

Performance Relationships in PVC-Plasticizer Dry Blending

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Synopsis

The phenomenon of plasticizer acceptance by poly(vinyl chloride) (PVC) in hot-process dry blending is examined via scanning electron microscopy, mercury intrusion porosimetry, and torque rheometer measurements. The effects of granule porosity, resin molecular weight, and synthesis recipe in PVC manufacture by the suspension process are related to the rate of plasticizer acceptance. For a PVC resin to dry blend, i.e., to become a free-flowing powder when mixed with plasticizer under hot-processing conditions, the resin granules must be porous. Porosity arises from interstices between primary PVC particles. At a given granule porosity, an increase in primary particle agglomeration adversely affects dry blend performance. At constant molecular weight and for resins manufactured by a given recipe, dry-blend performance is quantitatively described by granule porosity. With an increase in resin molecular weight, a greater granule porosity is required to maintain an equivalent dry-blend time (DBT). Accordingly, for most suspending agent recipes, DBT is dependent directly upon granule porosity and inversely upon molecular weight. However, if the suspending agent used in resin manufacture is an excessively rapid film former, dry-blend performance with molecular weight variation is dependent upon the suspending agent's concentration, not upon granule porosity, which must be adequate, nor upon the resin's molecular weight. An interfacial film-forming suspending agent enhances fusion of primary PVC particles at the suspension granule-water interface, increasing the granule's "pericellular membrane" thickness. This membrane, a PVC skin, does not significantly influence dry-blend performance with low- or intermediate-viscosity plasticizers. The particle skin does impede dry-blend rates with high-viscosity, poorly solvating plasticizers, but this effect can be negated in part by increasing the diameter of pore openings in the topographical skin. Dry blending occurs below the glass transition temperature (T_g) of PVC with low-viscosity plasticizers and above the T_g with high-viscosity, poorly solvating modifiers. The influence of resin and plasticizer variables indicates the dry-blend phenomenon to be a diffusion-controlled process. The rate of dry blending is dependent upon two mechanisms: (1) the rate of pore penetration—which exposes the plasticizer to a much greater surface area than if it remained exterior, encapsulating the granule—and (2) the rate of plasticizer diffusion into the PVC matrix.

INTRODUCTION

At sales of 3.1 billion pounds in 1970, poly(vinyl chloride) (PVC) represents the second largest plastic in the United States. Over 70% of this total is produced by the suspension polymerization process.

The process is a miniature bulk polymerization, with the monomer dispersed in an aqueous media. Impeller agitation and the suspending agent (a water-soluble polymer) control agglomeration of the dispersed monomer and thereby permit good heat transfer in the production of a diversity of products. PVC particles of low porosity for plastisol-additive applications, of intermediate porosity for general purpose use, and of extreme porosity for use in fluidized-bed applications can be manufactured by this single polymerization technique.

Plasticized applications consume most of the suspension PVC produced in the United States. Such uses require resin granules of intermediate porosity, as judged by the standard ASTM spatula test,¹ to efficiently hot-process dry-blend PVC for flexible products. The rate at which commercial additives, e.g., plasticizer and stabilizer, are accepted is dependent upon the structure of the granule and helps determine the manufacturing cost of the compound producer. The term dry blend indicates that, in time, the resin-plasticizer mixture becomes free flowing. Dependence of the dry-blending process upon granule properties such as size, shape, and exterior particle surface area is discussed by Park² and by Carleton and Mischuk.¹ Investigators in our laboratories attempted to relate granule porosity, determined by mercury intrusion porosimetry, with the rate of plasticizer acceptance and concluded that "the size distribution and total volume of these pores are directly related to plasticizer absorption, but do not entirely control dry blend behavior."³ Mazzur,⁴ employing a torque rheometer, correlated dry-blending rates with molecular structure of the plasticizer. In a recent study, Canadian investigators,⁵ employing a variety of physical techniques, concluded that the hot-process dry blending of PVC is a diffusion process dependent upon the resin granule's total surface area.

In this article, scanning electron microscopy (SEM) and mercury intrusion porosimetry (MIP) are correlated with dry-blend times determined with a C. W. Brabender torque rheometer to define the effect upon dry-blend performance of granule porosity, resin molecular weight, the recipe protective colloid, and the presence of a pericellular membrane.

EXPERIMENTAL

Materials

Plasticizers employed in the torque rheometer studies (Flexol DOP, di-2-ethylhexyl phthalate; Flexol 10-10, diisodecyl phthalate (DIDP); and Flexol 13-13, ditridecyl phthalate (DTDTP), Union Carbide products) were of commercial quality. Plasticizer viscosities at 90°C are 5.5, 8.0, and 13.0 cks, respectively. Plastisol fusion temperatures with PVC latices reflect solvation interactions. Minimum fusion temperatures of 105°C (DOP), 120°C (DIDP), and 157°C (DTDTP) are observed for the commercial plasticizers used in this study.

TABLE I. PVC Commercial Dry-Blend Resin Properties

Com- mercial resin	Dry-blend time, min. ^a		Internal porosity			Par- ticle ^b me- dian size, μ	Resin in- herent vis- cosity (0.2 g/dl in cy- clohex- ane), ^c dl/g	
	Diiso- decyl phthal- ate	Ditridecyl phthalate	Average		Total Volume intruded, cc/g			
			apparent pore radius, μ					
A	5.5	10.4	0.357		0.2441	125	1.00	
			0.384		0.2396			
			0.385		0.2450			
			<i>Ave.</i>	0.38	<i>Ave.</i>			0.243
B	6.8	16.0	0.372		0.2439	142	1.00	
			0.366		0.2392			
			0.373		0.2364			
			<i>Ave.</i>	0.37	<i>Ave.</i>			0.240
C	5.8	9.7	0.367		0.2394	150	1.02	
			0.412		0.2342			
			0.372		0.2339			
			<i>Ave.</i>	0.38	<i>Ave.</i>			0.236
D	7.3	12.8	0.508		0.2630	285	1.00	
			0.473		0.2502			
			0.515		0.2616			
			<i>Ave.</i>	0.50	<i>Ave.</i>			0.258
E	5.5	10.5	0.431		0.2755	280	1.10	
			0.458		0.2832			
			<i>Ave.</i>	0.44	<i>Ave.</i>			0.279
			0.352		0.2377			137
0.360		0.2441						
0.360		0.2441						
<i>Ave.</i>	0.36	<i>Ave.</i>	0.242					
G	5.4	10.3	0.454		0.2452	120	1.04	
			0.466		0.2634			
			<i>Ave.</i>	0.46	<i>Ave.</i>			0.254
			0.467		0.2312			120
0.476		0.2439						
<i>Ave.</i>	0.47	<i>Ave.</i>	0.238					
0.413		0.2480	150	1.02				
0.422		0.2199						
<i>Ave.</i>	0.42	<i>Ave.</i>			0.234			
0.330		0.2190			136	1.03		
0.339		0.2207						
<i>Ave.</i>	0.33	<i>Ave.</i>	0.220					
0.669		0.3667	325	0.95				
0.670		0.3697						
<i>Ave.</i>	0.67	<i>Ave.</i>			0.368			
0.341		0.2191			92	0.99		
0.339		0.2181						
<i>Ave.</i>	0.34	<i>Ave.</i>	0.219					

^a ± 0.5 min at 90°C.^b $\pm 15 \mu$.^c ASTM D-1243.

