared. Comparison of the parameters of hot (170°F .) and irreversible cold PTU gave the values shown in Table XII.

The effects of less severe grinding were also explored, using both another

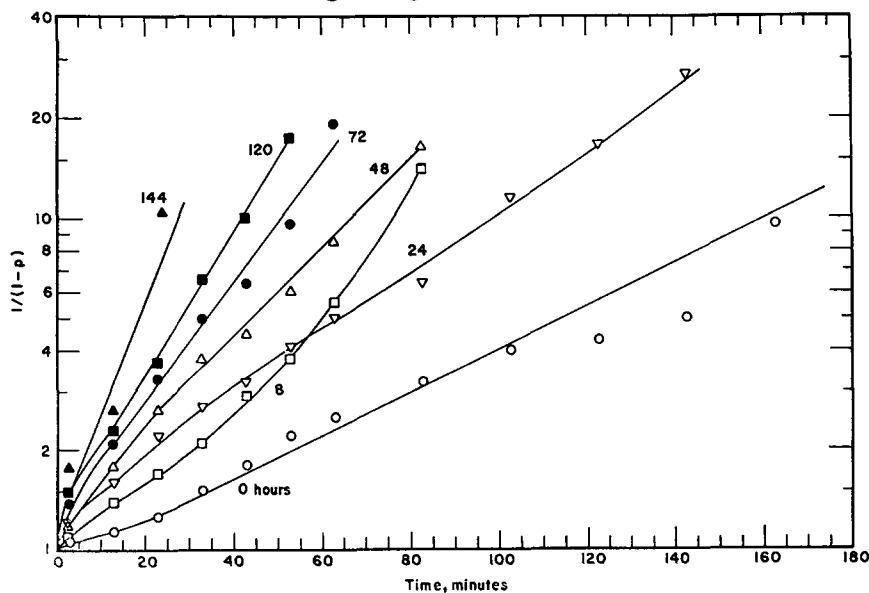


Fig. 13. Effects of grinding on hot PTU kinetics (polymer A, lot 98).

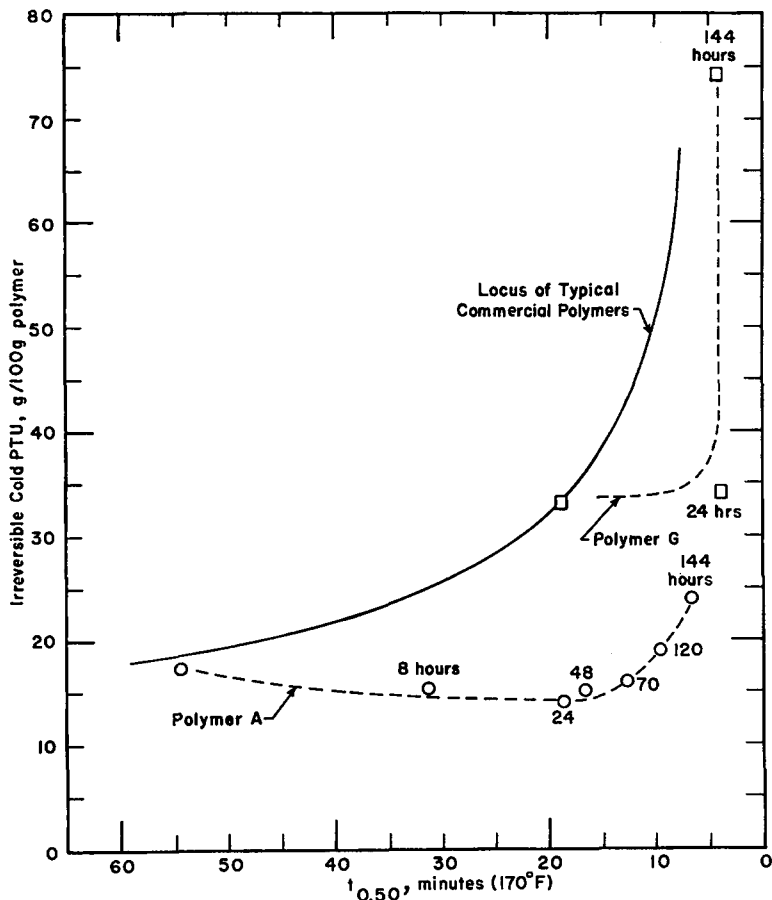


Fig. 14. Effect of grinding on parameters of PTU.

polymer A (lot 98) and polymer G (lot 275). Parameters relating to dryblending were measured at various intervals of grinding time. Qualitative observations of discoloration were also made; it became marked after 5 days with polymer A, and after 3 days with polymer G. The plots of $\log [1/(1-p)]$ versus time for hot PTU of the former are shown in Figure 13.

The progressive effects of grinding are shown on plots of $t_{0.50}$ versus irreversible cold PTU in Figure 14. The hot dryblending performance of both polymers improves immediately and continuously with grinding time. This improvement appears both as elimination of the induction period (attributed to skin effects) and also as an increase of slope. However, extensive grinding time is required before enough change occurs to improve the cold dryblending performance.

