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RHEOLOGICAL BEHAVIOR OF HIGH RESIN-LEVEL PLASTISOLS

By

Gary E. Williams

A Dissertation
Presented to the Graduate Committee
of Lehigh University
in Candidacy for the Degree of
Doctor of Philosophy
in
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1. ABSTRACT

The rheological behavior of plastisols that vary in volume fraction of resin from 0.567 to 0.670 was studied. Different particle-size "cuts" from Tenneco Chemicals, Inc.'s 1730 dispersion-grade-poly(vinyl chloride) resin and di-2-ethylhexyl phthalate (DOP), n-butyl benzyl phthalate (BBP), and di-2-ethylhexyl adipate (DOA) plasticizers were used to prepare the plastisols. In the range of concentrations studied, both shear-thickening and shear-thinning behaviors were observed. In all cases discontinuous-viscosity behavior was observed at a critical shear rate. This viscosity discontinuity depends strongly on the particle-size characteristics of the resin, and the compatibility of the plasticizer with the resin. This study has led to the following contributions.

1. A mixing technique was developed that permits the determination of the maximum volume fraction of resin possible to produce a fluid plastisol. This maximum volume fraction of resin, ϕ_{MIX}, is directly related to the particle-size characteristics of the resin, and the compatibility of the plasticizer with the resin.

2. The resin content of the plastisols studied was expressed in terms of a reduced volume fraction, ϕ_R, that was calculated with the following mixing rule,

$$\phi_R = \sum_{i=1}^{n} \sum_{j=1}^{m} x_i y_j \quad \phi/\phi_{MIX\ ij},$$

where x_i = volume fraction of the i^{th} liquid phase

y_j = volume fraction of the j^{th} solid phase

ϕ = total volume fraction of resin(s)

n = number of plasticizers

m = number of resins

and $\phi_{MIX\ ij} = \phi_{MIX}$ of the i^{th} plasticizer with the j^{th} resin.

Since this expression involves only the determination of ϕ_{MIX} for each resin/plasticizer combination, ϕ_R can be easily determined for variations in both the content of resin and the relative amounts of plasticizers and/or resins present in multiple component plastisols.

3. A model is developed that relates ϕ_R to the shear rate, $\dot{\gamma}d$, at which the viscosity discontinuity occurs. The model, $\log_{10} \dot{\gamma}d = -9.8568 + 10.437/\phi_R$, is shown to be valid for values of ϕ_R between 0.87 and 1.00. The above expression was also found to describe discontinuous viscosity behavior published by another investigator who used different resins. This model can be used as an aid in designing plastisols for specific flow properties.

2. INTRODUCTION

Poly(vinyl chloride) (PVC) pastes, or plastisols, are fluid dispersions of poly(vinyl chloride)-resin particles in plasticizers or blends of plasticizers to which pigments, fillers, stabilizers, and other components may be added.[1]

Hoffman[2,3] has reported that the flow characteristics of such dispersions become discontinuous as the amount of resin is increased. This work treats the rheological properties of high resin-level plastisols that develop such discontinuous flows at increasing shear rates. A technique is described for determining the maximum volume fraction of resin attainable in a plastisol. This maximum volume fraction of resin, ϕ_{MIX}, depends on the resin-particle-size characteristics, as well as the compatibility of the resin with the plasticizers. The viscosity-discontinuity dependence on the volume fraction of resin is presented for plastisols based on three plasticizers using several particle-size resins.

The discontinuity shear rate, $\dot{\gamma}_d$, (that shear rate where discontinuous viscosity behavior starts to occur) is empirically related to the resin volume fraction, ϕ, and the maximum volume fraction, ϕ_{MIX}. This relationship is simplified by the definition of a new variable, the reduced volume fraction, ϕ_R.

2.1 Perspective of Plastisols

Rheological behavior is of great importance in the technology of plastisols, primarily because of the diverse nature of plastisol application processes. Plastisols exhibit anomalous flow behaviors. The variations may be of at least three different types:

(a) η, the coefficient of viscosity, is independent of rate of shear (called Newtonian)

(b) η decreases as the rate of shear increases (called shear thinning)

(c) η increases with increasing rate of shear (called shear thickening)

In some cases all three behaviors -- Newtonian, shear-thinning, and shear-thickening -- have been found to exist in a single plastisol. In addition, some plastisols have been found to exhibit a decrease of η with time at a constant shear rate, a characteristic which is termed thixotropic behavior. Finally, the phenomenon of a yield stress, or shearing stress below which no flow occurs, has also been observed experimentally.

Plastisols have been accountable for the development of new low-cost processes because they are a liquid form of a PVC compound in the unprocessed state. These new techniques were made possible because the liquid form of PVC could be converted to a finished product (or "vinyl") simply through the application of heat to effect fusion into a solid mass. Hence, through proper formulation, plastisols can be modified for the most-efficient processing, as well as for the desired end-use properties. Plastisol-end products normally range from semirigid to soft and pliable materials. Their range of properties may be extended to include rigid forms through modification by mechanical mixtures with other polymers, as well as through special processing techniques.

Vinyls can exhibit a wide variety of flexibility, tensile strength, hardness, and abrasion resistance. Other desirable formulations may include nontoxicity, outdoor-weathering resistance, and resistance to chemicals, oils, and water. Plastisols can be pigmented to any color or may be produced in a transparent form.

The usefulness of plastisols was made possible through the development of PVC resins made by emulsion-polymerization processes. Resins made in this manner are termed dispersion resins. Work on such processes began in Germany at I. G. Farben as early as 1931 and resulted in commercial production by 1938. In the United States, production was begun in the early nineteen-forties by both Union Carbide and B. F. Goodrich.

The production of dispersion-grade resins used in plastisols differs greatly from that of the vast majority of PVC resins which are referred to as suspension or general-purpose resins. These general-purpose resins are prepared by suspension polymerization. Suspension resins fall typically in the 30 to 350-micron-diameter range of particle sizes and are granular in nature with a porous surface. By contrast, PVC resins that are polymerized using emulsion polymerization in which surface-active agents are employed result in a fine particle-size material in the range of 0.1 to 10 microns. These so-called dispersion-grade resins are talc-like in quality because of their fine particle size.

The successful industrial application of plastisol dispersions requires a working knowledge of their rheological properties of such systems. This work was motivated in part by the need for such knowledge. A detailed description of the practical use of poly(vinyl chloride) systems and the flow-dependent parameters of several application techniques are detailed in Appendix A. If the reader is not familiar with the industrial processing of plastisols, Appendix A should help set the perspective for this work.

Because of the diverse nature of plastisol application processes, it is essential to be able to formulate plastisols for a multiplicity of flow properties. However, the formulation process is difficult because ultimate vinyl properties must always be the main consideration. One cannot neglect these properties when formulating for the most-desirable plastisol rheology. This situation requires that one understand how various plastisol components can be altered to achieve the desired flow properties without adversely affecting ultimate vinyl properties after fusion. The following factors have been found to influence the flow properties of dispersions of PVC: (1) particle size and particle-size distribution of the polymer,[4-7] (2) nature of the plasticizer,[7,8] (3) concentration of the polymer,[4,9-12] (4) age of the dispersion,[10,13-15] (5) type and amount of surfactant present on the resin,[16] and (6) temperature.[17] In addition, other factors, such as the degree of dispersion due to mix preparation and the order in which ingredients are added during the mixing process, may further complicate flow properties. However, a gap is still present between relating and then integrating these factors to predict ultimate flow properties. The purpose of this study is to try to bridge this gap by investigating the effects of the resin characteristics and the nature and amount of plasticizers as they relate to predicting plastisol rheology.

2.2 Theory of Suspensions

Early analysis dealt with suspensions that were confined to low volume fractions of suspended materials (≤ 0.10 volume fraction of solid phase). Later work dealt with moderately concentrated suspensions (0.10 to 0.30 volume fraction of solid phase) and concentrated suspensions (≥ 0.30 volume fraction of solid phase). The critical area of plastisol rheology involves volume fractions of resins greater than or equal to 0.50, for which resin/resin (particle/particle), as well as resin/plasticizer (particle/vehicle), interactions become important.