TABLE II
Variable Molecular Weight PVC Resins Manufactured Under
Similar Process I Conditions

Resin	Dry-blend time with diisodecyl phthalate, min	Internal porosity				Resin inherent viscosity (0.2 g/dl in cy- clohex- anone), dl/g
		Average apparent pore radius, μ		Total volume intruded, cc/g		
I-A	5.1	0.441		0.236		1.01
		0.439		0.234		
		<i>Ave.</i>	0.44	<i>Ave.</i>	0.235	
I-B	6.2	0.411		0.224		1.01
		0.410		0.222		
		0.416		0.223		
		<i>Ave.</i>	0.41	<i>Ave.</i>	0.223	
I-C	7.3	0.398		0.198		1.00
		0.390		0.206		
		<i>Ave.</i>	0.39	<i>Ave.</i>	0.202	
I-D	7.0	0.359		0.293		1.42
		0.372		0.292		
		<i>Ave.</i>	0.36	<i>Ave.</i>	0.292	
I-E	8.0	0.351		0.260		1.41
		0.359		0.264		
		<i>Ave.</i>	0.35	<i>Ave.</i>	0.262	
I-F	7.9	0.350		0.263		1.40
		0.361		0.273		
		<i>Ave.</i>	0.36	<i>Ave.</i>	0.268	

Laboratory-prepared plasticizers, purified by vacuum distillation, were used in contact angle studies on PVC plaques, prepared in a metallurgic press at 10,000 psi, 85°C, from bulk-polymerized QYNL (Union Carbide) granules. The PVC dry-blend resins in Table I are commercially available materials, supplied by a variety of manufacturers. The resins in Tables II-IV were synthesized in production-size equipment; the recipes and process conditions used to produce the latter products are proprietary and will not be discussed.

Scanning Electron Microscopy

The scanning electron micrographs (SEM) illustrated were obtained with a Cambridge instrument. The specimens were prepared by implanting resin granules in a conductive glue, one part latex adhesive and three parts Aquadag (a colloidal graphite suspension in water). The latex adhesive was a 50/50 mixture of UCAR 891 or UCAR 40 (Union Carbide latices) with a laboratory prepared poly(2-ethylhexyl acrylate) latex. To avoid surface charging, the specimens were coated with a conductive gold surface. The specimen studs were mounted on a rotating

TABLE III. Variable Molecular Weight PVC Resins
Manufactured Under Similar Process II Conditions

Resin	Dry-blend time with diisodecyl phthalate, min	Internal porosity				Resin inherent viscosity (0.2 g/dl in cyclohex- anone), dl/g
		Average apparent pore radius, μ		Total volume intruded, cc/g		
II-A	6.2	0.655		0.118		0.62
		0.642		0.125		
		0.648		0.118		
		<i>Ave.</i>	0.65	<i>Ave.</i>	0.120	
II-B	7.0	0.638		0.128		0.65
		0.659		0.115		
		0.673		0.119		
		<i>Ave.</i>	0.66	<i>Ave.</i>	0.121	
II-C	7.0	0.659		0.113		0.61
		0.670		0.155		
		0.647		0.111		
		<i>Ave.</i>	0.66	<i>Ave.</i>	0.113	
II-D	3.5	0.460		0.323		0.94
		0.463		0.329		
		0.456		0.326		
		<i>Ave.</i>	0.46	<i>Ave.</i>	0.326	
II-E	4.8	0.457		0.262		0.93
		0.452		0.262		
		0.455		0.257		
		<i>Ave.</i>	0.45	<i>Ave.</i>	0.260	
II-F	5.2	0.417		0.264		0.95
		0.411		0.259		
		0.420		0.259		
		<i>Ave.</i>	0.42	<i>Ave.</i>	0.261	
II-G	6.7	0.442		0.237		0.93
		0.437		0.236		
		0.443		0.238		
		<i>Ave.</i>	0.44	<i>Ave.</i>	0.237	
II-H	3.8	0.377		0.296		1.00
		0.377		0.293		
		<i>Ave.</i>	0.38	<i>Ave.</i>	0.294	
II-I	4.5	0.427		0.281		1.01
		0.426		0.275		
		<i>Ave.</i>	0.43	<i>Ave.</i>	0.278	
II-J	5.0	0.386		0.255		0.99
		0.397		0.262		
		<i>Ave.</i>	0.39	<i>Ave.</i>	0.258	
II-K	5.6	0.433		0.262		1.00
		0.438		0.256		
		0.415		0.256		
		<i>Ave.</i>	0.43	<i>Ave.</i>	0.258	
II-L	6.2	0.410		0.255		1.02
		0.372		0.251		
		0.425		0.258		
		0.422		0.255		
		0.418		0.254		
		<i>Ave.</i>	0.41	<i>Ave.</i>	0.255	
II-M	8.0	0.403		0.236		1.01
		0.399		0.238		
		<i>Ave.</i>	0.40	<i>Ave.</i>	0.237	

TABLE IV
Variable-Process, High Molecular Weight PVC Resin Properties

Process and resin	Dry-blend time with diisodecyl phthalate, min	Internal porosity				Resin inherent viscosity (0.2 g/dl in cyclohexanone), dl/g
		Average apparent pore radius, μ		Total volume intruded, cc/g		
III-A	5.8	0.357		0.248		1.40
		0.362		0.251		
		<i>Ave.</i>	0.36	<i>Ave.</i>	0.250	
III-B	7.0	0.330		0.225		1.37
		0.343		0.230		
		<i>Ave.</i>	0.34	<i>Ave.</i>	0.228	
IV-A	5.8	0.364		0.286		1.37
		0.369		0.286		
		0.344		0.281		
IV-B	7.0	<i>Ave.</i>	0.36	<i>Ave.</i>	0.284	1.39
		0.353		0.282		
		0.351		0.299		
		0.361		0.286		
		<i>Ave.</i>	0.35	<i>Ave.</i>	0.289	

stage in a vacuum metal evaporator. A deposition angle, to the surface of the mounting stud, was employed while the stage was rotated. The procedure effectively coats the specimen and the mounting medium with a continuous, conductive gold coating. Cut particle specimens were prepared with a stainless steel razor blade. The granules adhered to the blade's edge (static electricity); this permitted easy implantation of the granules, with interior surfaces exposed. The principles of this electron-optical technique are reviewed by Kammlert⁶ and its utility in polymer and coating studies has recently been reported.⁷

Mercury Intrusion Porosimetry

The apparatus employed in mercury intrusion measurements is described by Winslow and Shapiro.⁸ Rootare and Nyce⁹ detail the principle and sources of error in such measurements. Intruded volumes are obtained from capillary displacement readings, and pore size distributions are calculated from the Washburn equation,¹⁰

$$r = \frac{-2\sigma \cos\theta}{P} \quad (1)$$

where r is the apparent pore radius being intruded by mercury of surface tension σ (480 dyn/cm), under a pressure P , and at a contact angle θ (130°) with the PVC surface. The resins examined in Tables II-IV have a narrow particle-size distribution and uniform granule structure.