Differences between the polymers A and G are evident. Grinding reduces the cold PTU of the former but increases the PTU of the latter. The irregular clustered particles of A evidently break up into more regular spherical particles which pack more closely. Particles of G, which are nearly

spherical to begin with, break up on grinding to more irregular particles which pack less efficiently. Evidently drastic grinding is required (to the point where decomposition is noticeable) in order that new cavities and interstices be formed before cold dryblending performance is improved. There is also a steady rise with grinding time of $PTU_F - PTU_0$ for both polymers which may be indicative of either (1) a greater distortion of the more ragged particles at high degrees of swelling which would lead to poorer packing or (2) a partial solution of degraded low molecular weight material.

It can be concluded that grinding improves the dryblending performance of PVC, although the rate of improvement appears to be controlled by the nature of the polymer. Any practical use of grinding, however, must take account of the tendency to decompose and discolor. Adequate stabilization must be developed.

Classification

Fractionation, as by screening or sedimentation, is another possible means for improving polymer quality. However, the separation of fractions of desirable dryblending or preblending properties by these methods is not practically effective. The distribution of sizes or densities (e.g., in Table V) falls within too narrow a spread. Within this distribution, the changes of parameters of PTU are small, and often random.

GENERAL CONCLUSIONS

The investigations reported here have selected plasticizer takeup as a basic measure of the capability of polymer to accept plasticizer in formulations for calendaring, milling, forming and extrusion. The ability to form hot dryblends is measured by hot PTU, and the ability to form cold preblends is measured by irreversible cold PTU. Simple tests for all of these quantities have been established.

Results of all experiments on the variation of dryblending and preblending characteristics with processing conditions support one important general conclusion. Good quality in regard to both hot dryblending and cold preblending may be produced in the reactor under suitable conditions. On the other hand, post-polymerization treatment of an initially poor polymer can easily give its good hot dryblending performance, and treatment of a polymer initially of good quality can make it outstanding. However, preliminary laboratory studies indicate that cold preblending performance will remain unchanged or actually be impaired unless the treatment is severe enough to break up the original particles.

The mechanisms of cold and hot PTU which have been demonstrated in the course of this study help to explain these conclusions. The intraparticle pores which account for irreversible cold PTU are formed during the polymerization reaction by the shrinkage of monomer volume on polymerization, augmented by other factors such as amount and nature of colloid, agitation speed, speed of reaction, temperature, pressure, per cent con-

version, and escape of monomer. After polymerization is complete, any attempt to increase the volume of these pores requires drastic treatment, such as grinding. On the other hand, improvement of the hot dryblending properties merely requires removal of the surface skin, as by mild solvent treatment.

The authors are deeply indebted to G. M. Therneau for his painstaking laboratory work. Much experimental information was generously made available by the General Tire and Rubber Company, and the contributions of E. J. Serwan, W. J. Hanlon, W. C. Warner, W. L. Kollar, E. Pfau, A. L. Antonio, and others are gratefully acknowledged. The editorial advice of F. C. Price is also acknowledged with thanks.

APPENDIX I: COLD PLASTICIZER TAKEUP (PTU) TEST FOR PVC

Materials and Equipment

Materials required are a 10-ml. buret, with shortened tip to increase rate of flow; a titration stand with a glazed tile base or ringstand, clamp, and tile plate; a stiff, stainless steel spatula with blade $\frac{1}{2}$ to $\frac{3}{8}$ in. wide; a torsion balance; high quality, commercial DOP (di-2-ethyl-*n*-hexyl phthalate).

Procedure

The procedure is as follows. The buret is filled with plasticizer to the zero mark, and any spillage wiped up. A 5.0 ± 0.05 g. portion of clean, dry PVC powder is weighed out, and the PVC transferred quantitatively to the buret stand or tile plate directly under the buret.

Approximately 0.5 ml. of plasticizer is run out onto the polymer, and with the spatula, distributed throughout the resin. This step is repeated until the mass shows indications of becoming fluid. Near the flow point the rate of addition is decreased to 0.1 or 0.05 ml. at a time. The flow point (end point of the titration) is the point at which the mixture, when thoroughly wetted and mixed, will flow off the spatula. This point is arbitrary, but is reproducible with a little practice.

The PTU as parts by weight of plasticizer per hundred of polymer is then calculated by the formula:

$$\text{PTU} = \frac{\text{Volume plasticizer (ml.)} \times 100 \times \text{density of plasticizer (g./cm.}^3)}{5}$$

or

$$\text{PTU} = \text{ml. plasticizer} \times 19.7$$

APPENDIX II: CENTRIFUGE TEST FOR IRREVERSIBLE COLD PTU OF PVC

Materials and Equipment

Equipment required is: an analytical balance; an International Clinical centrifuge (No. 400 series) equipped for four 50-ml. metal shields; four

glass tubes (29 mm. o.d. \times 85 mm.) with a 10-mm. o.d. capillary tube attached to the bottom (Fig. 3); glass wool; spatula with blade $\frac{1}{2}$ to $\frac{3}{8}$ in. wide; dioctyl phthalate plasticizer [high quality commercial di(2-ethyl, *n*-hexyl) phthalate]; four cork rings, 33 mm. o.d., 20 mm. i.d., 25 mm. length.