2.2.1 Dilute/Moderately Concentrated Suspensions

Einstein[18,19] was the first (1906, 1911) to present a theoretical analysis of the effective viscosity of suspensions pertaining to the limiting conditions of spherical solid particles at infinite dilution (no interparticle attraction or repulsion). He expressed his results in the form,

$$\frac{\eta}{\eta_S} = 1 + 2.5\phi \text{ as } \phi \to 0, \qquad (1)$$

where η = suspension viscosity

η_S = viscosity of liquid phase

and ϕ = volume fraction of solid phase.

Since then, extensive theoretical and experimental investigations have been devoted to the effect of concentration on viscosity of suspensions. This work has been summarized adequately in several review articles.[20-24]

A typical plot of η_R, the reduced or relative viscosity (the viscosity of the suspension divided by the viscosity of the dispersing medium) versus ϕ is shown in Figure 1. The packing fraction at which the viscosity apparently becomes very large, ϕ_P, is also shown.

Many functions have been proposed to represent the variation in η_R shown in Figure 1. Most of these relationships suffer from the limitation that they do not consider non-Newtonian-viscosity behavior, i.e., η_R is formulated independent of shear

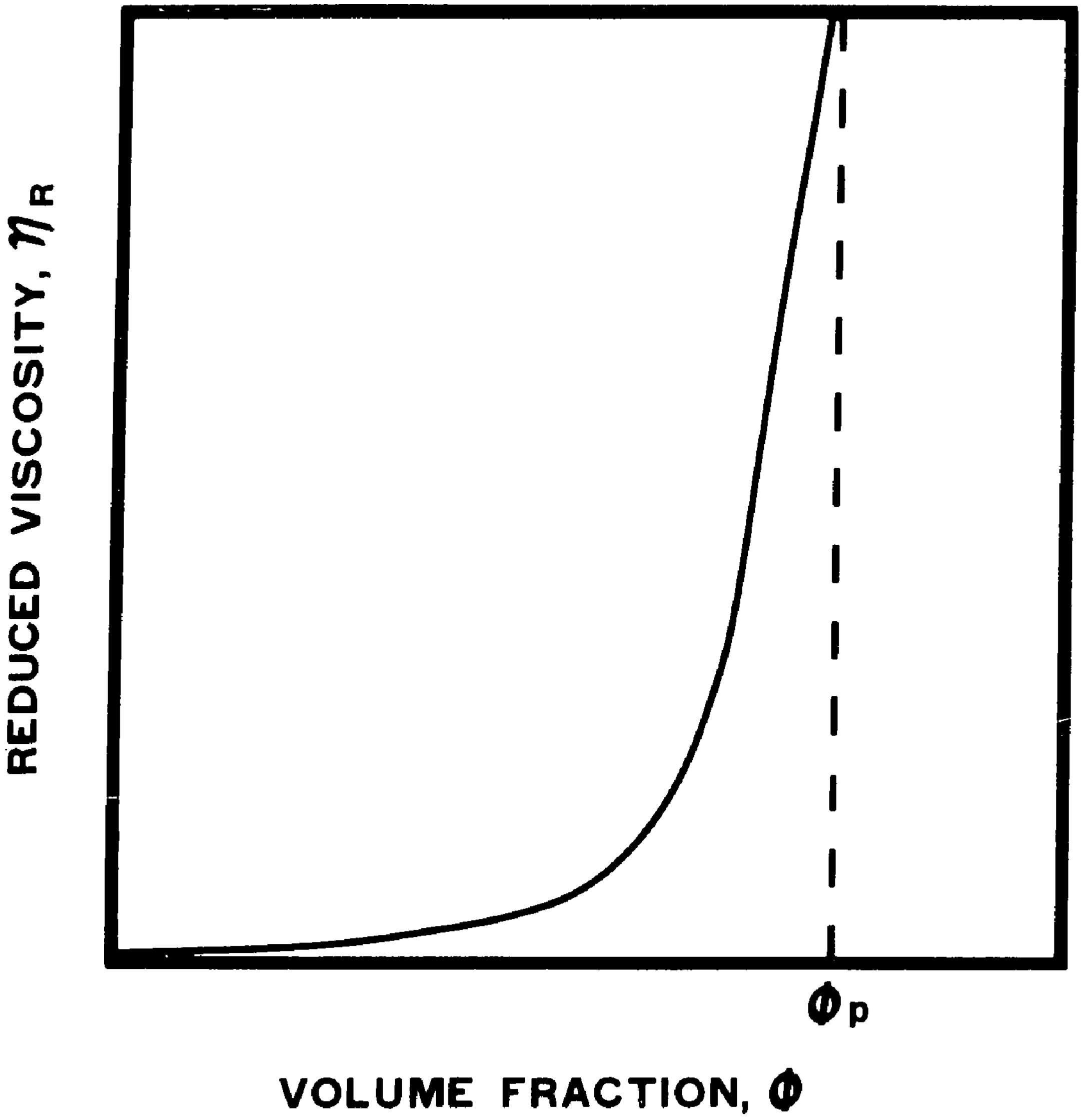


Figure 1

Typical Dependence of Reduced Viscosity on Volume Fraction rate. Nonetheless, these published relationships are presented because of the contributions they have made to the understanding of suspension rheology.

Mooney[25] (1946) extended Einstein's work to include first-order interactions. He demonstrated that his correlation could successfully be used to correlate independent experimental data from various sources, using

$$\frac{\eta}{\eta_S} = \eta_R = \sqrt{\frac{1 + 0.5\phi}{1-\phi}} \exp \frac{1.25}{1-\phi}. \qquad (2)$$

A theoretically based exponential function was developed by Vand[26] (1948):

$$\eta_R = \exp[2.5/(1-0.609\phi)]. \qquad (3)$$

In addition, Einstein's equation has been modified by Guth and Simha (1936)[57] to the form:

$$\eta_R = 1 + 2.5\phi + 14.1\phi^2. \qquad (4)$$

Robinson[27] (1949) attempted to derive a relationship with two parameters -- one of which had simple physical significance — valid over the entire range of suspension concentration. His expression,

$$\eta_R = 1 + k\phi/(1-s'\phi), \qquad (5)$$

where k = empirical constant

and s' = relative sediment volume,

includes the coefficient k which was taken to be a frictional coefficient and thus to depend on the shape, surface roughness, and other properties of the particle. In order to fit his own data on the viscosity of glass spheres in various solvents, Robinson had to make assumptions in Eq. (5) which were inconsistent with Einstein's Eq. (1) at low concentrations.

DeBruijn[28] (1951) felt that the absolute particle diameter was one parameter of importance. For particles with diameters less than 1 to 10 microns, colloid-chemical forces become important, causing non-Newtonian flow behavior. The result is a relative viscosity that increases as particle size is decreased, but which decreases to a limiting value as the shear rate is increased. For particles larger than 1 to 10 microns, deBruijn believed that inertial effects due to the restoration of particle rotation after collision result in an additional energy dissipation and a consequent increase in relative viscosity with increasing particle diameter.

2.2.2 Concentrated Suspensions

Simha[29] (1952) developed an expression

$$\eta_R = (54/4f^3)\left[\phi^2/(1-\phi/\phi_{MAX})^3\right], \quad \text{as } \phi/\phi_{MAX} \rightarrow 1, \qquad (6)$$

where f = empirical constant $1<f<2$

and ϕ_{MAX}= concentration of solids at close packing conditions.

Eq. (6), through the parameter f, takes into account the average intermolecular distance between molecules and the distance over which a hydrodynamic disturbance produced by one molecule can effect a second one in the presence of intervening particles.

Thomas[20] (1965) proposed that for more concentrated suspensions, it is necessary to account for the hydrodynamic interaction of particles, particle rotation, collision between particles, mutual exclusion of particles, doublet and higher-order agglomerate formation, and ultimately mechanical interference between particles as packed-bed concentrations are approached. He stated that the greatest difficulty in arriving at a theory for these concentrated suspensions is the fact that the random structure of the suspension cannot, in general, be represented by a single model. His model took the form:

$$\eta_R = 1 + 2.5\phi + 10.05\phi^2 + 0.00273\exp(16.6\phi). \qquad (7)$$

In 1967, Frankel and Acrivos[30] used an asymptotic technique to derive the functional dependence of effective viscosity on concentration for a suspension of uniform solid spheres, in the limit as concentration approaches its limiting value. This result, containing no empirical constants, was intended to complement the classical Einstein formula, Eq. (1). Their relationship

$$\eta_R = 1.125\left[\frac{(\phi/\phi_{MAX})^{1/3}}{(1-\phi/\phi_{MAX})^{1/3}}\right], \quad \text{as } \frac{\phi}{\phi_{MAX}} \to 1, \qquad (8)$$

was tested with experimental data available at that time and was found to agree quite well with the measurements for concentrations greater than $0.8\phi/\phi_{MAX}$.