Dry Blend Times

The dry blend time, i.e., the time required for the PVC resin powder and plasticizer mixture to become free flowing, was measured using a C. W. Brabender Plasticorder, Model PLV-33AA, with a 600-ml Sigma mixer head. The procedure and method of analysis for the constant-temperature studies (Tables I-IV) are approximate with those previously described.^{4,5,11} The Sigma mixer head was preheated to 90°C. The formulation at ca. 72°C, included resin, 200 g; plasticizer, 103 g; Mark M, a Ba-Cd complex stabilizer mixture (Argus Chemical Co.), 9 g; and Atomite, a wet-ground calcite (Thompson and Wieman Co.), 84 g. In programmed temperature studies the formulation (minus the Atomite filler) and the mixer head were preheated to 40°C, and a 2°C/min increase in head temperature was maintained until 5 min after maximum torque, observed when the mixture becomes free flowing. Plasticizer at room temperature was added to the preheated resin, in both constant and programmed temperature studies, via a plasticizer distribution funnel manufactured by the C. W. Brabender Company.

RESULTS AND DISCUSSION

In the polymerization of any halide or pseudohalide substituted ethylene derivative, the polymer is insoluble in its monomer. This feature provides the nucleus for a diversity of products in the suspension polymerization of

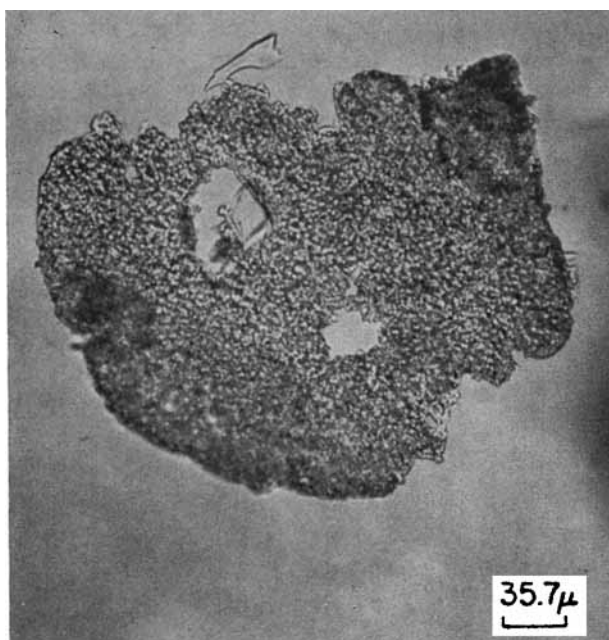


Fig. 1. Microtome (thin-section electron micrograph) of PVC granule.

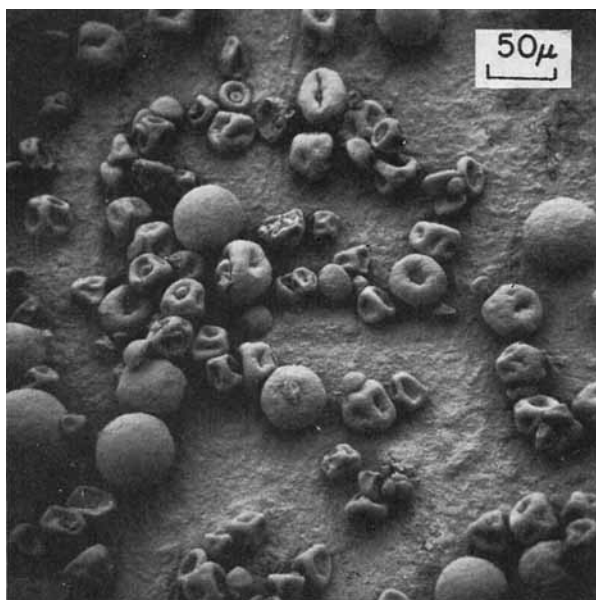


Fig. 2. SEM micrograph of PVC granules (QYPM-4) used in plastisol-additive applications.

vinyl chloride. Traditionally, most PVC morphology studies are undertaken by microtome analysis¹²⁻¹⁴ (examination of thin PVC particle sections via electron micrographs, see Fig. 1). Primary PVC particles at high conversion are approximately 1-3 μ in diameter. Within the precision of such measurements a discernible trend in particle diameters is not observed with polymerization temperature or process.

When the primary particle structures are fused, a low-porosity granule suitable for plastisol-additive applications is produced. A commercial resin of this type is shown in Figure 2 with an interior examination (Fig. 3) of one of the larger spherical particles. An average surface sorption for such resins, as depicted by the room temperature ASTM spatula test,¹ is approximately 50 phr. PVC granules normally used for hot-processing flexible applications have greater porosity; room-temperature sorption values vary between 90 and 120 phr. Exterior and interior particle characteristics for this dry blend-type resin (used in extrusion, molding, and calendaring applications) are shown in Figures 4 and 5. Products used in fluidized-bed applications have large room-temperature sorption properties, 180-220 phr. The ease with which plasticizer acceptance can occur, through capillary action, is apparent in the SEM (Fig. 6). The resin illustrated, QYNL, is not a suspension process product. QYNL represents an optimum in blotter-type resins; suspension resins can be made which approach its porosity and particle size characteristics.

Total intruded volumes (mercury-intrusion porosimetry measurements) for the three resin types are 0.014, 0.236, and 0.322 cc/g, respectively, over

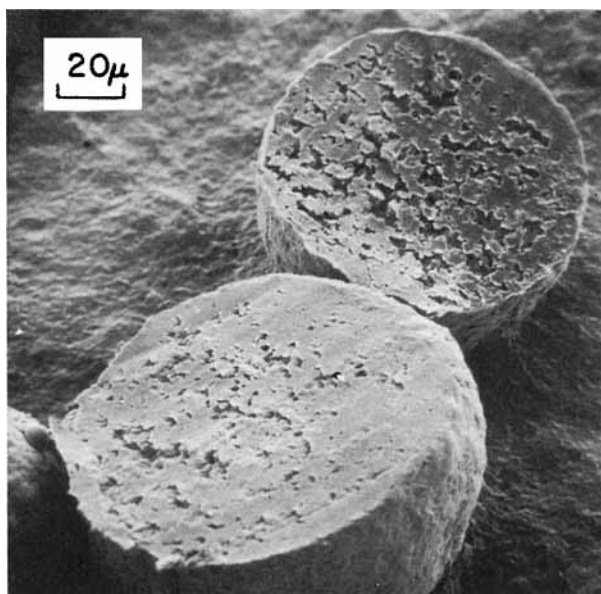


Fig. 3. SEM micrograph of cut QYPM-4 granule.