Procedure

The procedure is as follows. A small bit of folded glass wool is first placed in the bottom of the tube to prevent spilling of the resin, and the tube and glass wool weighed. A 10-g. portion of the PVC is then weighed into the tube, and 20 ml. of DOP (DOP/PVC = 2/1 ratio) added. The PVC and plasticizer are then mixed with the small spatula, care being taken not to disturb the glass wool.

The tube is placed in the metal shield in which a cork ring has been inserted. The cork ring will cushion the tube as well as provide a space for the excess DOP. Filled shields are placed in the centrifuge in a balanced arrangement.

The centrifuge is set to turn at 1300 rpm and run for 5 min. The excess DOP in the shields is emptied out; the centrifuge is run again for 5 min. and shields are emptied again.

The run is continued until 30 min. have passed while centrifuging. The tube and its contents is then weighed, replaced, centrifuged again for 4 min. and weighed again. If the change in weight is 0.01 g. or less, the run is complete; if not, centrifuging is continued until these conditions are met.

The difference between the final weights recorded above and the tube, glass wool, and PVC is the amount of DOP retained. From this difference,

Irreversible PTU = 10 (Difference) = 10 (Final weight-tare weight-10)
Each determination should be made in duplicate.

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Résumé

La facilité de polymériser le chlorure de polyvinyle en suspension (PVC) est reliée à son pouvoir d'accepter suffisamment de plastifiant tout en restant une poudre sèche et facilement malléable. L'incorporation satisfaisante de plastifiant, appelée prémélange

à froid ou mélange-sec à chaud, dépend de facteurs physicochimiques de base. Le prémélange à froid correspond à un remplissage purement géométrique des pores et fissures entre les particules, alors que le mélange-sec à chaud dépend en plus d'une absorption fonction du temps. Des tests quantitatifs de laboratoire pour ces deux effets ont été développés et standardisés, quand ils sont appliqués à des échantillons expérimentaux et commerciaux de PVC et leurs fractions, les tests donnent des résultats qui montrent une légère corrélation avec les propriétés d'accroissement des particules. Cependant, la corrélation entre les tests par le prémélange à froid et le mélange-sec à chaud est important, indiquant que les mêmes facteurs sont responsables des deux. Les tests fournissent également de bons rendements en polymère pour le comportement réel de croissance. Il est possible de contrôler la géométrie des particules au moyen des variables de progression de la polymérisation en suspension et de régler ensuite le comportement du prémélange à froid; ces effets sur le mélange sec à chaud ne sont pas aussi évidents. Le broyage après polymérisation altère remarquablement les surfaces des particules de PVC et peut améliorer substantiellement le pouvoir de mélange sec à chaud. Un broyage rigoureux est nécessaire pour changer la géométrie des particules d'une façon suffisante pour provoquer une amélioration notable du prémélange à froid.

Zusammenfassung

Die Verarbeitbarkeit von suspensionspolymerisiertem Polyvinylchlorid (PVC) hängt mit dessen Fähigkeit zusammen, genügend Weichmacher unter Beibehaltung der Eigenschaften eines trockenen, frei fließenden Pulvers aufzunehmen. Die erfolgreiche Einführung des Weichmachers, die sogenannte kalte Vormischung oder heisse Trockenmischung, ist von grundlegenden physikochemischen Faktoren abhängig. Die kalte Vormischung entspricht einem rein geometrischen Ausfüllen von Poren und Spalten innerhalb der Teilchen, während für die heisse Trockenmischung ausserdem noch ein zeitabhängiger Absorptionsvorgang massgeblich ist. Zur Untersuchung dieser beiden Effekte wurden quantitative Laboratoriums-Testmethoden entwickelt und standardisiert. Die Ergebnisse der Anwendung dieser Methoden auf experimentelle und kommerzielle PVC-Proben und deren Fraktionen stehen nur in schwacher Beziehung zu den makroskopischen Eigenschaften der Teilchen. Dagegen besteht zwischen den bei der kalten Vormischung und der heissen Trockenmischung erhaltenen Testergebnissen eine enge Korrelation. Dies weist darauf hin, dass in beiden Fällen die gleichen Faktoren massgeblich sein dürften. Ausserdem lässt sich auf Grund der Testergebnisse das tatsächliche Verhalten der Polymeren bei der Verarbeitung gut abschätzen. Man kann die Teilchengrösse durch die Wahl der Reaktionsbedingungen bei der Suspensionspolymerisation kontrollieren und somit das Verhalten bei der kalten Vormischung beeinflussen. Der Einfluss auf die heisse Trockenmischung ist weniger klar. Durch Mahlen des Polymeren nach der Polymerisation wird die Oberfläche der PVC-Teilchen stark verändert, wodurch die Kapazität bei der heissen Trockenmischung wesentlich erhöht werden kann. Die zu einer deutlichen Verbesserung bei der kalten Vormischung nötige Änderung der Teilchengometrie kann nur durch starkes Mahlen erreicht werden.

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