Frankel and Acrivos also found that their expression was not in agreement with any of the semiempirical or empirical expressions that prior to 1966 had been proposed for highly concentrated suspensions including one derived by Eiler[31]:

$$\eta_R = (25/16)\left[\phi^2/(1-\phi/\phi_{MAX})^2\right]. \qquad (9)$$

A number of other investigators studied specifically the flow behavior of concentrated suspensions, many of them emphasizing the effects of particle size and particle-size distribution as it affects particle packing.

Metzner and Whitlock's paper in 1958[32] represents probably the first attempt to compile all available quantitative data on dilatancy (shear thickening). They attributed the onset of shear-thickening behavior to be a function of particle size and concentration, and viscosity of the suspending fluid. No mathematical models were proposed for predicting the flow behaviors.

Lewis and Nielsen[33] (1968) were the first to report rheological data for suspensions with a dispersed phase composed entirely of permanent aggregates of controlled size, size distribution, and shape. They found that the rheological behavior of their system (glass beads in a highly viscous fluid) could be predicted by Mooney's equation (Eq. (2)).

Morgan[34] (1968) studied the phenomenon of rheological dilatancy in an aqueous pigment suspension and determined that shear-thickening resulted from a progressive increase in flocculation due to shear. He felt that this finding was consistent with the findings by previous investigators in that the extent of shear-thickening increases with increasing particle concentration. He theorized that an increase in particle concentration increased the frequency of inter-particle collisions during flow, with the result that a given level of flocculation is attained at a lower rate of shear.

Both Farris[35] (1968) and Lee[36] (1970) examined the effects of particle size and particle-size distribution by considering the packing phenomenon. Farris developed a theory that related the viscosity-concentration behavior of multimodal suspensions of rigid particles to the viscosity-concentration behavior of the unimodal components. Lee developed an analytical technique for calculating the packing of n-component mixtures of spheres using the idealized packing of binary mixtures.

Chong, Christiansen, and Baer[37] (1971) studied the rheology of concentrated suspensions. Using their own data and data from many other sources, they developed the expression:

$$\eta_R = \{1 + 0.75 \left[\phi/\phi_\infty \,/(1-\phi/\phi_\infty)\right]\}, \qquad (10)$$

where ϕ_∞ = maximum volume solid loading.

This correlation indicates that the relative viscosity of suspensions of spherical particles is independent of particle size and particle-size distribution and is only a function of the reduced volume concentration, ϕ/ϕ_∞. If the maximum solids concentration, ϕ_∞, for monodispersed suspensions is taken to be equal to 0.605, Eq. (10) reduces to Eq. (1) at dilute concentrations. The reduced viscosity can be predicted from their correlation if the maximum solids concentration is known as a function of particle-size distribution.

Eagland and Kay[38] (1970) also studied the rheological properties of concentrated polymer dispersions. Their study showed the importance of the degree of dispersion on rheological investigations. In addition, they reported a marked increase in shear-thinning behavior that accompanied a decrease in particle size.

Other investigators including Gillespie[39-41] (1960, 1963) and Smith[42] (1972) examined the rheology of colloidal systems; however, only shear-thinning effects were discussed.

2.2.3 Plastisols

The general area of plastisol technology is covered well in both Sarvetnick's[1] and Penn's[43] books. Early investigators[4,9,10,12,44,45] examined the kinds of instruments that could be used in plastisol rheology and discussed in some generality plastisol-flow anomalies.

A number of other investigators[5,7,11,13-16,46-53] have looked at various aspects of plastisol rheology; however, only two studies will be discussed in detail because of their importance to this study.

Johnston and Brower[54] (1970) used the critical-volume concept to develop what is probably one of the best expressions available for the relationship between the apparent viscosity (at a shear rate of 1 $\sec^{-1}$) of plastisols and the volume fraction of resin. Their expression, Eq. (11), was found to be valid --

$$\log_{10}\eta_R = (1.33 - 0.84\phi/\phi c)\ \left[\phi/(\phi c - \phi)\right], \qquad (11)$$

where ϕ_c = critical volume of resin --

for several resin/plasticizer systems and thus not invalidated by variations in particle size and particle-size distribution. The equation was also shown to be equally applicable to suspensions of glass beads in plasticizers. The critical volume fraction is defined as the volume fraction of resin particles that have absorbed the plasticizer to the point where it no longer fills completely the interstices between the particles and consequently the viscosity becomes extremely high. The authors point out, however, that it is not easy to extrapolate viscosities to high shear rates (or for that matter any shear rate different from 1 $\sec^{-1}$) from their equation since the viscosity of the paste changes in a complicated manner. In fact, the authors do not suggest how such an extrapolation might be made.

The determination of ϕ_c in their equation was initially done by extrapolating η_R versus ϕ data to determine the value of ϕ at which η_R approaches a very large value. Eq. (11) was derived by computer fitting their experimental data. In this fashion, ϕ_c could be determined from a few viscosity measurements.

In another significant work, Hoffman[2,3] found that monodisperse suspensions of polymeric resins exhibit shear-thickening behavior that transforms into a discontinuous viscosity behavior when the volume fraction of solids is raised above 0.50. His experimental evidence supported his hypothesis that the discontinuity was caused by a flow instability in which surfaces of spheres, packed in a two-dimensional hexagonal packing at low shear rates, break up into a less-ordered array of spheres. Referring to the works of Metzner and Whitlock[32], Morgan[34], and Gillespie[13], Hoffman hypothesized the following model for viscometric flows.

Forces of attraction and repulsion acting between particles in the suspension interact with forces of the shear field to cause the formation of surfaces of two-dimensional, hexagonally packed spheres that pass one over another in the direction of flow. As one increases the relative velocity of these neighboring surfaces of spheres, the shear stress transmitted from one surface to the next through the interstitial fluid is increased. Some critical value of the shear stress is finally reached at which the shear-stress couple on the surfaces of the hexagonally packed spheres is just sufficient to overcome the forces between the spheres which hold them in place. When this happens, sections of the ordered surfaces roll up into eddies and the onset of disordered flow occurs. The extra energy dissipated by the spheres when they collide with one another during flow causes a discontinuous jump in the apparent viscosity at the instability point.

Hoffman provided evidence of his theory from (1) viscosity curves for suspensions containing monosized PVC spheres at various volume-fraction levels; (2) light-diffraction results from the ordered and unordered arrays of spheres obtained at various shear rates; and (3) photographs of the ordered planes of hexagonally packed spheres.

2.2.4 Direction of Research

Drawing on the works of Johnston and Brower, and Hoffman, this study is aimed at more fully investigating plastisol rheology, concentrating on discontinuous-viscosity behavior as influenced by the particle-size characteristics of the resin and the nature and amount of plasticizer, employing the critical-volume concept wherever possible. In this manner the findings of these authors can be further extended and understood.

No single equation exists which accounts both for the dual effects of volume and shear-rate conditions, to say nothing of such additional phenomena as thermodynamic interactions in reactive dispersants. The ultimate goal of this study was to develop such a quantitative expression that can be used in predicting 'a priori' plastisol flow properties, given certain quantitative parameters determined experimentally. These parameters include the viscosity of the plasticizer(s), the volume concentration of the resin, and the maximum volume fraction of resin which can be used and still form a fluid plastisol.

3. EXPERIMENTAL

3.1 Resins

Plastisol resins are polymerized in latex form as follows: First, vinyl chloride (VCM) is added to the water phase, in which it disperses as colloidal droplets. Some monomer dissolves in the water and migrates to a polymerization site where the VCM adds to other VCM units to form a polymer. This polymer grows to a molecular weight that is controlled by the temperature of the reaction. Free-radical-producing species (initiators) are required to initiate the reaction and to keep it going. Emulsifier is used to keep the colloidal emulsion particles from coagulating after they form.