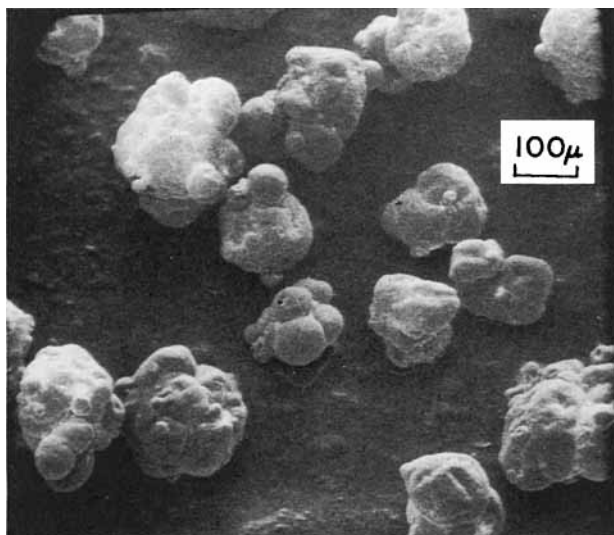


Fig. 4. SEM micrograph of PVC granules (QYTQ-7) used in dry-blend applications.

pressures corresponding to 0.26–3.0 μ apparent pore diameters. Intruded volumes as a function of apparent pore diameters are illustrated in Figure 7. Computer analysis of porosity data for the three resin types reveals that porosity associated with higher than a 3.0 μ apparent pore diameter is due to interparticle voids. A similar conclusion was reached in previous studies³ with 29 μ glass beads.

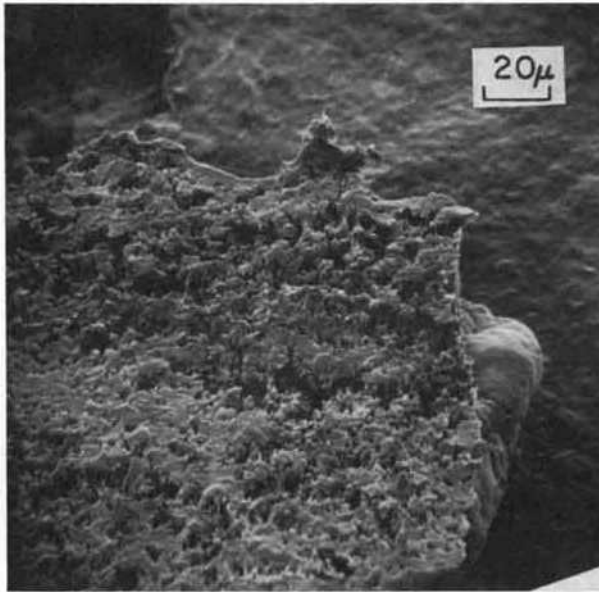


Fig. 5. SEM micrograph of cut QYTQ-7 granule with primary PVC particles exposed.

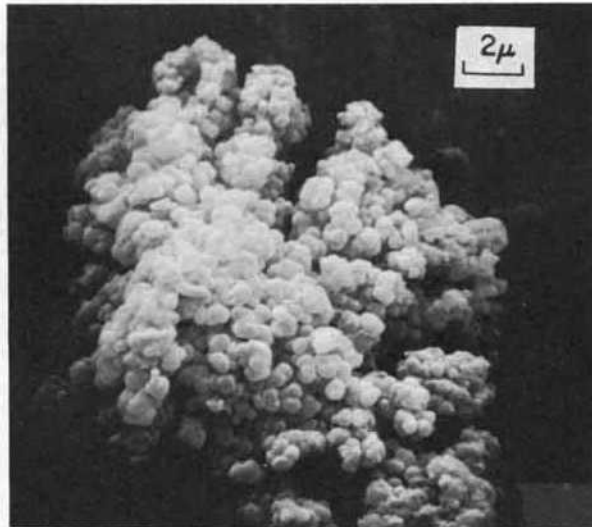


Fig. 6. SEM micrograph of PVC blotter resin, QYNL.

Performance Relationships in PVC Hot-Process Dry Blending

Intraparticle Porosity

Commercial dry-blend resins, representative of the industry, are listed with pertinent granule analyses in Table I. Scanning electron micrographs of seven resin granules illustrating a wide variety in topographic structure are shown in Figures 8-14. Resin characteristics were related via linear

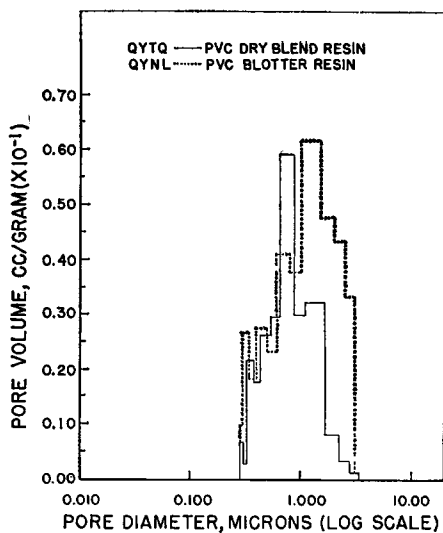


Fig. 7. MIP data: porosity distribution of QYTQ-7 and QYNL granules.

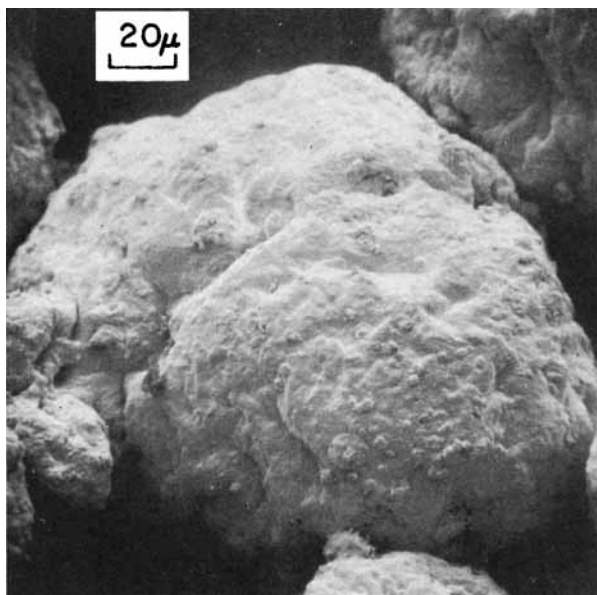


Fig. 8. SEM micrograph of commercial resin A granule.