To convert the PVC latex into a useful form, the resin must be separated from the water phase. This step is generally accomplished by drying the latex in a spray dryer, where under considerable pressure the latex stream is broken up into fine spray droplets, then mixed with hot air which flashes away the water. The resin drops to the bottom of the dryer where it is conducted on a stream of air to a grinder. The grinder acts to reduce the size of any resin clusters that may have developed in the latex or in the dryers.

Another way of removing water from the latex is through use of suction filters and/or pressure filters.[55] These techniques result in less agglomeration of the PVC particles.

A commercially available, vacuum-dried resin, Tenneco 1730, was chosen for this experimental study. Prepared by Tenneco Chemicals, Inc., it contains a small number of agglomerated particles formed after drying. The 1730 resin was classified into three separate size ranges by the Majac Division of the Donaldson Company, Inc. using their Acucut air classifier.[56]

This particular classifier is designed to disperse and classify PVC particles into coarse and fine fractions. High-energy dispersing air enters a rotor radially around the entire outer edge, while feed particles enter the dispersing air zone through an inlet in the rotor ring. In the classification zone, particles are acted upon by an outwardly directed centrifugal force and an inwardly directed drag force. Air carries the dispersed fine particles spirally inward to the central fine-fraction outlet. Coarse particles move outward around the rotor periphery to the coarse-fraction outlet. The desired "cut" is selected by adjustment of air-flow rate, rotor speed, or both. Figures 2 and 3 illustrate the principle.

The Tenneco 1730 resin was classified by attempting to separate the resin into two separate "cuts" of 1.0 and 2.0 microns particle diameter. Some difficulty was encountered in achieving this precisely; however, three separate sizes in addition to the "Raw Feed" 1730 were obtained. The flow chart depicted in Figure 4 indicates how the various size ranges were obtained.

Figure 5 shows the particle-size analysis of the 1730, 1730-2F 1730-1F, and 1730-2C resins as determined by Coulter Counter analysis by Majac. Although the 1730-2C resin should have a larger proportion of particle sizes as compared with the unseparated 1730, Coulter Counter analysis did not indicate this to be true. Both the 1730 and the 1730-2C fractions were rechecked by Majac, with the same results as indicated in Figure 5. Differences in particle size were observed in scanning-electron micrographs taken of the test resins. These photographs are included later in this section.

Table I shows the arithmetic and linear mean diameters of the various resins based on Coulter Counter results.

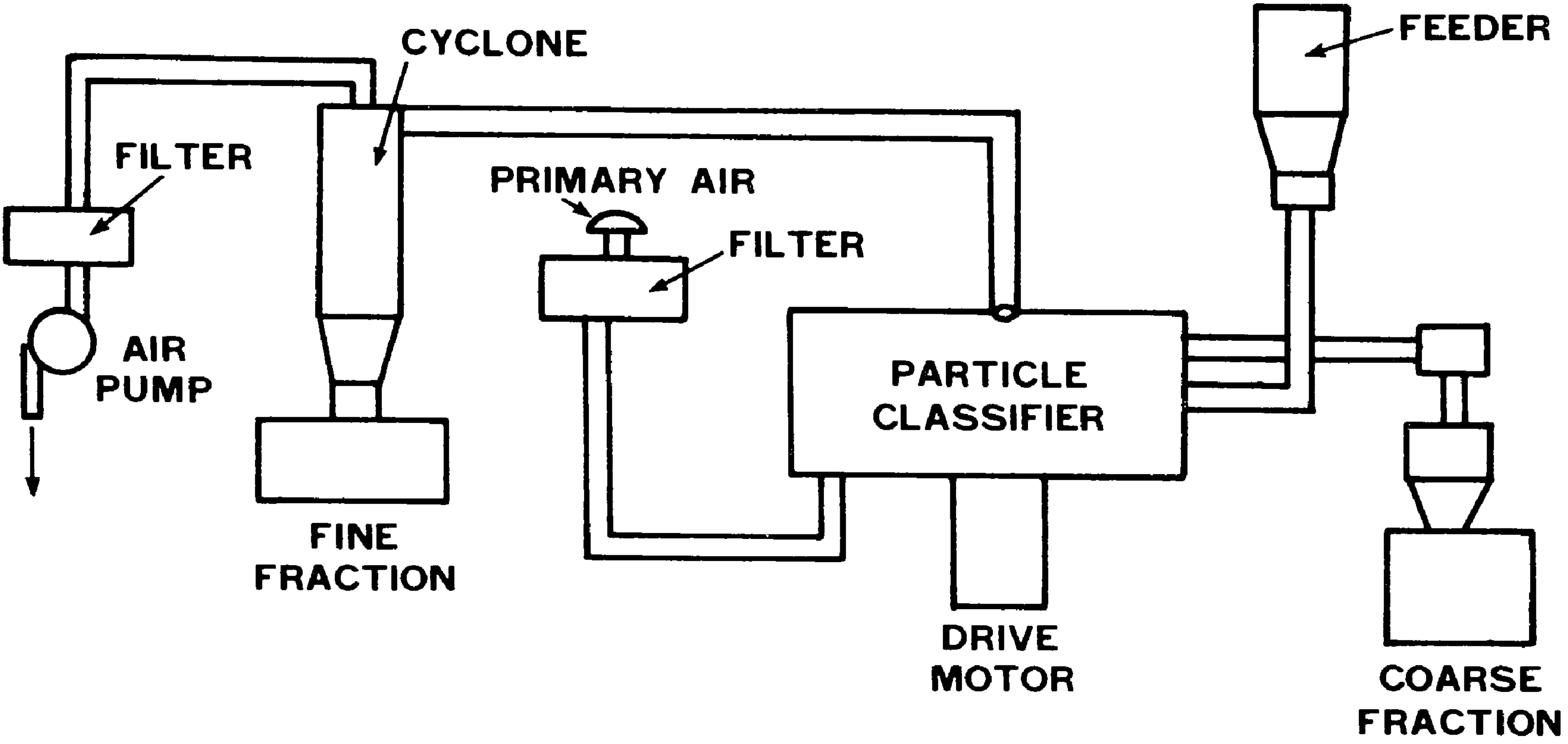


Figure 2

Majac Classifier

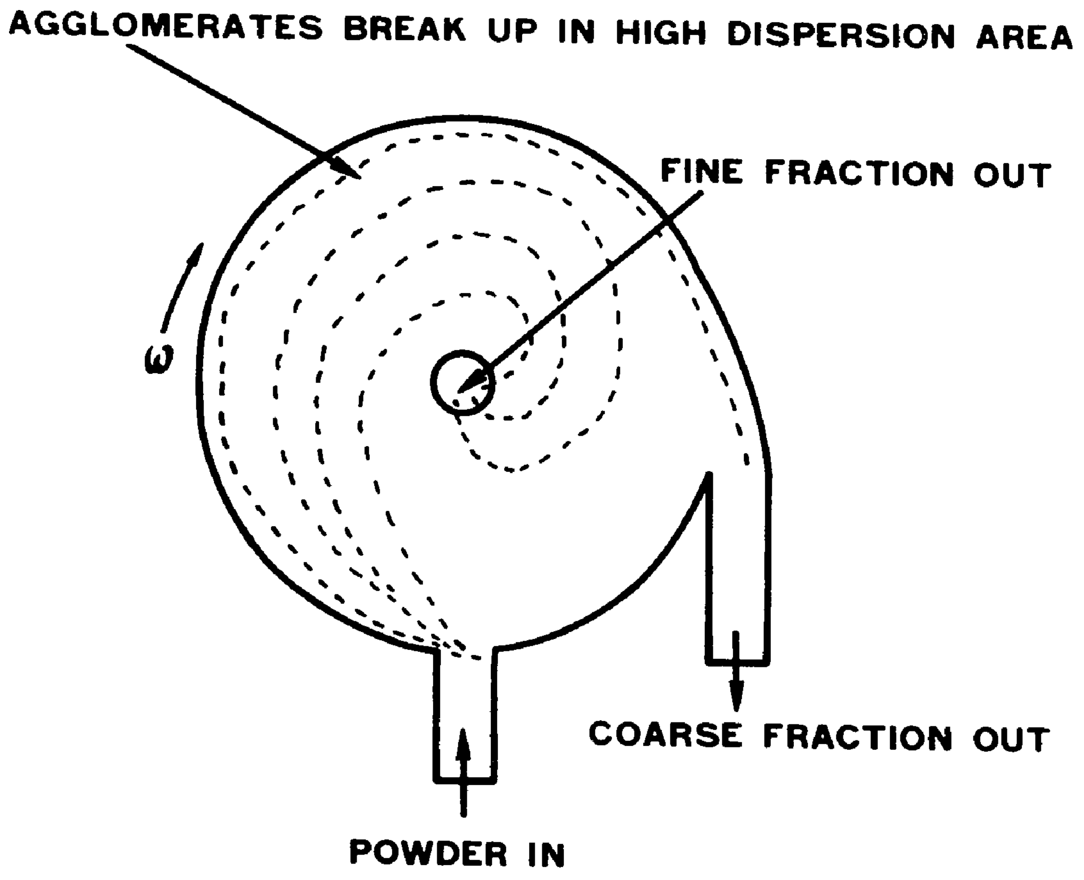


Figure 3

Majac Particle Classifier

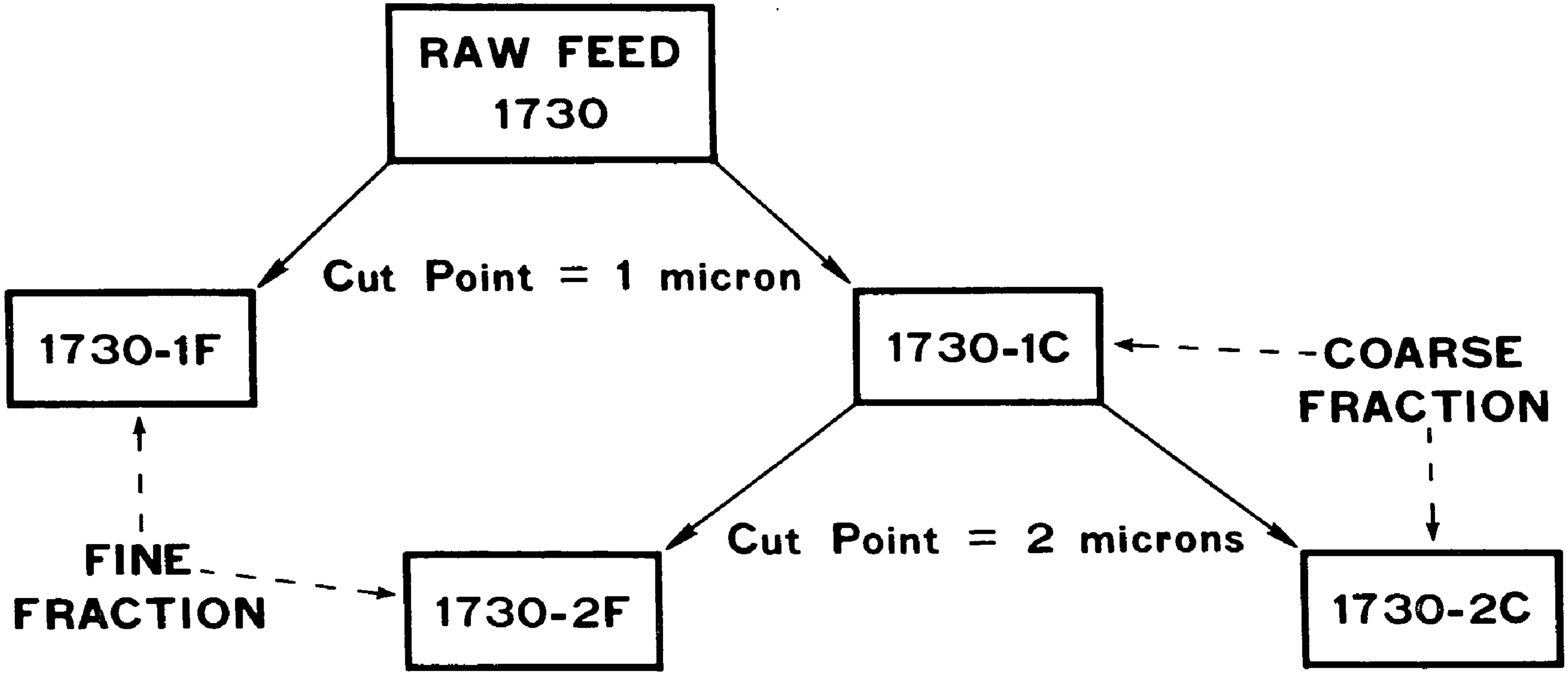


Figure 4

Classification of 1730 Resin

Figure 5

Particle-Size Analysis of Separated 1730 Dispersion Resin

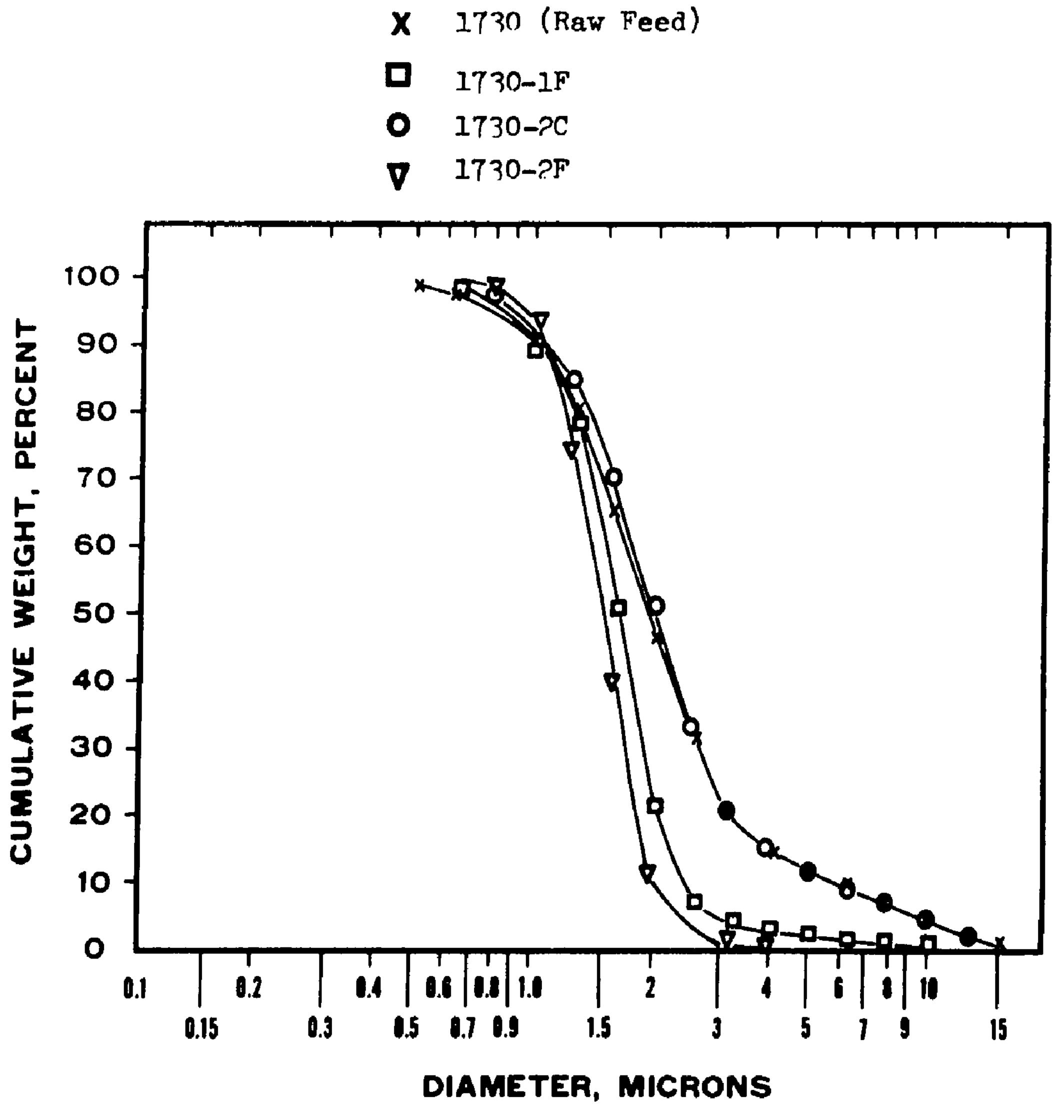


TABLE I

Particle-Size Diameter Averages of 1730 Resins

Resin Cut	Arithmetic Mean, $\bar{d}$, microns*	Linear Mean, d_1, microns**	$d_1/\bar{d}$
1730	2.88	5.55	1.93
1730-1F	1.75	2.30	1.31
1730-2F	1.55	1.68	1.08
1730-2C	2.87	5.20	1.81

$$*\bar{d} = \sum_{i=1}^{N} x_i D_i / \sum_{i=1}^{N} x_i \qquad (12)$$

$$**d_1 = \sum_{i=1}^{N} x_i D_i^2 / \sum_{i=1}^{N} x_i D_i \qquad (13)$$

where x_i = weight fraction

D_i = particle diameter

and N = number of fractions.