multiple regression analyses^{15,16} with the times required for the PVC-plasticizer mixtures to dry blend, i.e.,

$$DBT = A \pm B(r_p) \pm C(v_t) \pm D(a_s) \pm E(P_{50}) \pm F(P_d) \pm G(P_s) \quad (2)$$

where r_p is the average apparent pore radius, v_t is the total intruded volume, and a_s is the internal surface area of PVC granules possessing a

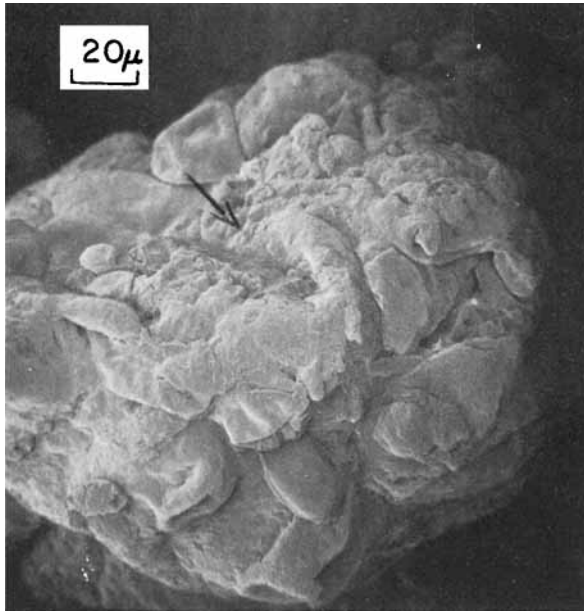


Fig. 9. SEM micrograph of commercial resin C granule.

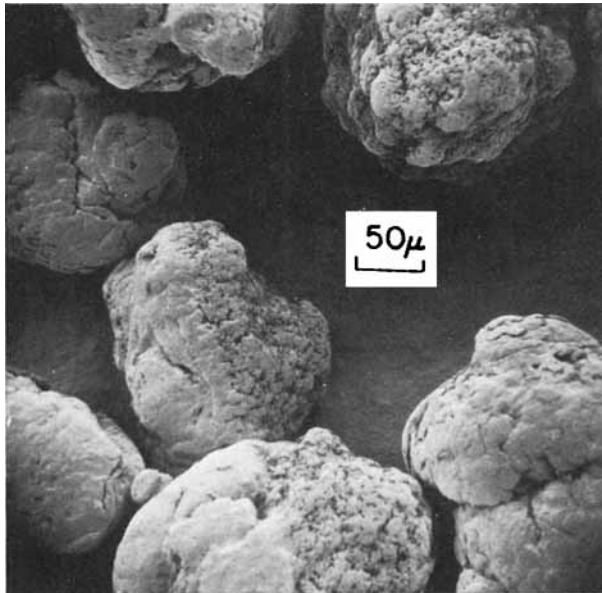


Fig. 10. SEM micrograph of commercial resin E granules.

median size P_{50} , with size distribution characteristics P_d (dispersion) and P_s (skewness). Granule size distributions of the resins were relatively narrow; consequently, resin dispersion and skewness parameters did not relate with dry-blend performance in any of the regression analyses.

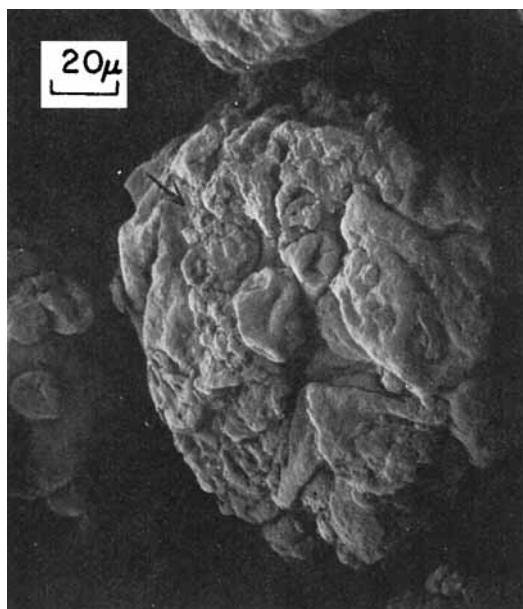


Fig. 11. SEM micrograph of commercial resin H granule.

The independent variables of significance are listed in Table I. In the diisodecyl phthalate analysis, an equation is obtained, eq. (3), which accounts for 72% of the variation in DBT , with an F -ratio of 10.1 and a standard deviation of 0.552 for the dependent variables:

$$DBT(DIDP) = 12.2 - 30.6(v_i) + 0.0095(P_{50}) \quad (3)$$

where $DBT(DIDP)$ is the dry-blend time with diisodecyl phthalate, v_i is the total intruded volume of the PVC granules, and P_{50} the median particle size. Intraparticle porosity is the dominant independent parameter in eq. (3). With the many process and recipe variations possible in this selection of commercial resins, the relationship is surprisingly good. Data for PVC resins (Table II) of the same molecular weight but manufactured under similar process and recipe conditions provide a quantitative relationship, eq. (4): 98% accountability, F -ratio of 63.5, and a standard deviation of 0.193:

$$DBT(DIDP) = 25.7 - 47.1(v_i). \quad (4)$$

Independent analysis of other PVC resins of variable porosity made with a constant recipe and having comparable molecular weights also yield independent, quantitative relationships between $DBT(DIDP)$ and v_i . An equation between DBT and an artificial parameter, the granule's total internal surface area, a_s (calculated via an assumed cylindrical pore model

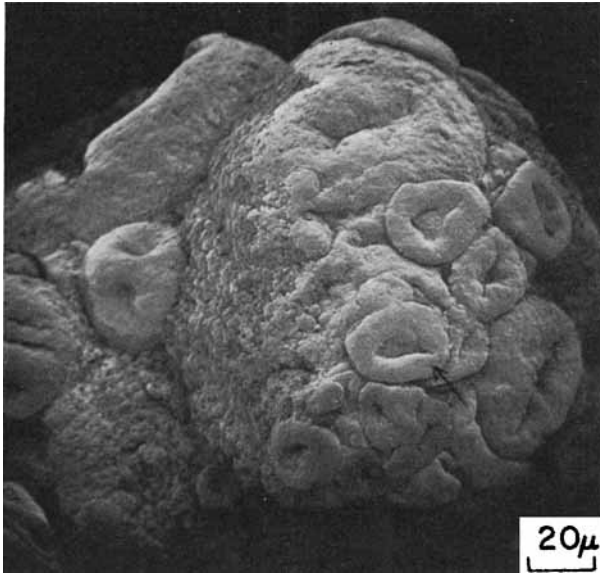


Fig. 12. SEM micrograph of commercial resin J granule.