Table I illustrates that the 1730-2F resin cut has the smallest particle size and narrowest particle-size distribution, followed by 1730-1F, 1730-2C, and 1730, respectively.

In addition to Coulter Counter analysis, each of the resin cuts were individually characterized, so as to be able to isolate the particle size and particle-size distribution differences. Scanning electron micrographs (SEM) of each cut size were taken and are shown in Figure 6.

From these photographs, one can see the differences present among the resins. Resins 1730-1F and 1730-2F possess nonagglom-

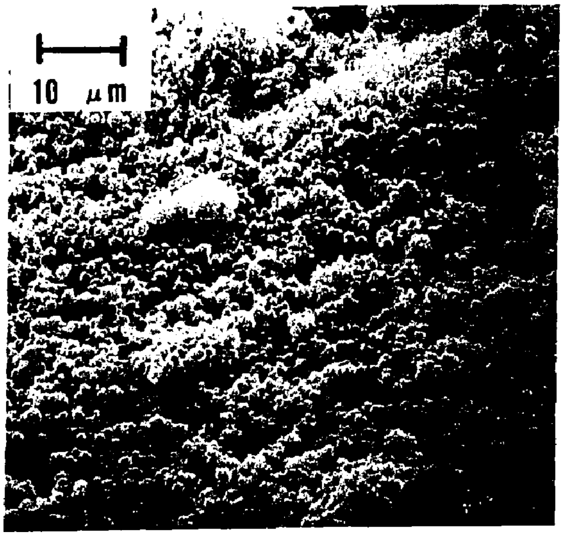


Figure 6a
SEM of 1730 Resin
1000X

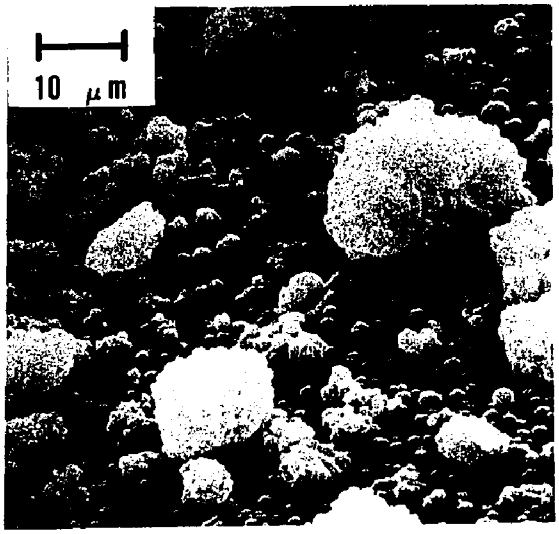


Figure 6b
SEM of 1730-2C Resin
1000X

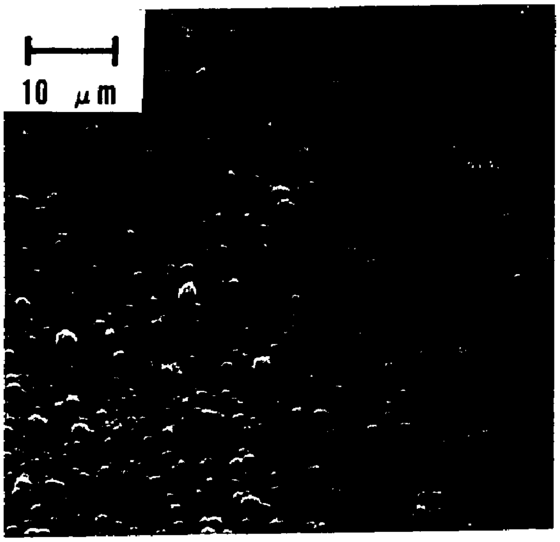


Figure 6c
SEM of 1730-IF Resin
1000X

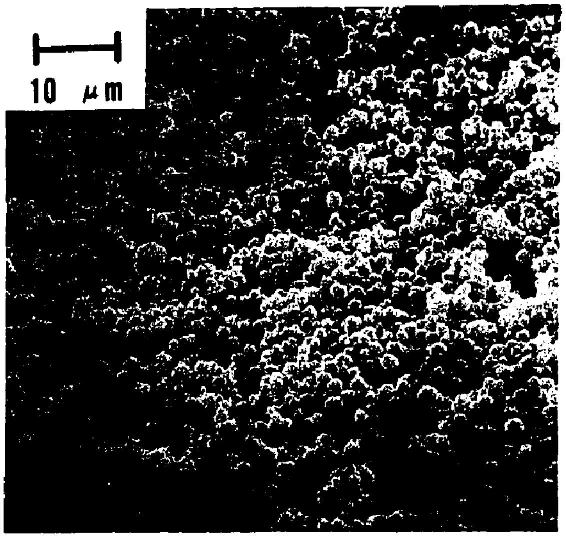


Figure 6d
SEM of 1730-2F Resin
1000X

erated particles, whereas the 1730 and 1730-2C resins contain such agglomerations. Note, however, that the 1730-2C resin contains a larger proportion of these agglomerations. Although the Coulter Counter analysis did not pick up any significant differences between the 1730 and 1730-2C resins, the SEMs clearly show such differences.

Molecular-weight averages of the four resin cuts were also obtained using conventional gel permeation chromatography (gpc) techniques.

TABLE II

Molecular-Weight Averages for Test Resins

Resin	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_z/\overline{M}_w$
1730	17,500	99,300	205,000	5.67	2.07
1730-1F	14,000	99,500	209,000	6.66	2.11
1730-2F	15,250	98,250	201,500	6.44	2.05
1730-2C	18,500	98,500	207,000	5.32	2.10

Table II indicates that the molecular weights for all the resins are identical within experimental error.

The type and amount of surfactant present on the resins was determined by methanol extraction techniques. All resins were found to contain approximately 0.9 weight percent fatty acid-type surfactant. In addition, the four resins each were found to have a density of 1.41 g/ml, using a conventional pycnometer.

This is perhaps the first time that rheological studies of plastisols have been attempted using various particle sizes of dispersion-grade resins produced from the same original resin lot. With this procedure, differences due to polymerization conditions, drying conditions, and type and amount of surfactant present can be eliminated. Only the effects of particle size and particle-size distribution have been studied.

3.2 Plasticizers

By imparting fluidity to PVC resins, plasticizers are the key ingredient that make plastisols possible. In 1951, the Council of International Union of Pure and Applied Chemistry defined a plasticizer as a substance or material incorporated in another material to increase its workability and its flexibility or distensibility.[58] Plasticizers are high-boiling, chemically and thermally stable organic liquids. Their action is essentially permanent, as opposed to the temporary function of solvents.

Many different chemical compositions can function as plasticizers, however, for economic and/or performance considerations only about five hundred are listed as commercially available at present.[59] Less than one hundred are important in PVC, and not all of these find use in plastisol formulations.

In addition to aiding in processing and imparting flexibility, the requirements on PVC plasticizers are many.[1] Appendix B gives a listing of these functions and goes into some detail on the most important aspects of plasticizer properties.

Three plasticizers—di-2-ethylhexyl phthalate (DOP), n-butyl benzyl phthalate (BBP), and di-2-ethylhexyl adipate (DOA)— were chosen for this study. It is felt that the three represent a cross section of the most-important PVC plasticizers.

DOP

This plasticizer is by far the most-versatile and widely used PVC plasticizer. Although it is not outstanding in any single property, DOP exhibits good performance in the following respects: stability to light, heat, and chemicals; resistance to extraction by oil and water; compatibility with a variety of substances; little or no taste, color, odor, toxicity, or allergic reaction, and good electrical properties. DOP is rated "fair" with respect to volatility, temperature performance, and flammability. The important physical properties of DOP are listed in Table III.

BBP

Butyl benzyl phthalate is a primary plasticizer for resins of the PVC type. A true coester, it is a widely used fast-solvating plasticizer. It is particularly advantageous for improving ease of processing on mills, calenders, or extruders. BBP makes possible regular production rates at lower temperatures, or higher rates at similar temperatures. In addition, it imparts superior stain resistance, good solvent-extraction resistance, and low density to vinyl films. It has rather poor low-temperature properties, and heat and light stability are inferior to DOP. The important physical properties are listed in Table III.

TABLE III

Physical Properties of DOP, BBP, and DOA Plasticizers

Property	DOP	BBP	DOA
Chemical Formula	$C_{24}H_{38}O_4$	$C_{19}H_{20}O_4$	$C_{22}H_{42}O_4$
Molecular Weight	390	312	371
Density[a], 25.0°C g/ml	0.98336	1.12078	0.92452
Viscosity[b], 25.0°C poise	0.569	0.470	0.119
Boiling point/range	230°C @ 5mm	370°C @ 760mm	208-218°C @ 4mm
Freezing Point	-55°C	-35°C	-70°C
Flash point (ASTM D 92-46)	425°F	390°F	377°F
Refractive index	1.486 @ 20°C	1.536 @ 25°C	1.446 @ 25°C
Solubility parameter $(cal/ml)^{1/2}$	8.8	9.9	8.4
Flory-Huggins Interaction parameter, χ	-0.03	0.10	0.28
Dielectric constant @ 25°C	5.2 @ 1Kc 5.18 @ 10Kc 5.18 @ 100Kc	6.45 @ 1Kc 6.41 @ 10Kc 6.40 @ 100Kc	4.13 @ 1Kc 4.13 @ 10Kc 4.13 @ 100Kc
Fusion Temp.[c]	84°C	69°C	111°C
Minimum fluxing temp.[d]	105°C	75°C	120°C
Clear point[e]	127°C	89°C	144°C

---

[a] Experimentally determined by conventional pycnometer techniques.

[b] Experimentally determined by Haake Rotovisco Viscometer.

[c] The temperature at which torque in a Plasti-Corder begins to increase rapidly at the onset of fusion.[60]

[d] The lowest temperature at which a plastisol develops sufficient physical integrity to permit being lifted from a fusion plate.[61]

[e] The temperature at which a plastisol becomes clear.[62]

DOA

Di-2-ethylhexyl adipate is one of the dibasic acid esters commonly known as low-temperature plasticizers. These low-temperature plasticizers are said to impart "hand and drape" to PVC sheeting and coated fabric constructions. Although the low-temperature performance is superior to DOP, DOA does not have the degree of compatibility and performance of DOP. In practice, DOA is usually blended with branched-chain phthalates to improve the low-temperature performance of the resulting product. In addition, DOA is used in plastisols to reduce viscosity. The important physical properties are listed in Table III.

The property differences among the three plasticizers are illustrated by the data presented in Table III. The most important property differences for this study -- viscosity, density, and compatibility -- are summarized below:

$$\text{Viscosity}_{\text{DOP}} > \text{Viscosity}_{\text{BBP}} > \text{Viscosity}_{\text{DOA}}$$

$$\text{Density}_{\text{BBP}} > \text{Density}_{\text{DOP}} > \text{Density}_{\text{DOA}}$$

$$\text{Compatibility}_{\text{BBP}} > \text{Compatibility}_{\text{DOP}} > \text{Compatibility}_{\text{DOA}}$$

3.3 Mixing Procedure

Although the majority of experimental work centered around the measurement of viscosity characteristics of the aforementioned resins and plasticizers, the development of some key experimental techniques and corroboration of previously made assumptions were necessary.

The mixing procedure used to combine the resin and plasticizer is known to influence the ultimate flow properties.[63-65] After reviewing existing literature, it was determined that a technique should be used to determine the degree of dispersion after mixing is completed. A Hegman Gauge (or Fineness of Grind gauge) was utilized to test the degree of dispersion. This gauge is commonly used to measure the degree of dispersion in pigment dispersions. The procedure used to mix all the plastisols is listed below:

1. Weigh out the liquid plasticizer in a tared 250 ml beaker.
2. Add the total amount of resin.
3. Hand mix with a spatula for a total of 10 to 15 minutes. At this time check for the degree of dispersion using the Hegman Gauge.
4. If plastisol is not properly dispersed (scale reading greater than 0.3 mils), mix for another 5 minutes and check with Hegman Gauge.
5. When the scale reads 0.3 mils or less, the mixing is stopped.

This mixing procedure has yielded utility in mixing all the plastisols investigated in this research study. Reproducibility obtained with this technique is discussed in Section 4.1.

3.4 Plastisol Formulations

A variety of plastisols with various combinations of the aforementioned resins and plasticizers were prepared for this study.

Analysis of rheological behavior has been found to be best accomplished using volume-fraction concentrations rather than weight-fraction concentrations. The following equations were used to convert weight fractions to volume fractions:

$$\mathrm{Vol}_R = \mathrm{Wt}_R/\rho_R, \tag{14}$$

where Vol_R = volume of resin

Wt_R = weight of resin

ρ_R = density of resin

and

$$\mathrm{Vol}_p = \mathrm{Wt}_p/\rho_p, \tag{15}$$

where Vol_p = volume of plasticizer

Wt_p = weight of plasticizer

ρ_p = density of plasticizer

and

$$\Phi = \mathrm{Vol}_R/(\mathrm{Vol}_R + \mathrm{Vol}_p), \tag{16}$$

where Φ = volume fraction of resin.

Combining Eqs. (14), (15), and (16) one finally obtains

$$\Phi = (\mathrm{Wt}_R/\rho_R)/(\mathrm{Wt}_R/\rho_R + \mathrm{Wt}_p/\rho_p). \tag{17}$$

The accuracy of Eq. (17) is dependent on the assumption that the individual volumes of the resin and plasticizer are equal to the volume of the mixed plastisol, i.e.,

$$\mathrm{Vol}_{pl} = \mathrm{Vol}_R + \mathrm{Vol}_p, \tag{18}$$

where Vol_{pl} = volume of plastisol.

The validity of Eq. (18) was verified by using the pycnometer technique to measure the density of the plastisol. The procedure consisted of preparing a plastisol using the weight-volume relationship of Eq. (17). After measuring the plastisol density, the "actual" volume fraction was determined using Eq. (19),

$$\Phi = (Wt_R/\rho_R)/(Wt_{pl}/\rho_{pl}), \qquad (19)$$

where Wt_{pl} = weight of plastisol

and ρ_{pl} = density of plastisol

This experiment confirmed the assumptions made in deriving Eq. (17). More details on the comparisons will be presented in Section 4.1.

Table IV presents a listing of all the plastisols tested in this study.

3.5 Φ_{MIX} Determinations

As a way to further characterize the maximum packing possible with a specific particle-size distribution, a number of techniques have been used by other investigators. Most, however, involve the extrapolation of data outside of measurable limits, such as the technique used by Johnston and Brower.[54] A new, simpler technique was developed for this research that provided a measure of the maximum volume fraction of resin that would form a suitable plastisol, designated Φ_{MIX}. It was determined by the following procedure:

1. A known amount of resin was added to a tared 150 ml beaker.
2. Plasticizer was added in finite increments to the resin and hand-stirred with a spatula.
3. Additional plasticizer was added and stirred until a smooth paste resulted. This point was considered to be a maximum volume fraction of resin and Φ_{MIX} could be calculated using Eq. (17).