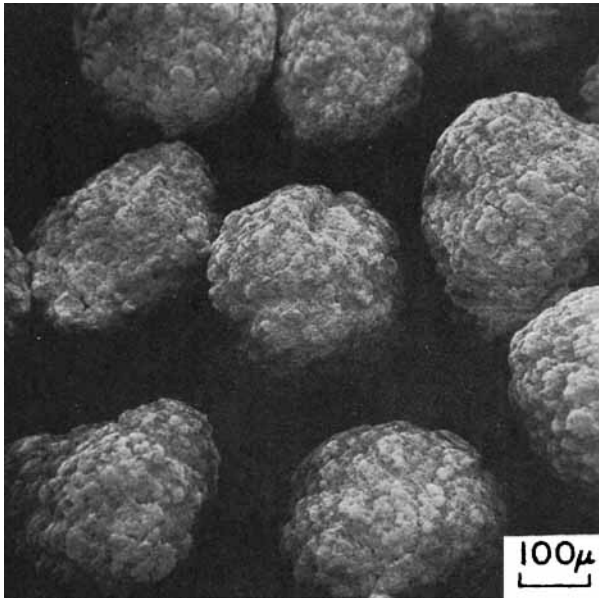


Fig. 13. SEM micrograph of commercial resin K granules.

from v_t and the average apparent pore radii), can be obtained, but scanning electron micrographs of cut particles, i.e., Figure 5, clearly demonstrate nonidealized pores. Under constant process and recipe conditions, a direct relationship between v_t and \bar{a}_s is probable.

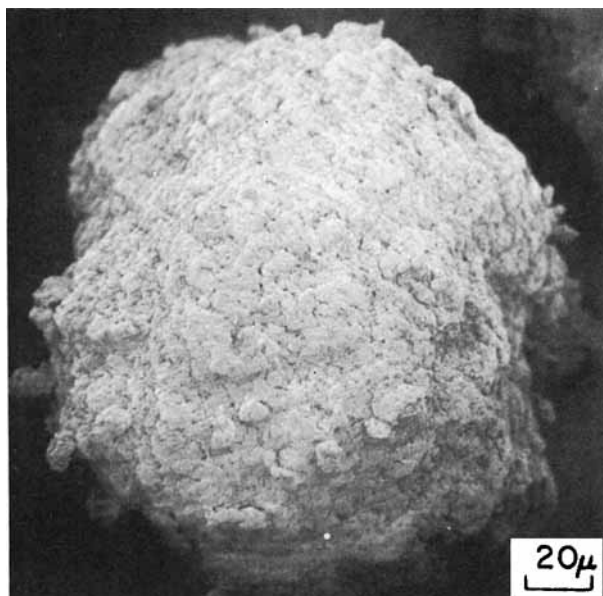


Fig. 14. SEM micrograph of commercial resin L granule.

Plasticizer Solvation and Viscosity

Topographic differences are not evident after the resin has undergone hot-processing; compare Figures 15, 16, and 17 with Figures 9, 12, and 13, respectively. In Figures 15–17, it is apparent that during pore penetration the plasticizer also is penetrating the PVC matrix through the resin granule's exterior membrane. This interaction and the external shear in hot-processing equate topographic differences.

These observations provide insight in understanding the multiple-regression relationship, eq. (5), defining commercial PVC dry-blend times (Table I) with ditridecyl phthalate (DTDP), a plasticizer more viscous and of poorer solvating characteristics than DIDP,

$$DBT(DTDP) = 19.0 - 17.1(r_p) \quad (5)$$

where r_p is the average apparent pore radius. The per cent variation in DBT , accounted for by the average apparent pore radius r_p , is low (42%), in part because the range in r_p is small compared with variations in DBT . A significant F -ratio of 6.5 is observed in the analysis.

The regression analysis is predicted in part by the Rideal-Washburn equation,¹⁷ recently discussed for several application areas,^{18,19}

$$t = \frac{2\eta l^2}{r \sigma \cos\theta} \quad (6)$$

where t is the time taken for a liquid of viscosity η and surface tension σ to penetrate a given pore of radius r and length l , and θ is the contact angle

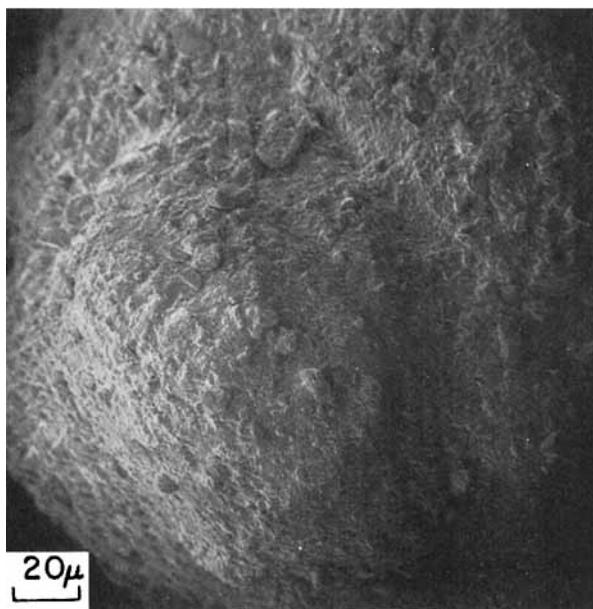


Fig. 15. SEM micrograph of dry-blended commercial resin C granule.

between plasticizer and the pore surface. Attempts to measure the contact angle of various phthalate esters, with side groups varying from C_3 to C_{16} , fail because the plasticizers wet PVC plaques. In agreement with expected slight variations in σ and θ , spreading areas in these studies did not vary with ester chains greater than six carbon atoms. Therefore, the dominant factors influencing pore penetration in theory, i.e., eq. (5), are plasticizer viscosity and the granule's pore radii.

Comparison of the distribution of the intruded volume as a function of pore opening diameters (Fig. 18) in commercial resins B and H (Table I) illustrates the influence of r_p . The resins have approximate intruded volumes, but the porosity in resin H is associated with greater pore openings. A difference in *DBT* is not observed with DOP and only a minute difference is observed with DIDP, but an *ca.* six minute variation is noted with the most viscous plasticizer, DTDP. Less dramatic but similar comparisons can be made between other resins in Table I. In many instances, such comparisons cannot be made because of simultaneous variations in primary particle stabilization, an important factor discussed in the last section.

Under similar resin conditions, the pore opening radii of the granules and the solvation and viscosity characteristics of the plasticizer interact in a complementary manner which does not allow estimation of their relative contributions. The interplay of the variables is apparent in programmed temperature increase studies with the torque rheometer (Fig. 19). The greater torque and broader compound temperature range with DIDP, rela-

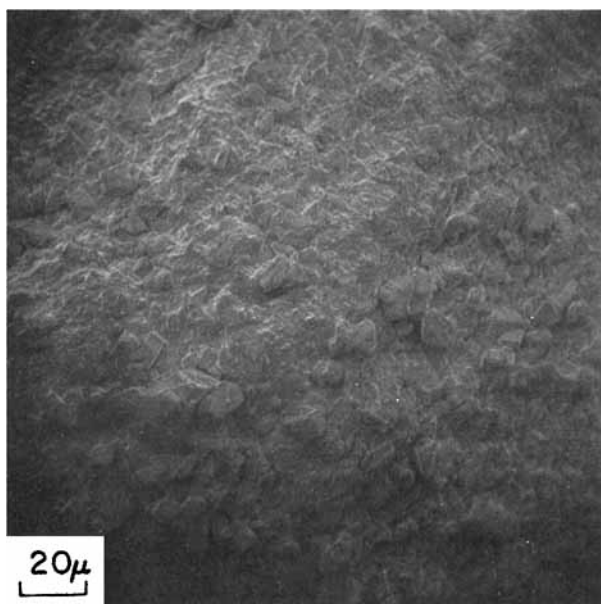


Fig. 16. SEM micrograph of dry-blended commercial resin J granule.

tive to DOP, are primarily related to poorer solvating characteristics^{2,4,20,21} and higher viscosity. The solvation difference between DOP and DIDP is not sufficient to result in a difference in dry-blend temperature variation (5°C between resins for both plasticizers, Fig. 19); however, with DTDP (not illustrated) a greater difference, 9°C, is observed. The resin having the larger r_p (IA, Table II) possesses the lower dry-blend temperature, 114°C, with DTDP. Based upon extensive data of this type, the authors place strong emphasis upon the role of r_p in PVC dry blending with increasing molecular weight plasticizers.

Resin Molecular Weight

At comparable porosity, dry-blend times are greater the higher the molecular weight of the resin (Table III). The intermediate and high molecular weight resins in Table III yield independent relationships between v_i and $DBT(DIDP)$, e.g., eq. (4). Insufficient variation in the parameters of the low molecular weight PVC resins ($\eta_{inh} = 0.61 - 0.65$) does not permit definition of such a relationship. Only temperature and a slight adjustment in recipe quantities with temperature are varied in the synthesis of different molecular weight resins. Regression analysis, using inherent viscosities at 0.2 g/dl in cyclohexanone as a reflection of PVC molecular weight, yields eq. (7),

$$DBT(DIDP) = 4.1 - 35.9(v_i) + 11.1(\eta_i) \quad (7)$$

a relationship with 75% accountability, F -ratio of 15.2 and standard deviation of 0.731. A more quantitative relationship, eq. (8) (93% ac-

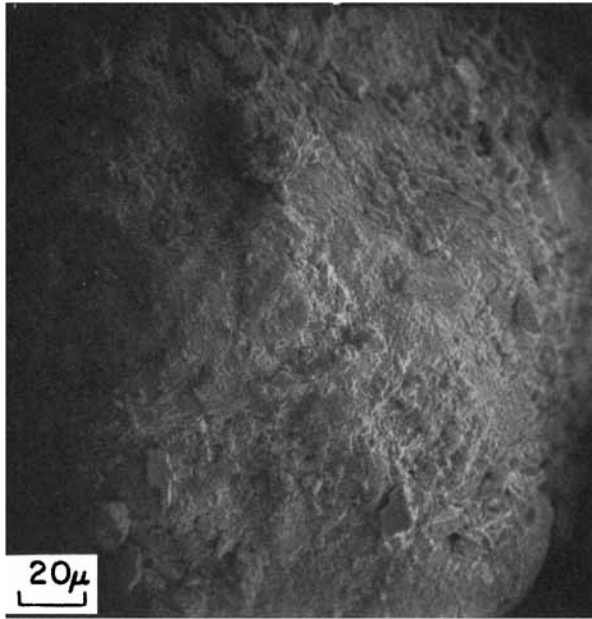


Fig. 17. SEM micrograph of dry-blended commercial resin K granule.

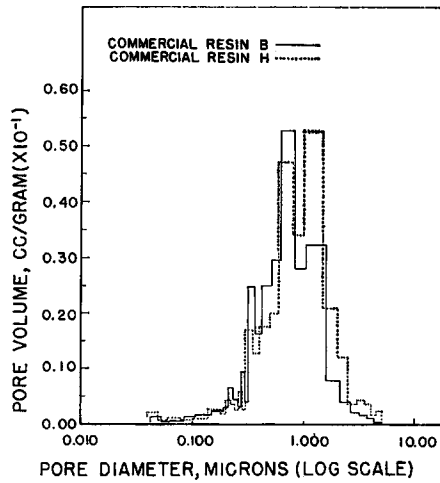


Fig. 18. MIP data: porosity distribution of commercial resins B and H granules.

countability, F -ratio of 40.0, and standard deviation of 0.409), is obtained with continued regression,

$$DBT(DIDP) = -4.8 - 57.1(v_1) + 29.1(\eta_1) - 66.2(X_3) \quad (8)$$

where X_3 is an interaction parameter between v_1 and the suspending agent concentration.

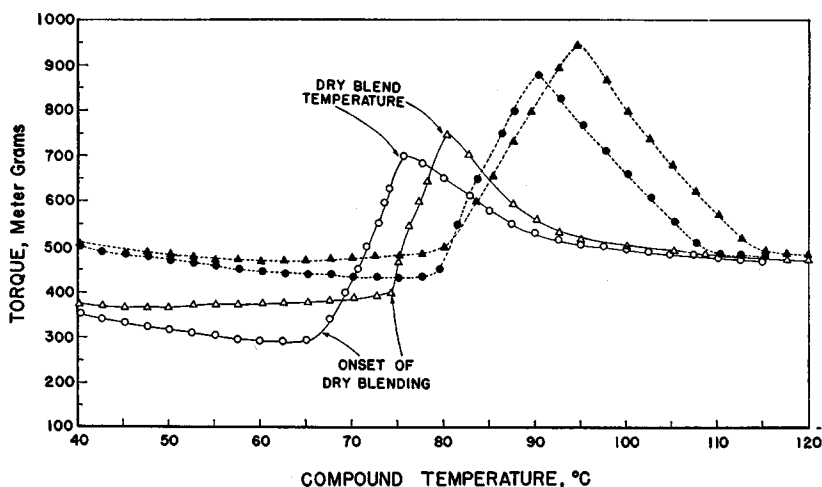


Fig. 19. Programmed temperature torque rheometer measurements. Interaction of variable porosity granules (Table II) with plasticizers of variable viscosity and solvation characteristics: ○ resin I-A with DOP; ● with DIDP; △ resin I-B with DOP; ▲ with DIDP.

Grotz²² observed the diffusion rate of dioctyl phthalate into PVC plaques to be dependent upon the polymer's molecular weight. Differential thermal analysis studies²³ of dry-blended resins recognize the role of diffusion but do not indicate the importance of intraparticle porosity. The observation that greater granule porosity is required with increasing molecular weight to maintain equivalent dry blend times strongly suggests the dry-blend phenomenon to be a two-step process: (1) penetration of the particle's interior and (2) diffusion into the PVC matrix.

The Exterior Membrane and Primary Particle Stabilization

Certain suspending-agent recipes provide resins for which eqs. (7) or (8) are not valid. A suspending agent which is an excessively rapid, interfacial film former, as defined by coalescence studies,²⁴ can be used to synthesize different molecular weight resins containing proportional granule porosities. However, when analyzed as a group (with v_i and resin inherent viscosities as variables), dry-blend performance is quantitatively described by the suspending agent concentration. A rapidly forming boundary film promotes adherence of primary PVC particles brought to the interface via centrifugal forces within a sheared, dispersed phase²⁵ and facilitates a thick, fused vinyl skin at the granule-water boundary. A slow film-forming suspending agent results in a thinner granule skin (Fig. 5) and accounts for the minor contribution of the third parameter (X_3) in eq. (8). A rapid film-forming suspending agent also will provide extreme stability to the dispersed droplets, which upon agglomeration maintain their identity. At least four of these agglomerates are evident within the PVC granule

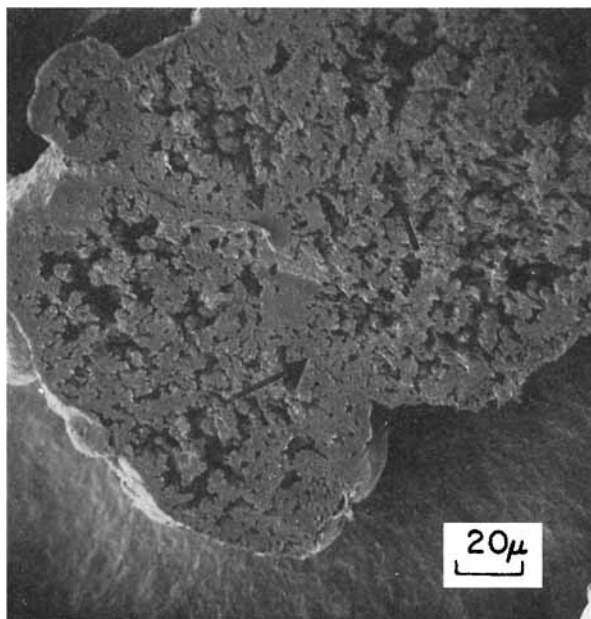


Fig. 20. SEM micrograph of cut PVC granule illustrating the effect of rapid film-forming suspending agent recipes on interfacial primary particle fusion.

(arrows point to the convex peripheries) in Figure 20; rather high primary particle densities exist in the convex gradations. This type of structuring is not detectable in microtome analysis. There is in effect a "pericellular membrane."¹³ It is not a suspending agent membrane as interpreted from microtome analysis; the membrane is a fused vinyl skin. If sufficient size pore openings are not available in the exterior high-density skin, the plasticizer must solvate this skin in order to penetrate the granule.

The relatively low accountability noted for eq. (3) is due, in part, to a variation in PVC skin thickness among the various commercial resins and the total absence of a skin in two of the resins, K and L (Fig. 13 and 14). Resin L is a U.S. licensee-produced (Pechiney-St. Gobain), two-stage bulk resin.^{14,26} In the absence of a monomer-water interface, particle growth occurs without the formation of a granule skin. Based upon the SEM (Fig. 13) of resin K (Dow's Q 3596 resin), such particles are synthesized via a two-stage²⁷ nonconventional suspension process. In this process, a monomer-water interface is not present during the first 20% conversion. A suspending agent supposedly responsible for the granule's "pericellular membrane" is present throughout the polymerization process.

Resins in Table II, III, and IV are made via different suspending agent recipes. In a given molecular weight resin comparison, it is evident that comparable dry-blend times require less granule porosity with certain recipes. This variance is the result of a difference in primary particle stabilization. Primary particle fusion, clearly demonstrated at high

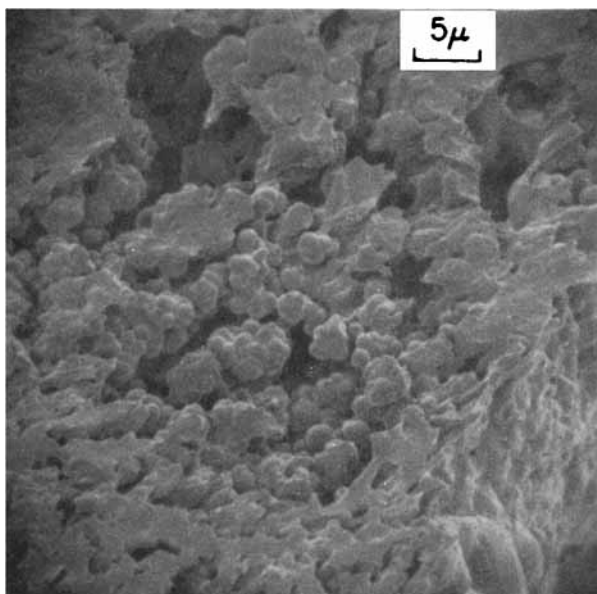


Fig. 21. SEM micrograph of cut PVC granule illustrating primary particle agglomeration and fusion within the resin granule.

magnification in Figure 21, lowers the granule's interior surface area at a given intruded volume. Good primary particle stabilization complemented by a narrow particle-size distribution permits superior dry-blend performance with high resin bulk density, both critical parameters in application areas. Nelson and Alfrey²⁷ recognize this in the synthesis of Dow's Q-3596 resin (commercial resin K, Table I, Fig. 13). Good primary particle stabilization also is obtained in the two-stage Pechiney-St. Gobain process (resin L). Superior dry-blend performance in these two resins and in many conventional commercial suspension vinyl polymers, where primary particle stabilization can be obtained with good resin heat stability, is consistent with Wallace, Kozak, and Noel's observation⁵ that the granule's total surface area is the controlling factor in plasticizer acceptance.

CONCLUSIONS

Good plasticizer acceptance in hot-process PVC dry blending occurs in two essentially consecutive steps: (1) penetration of the granule's pore structure and (2) diffusion into the PVC matrix. For fast dry blending, pore penetration must be rapid. With increasing viscosity and decreasing solvation characteristics of the plasticizer, pore penetration can become the rate-determining step as the interfacial film of a PVC granule thickens, without a parallel increase in the topographic pore diameters of the skin. Such conditions are encountered with rapid interfacial film-forming suspending agent recipes. Good primary particle stabilization

within each granule enhances dry-blend performance by increasing the resins' surface area, thereby aiding plasticizer diffusion into the PVC matrix.

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