TABLE IV

Experimental-Formulations Tested

Formulation Designation	Resin	Volume Fraction of Resin, ϕ	Volume Fraction of Total Plasticizer DOP	DOA	BBP
A	1730	0.580	0.000	1.00	0.000
B	1730	0.585	0.000	1.00	0.000
C	1730	0.600	0.000	1.00	0.000
D	1730	0.605	0.000	1.00	0.000
E	1730	0.610	0.000	1.00	0.000
F	1730	0.630	0.000	1.00	0.000
G	1730	0.640	0.000	1.00	0.000
H	1730	0.650	0.000	1.00	0.000
I	1730	0.660	0.000	1.00	0.000
J	1730	0.670	0.000	1.00	0.000
K	1730	0.585	1.00	0.000	0.000
L	1730	0.605	1.00	0.000	0.000
M	1730	0.635	1.00	0.000	0.000
N	1730	0.644	1.00	0.000	0.000
O	1730	0.576	0.000	0.000	1.00
P	1730	0.585	0.000	0.000	1.00
Q	1730	0.605	0.000	0.000	1.00
R	1730	0.620	0.000	0.000	1.00
S	1730	0.605	0.500	0.500	0.000
T	1730	0.605	0.000	0.500	0.500
U	1730	0.605	0.333	0.333	0.333
V	1730	0.605	0.250	0.250	0.500

TABLE IV, continued

Formulation Designation	Resin	Volume Fraction of Resin, ϕ	Volume Fraction of Total Plasticizer DOP	DOA	BBP
W	1730	0.605	0.500	0.000	0.500
X	1730-2F	0.585	0.000	1.00	0.000
Y	1730-1F	0.586	0.000	1.00	0.000
Z	1730-2C	0.586	0.000	1.00	0.000

The reproducibility of this technique was tested by repeating the experiment with a number of the different resin/plasticizer combinations and found to be accurate within 1.0%. Complete results and a more detailed analysis of this technique are found in Section 4.2.

3.6 Rheological Measurements

The rheological flow data of the plastisol formulations listed in Table IV were obtained with a Haake Rotovisco RV1 Rotating Viscometer. Operation details are described in the literature.[66]

The Rotovisco was used with the bob-cup experimental systems. The characteristics of these systems are described in Appendix C. The correction factors that were applied to the data are illustrated in Appendix D. These corrections were applied to correct for the non-Newtonian nature of the plastisols as affected by the specific bob-cup attachment. Such corrections are described in detail in the literature.[66,67]

The testing procedure followed was to mix the desired plastisol as previously described in Section 3.3. The plastisol is immediately placed in the cup and allowed to age at 25°C for 10 to 15 minutes. Following this, the rheological data are obtained by varying the shear rate and recording the corresponding shear-stress observation. Care was taken to choose, where possible, the specific bob-cup combination that would yield the widest range of shear rate observations, including $\dot{\gamma}_d$. Typical handling of the data obtained with the viscometer is illustrated in Appendix E.

4. RESULTS AND DISCUSSION

The development of a technique to determine maximum resin volume fractions, ϕ_{MIX}, and the use of the ϕ_{MIX} values to establish a relationship with discontinuous-viscosity behavior are two important results of this research study. This section will provide analysis of the experimental data obtained and will discuss the important implications of these results.

4.1 Density Check and Mixing Procedure

As discussed in the experimental section, a verification was made of the assumptions inherent in Eq. (17) using a pycnometer to measure the actual density of the plastisol. The procedure consisted of preparing a plastisol using the weight/volume relationships of Eq. (17), and then determining the "actual" volume fraction (VF) of resin by using Eq. (19). Table V illustrates the results.

TABLE V

Volume Fraction of Resin Determinations

Formulation Designation	Plastisol	Measured Plastisol Density, g/ml	ϕ Eq. (17)	ϕ Eq. (19)	% Diff $\frac{\phi_{17}-\phi_{19}}{\phi_{17}}$ X100
B	0.586VF 1730/DOA	1.2060	0.586	0.584	0.3
K	0.585VF 1730/DOP	1.2367	0.585	0.587	0.3
J	0.670VF 1730/DOA	1.2737	0.670	0.683	1.9

As shown in Table V, the differences in ϕ between samples

B and K were found to be 0.3%. A larger difference, 1.9%, was found for sample J, which represents the highest volume fraction of resin plastisol prepared. The good correlation obtained from this experiment verifies the assumptions made to derive Eq. (17), i.e., the density obtained when combining a resin and a plasticizer is simply the weight-average additions of each component's density. There is no change in volume due to thermodynamic interactions in the systems studied.

The reproducibility of the mixing procedure described in the experimental section is illustrated in Table VI. The procedure consisted of mixing and obtaining viscosity/shear-rate measurements of 0.585VF 1730/DOP plastisol (Sample 1). One week later, 0.585VF 1730/DOP plastisol (Sample 2) was mixed and viscosity/shear-rate measurements obtained. Comparative viscosity measurements of these two plastisols are shown below.

TABLE VI

Comparative Haake Rotovisco Data

Shear Rate (sec^{-1})	Viscosity 0.585VF 1730/DOP Hegman Gauge =0.3 mils Sample 1	Viscosity 0.585VF 1730/DOP Hegman Gauge = 0.1 mils Sample 2	% Difference $\frac{\text{Visc.\#2}-\text{Visc.\#1}}{\text{Visc.\#2}} \times 100$
5.92	92.70 poise	88.36 poise	4.91
8.89	103.21	99.35	3.88
17.77	140.91	137.05	3.86
26.66	206.5	198.04	2.56
		Average Difference	3.80%

Considering all the variables involved, the mixing procedure yielded two plastisols having almost identical rheological behavior. Thus the mixing procedure yields reproducible results and minimizes any effects that improper mixing may have on influencing ultimate plastisol rheology.

4.2 Φ_{MIX} Determinations

The development of an experimental technique for measuring the maximum volume fraction of resin, Φ_{MIX}, is an important result of this study. Previously, extrapolation and/or curve-fitting techniques were used to predict maximum volume resin concentrations. The mixing technique is much more akin to the actual preparation of plastisols being used commercially.

As described in the experimental section, the technique is straightforward and reproducible. It does accurately reflect what other experimenters have as maximum concentrations -- the point at which all the resin particles are coated and voids are "almost" completely filled.

Table VII lists the experimentally obtained values of Φ_{MIX} for all combinations of resins and plasticizers investigated in this study.

TABLE VII

Experimentally Obtained Values
of Maximum Volume Fraction of Resin, Φ_{MIX}

Resin	Plasticizer	Φ_{MIX}
1730	BBP	0.620
1730	DOP	0.642
1730	DOA	0.667
1730-1F	BBP	0.615
1730-1F	DOP	0.627
1730-1F	DOA	0.646
1730-2F	BBP	0.595
1730-2F	DOP	0.612
1730-2F	DOA	0.642
1730-2C	BBP	0.581
1730-2C	DOP	0.608
1730-2C	DOA	0.615

The more compatible the plasticizer ($\text{compatibility}_{BBP} > \text{compatibility}_{DOP} > \text{compatibility}_{DOA}$), the lower the maximum amount of resin that can be added for a given resin. This is due to the **imbibition** of a larger amount of the more compatible plasticizer on the resin particle, thereby requiring additional plasticizer to fill the interstices. This is another way of saying that the particle/vehicle interactions become greater as the compatibility of the plasticizer is increased.

The maximum volume fraction of resin, ϕ_{MIX}, is not related in a simple manner to the particle-size characteristics of the resin or the nature of the plasticizer. Thus, ϕ_{MIX} must be determined experimentally for each resin/plasticizer combination. ϕ_{MIX} represents a measure of particle/particle interactions. The smaller the value of ϕ_{MIX}, the greater the particle/particle interaction.

Figure 7 shows the relationship between ϕ_{MIX} and differences in the solubility parameters of the plasticizer and resin. This information will be discussed later in this report.

4.3 Reduced Volume Fraction, ϕ_R

In an effort to normalize volume-fraction data to reflect specific volume effects, a factor, ϕ_R, was developed as a measure of the deviation from ϕ_{MIX}.

$$\phi_R = \sum_{i=1}^{n} \sum_{j=1}^{m} x_i y_j \quad \phi/\phi_{MIX\ ij}, \qquad (20)$$

where x_i = volume fraction of the i^{th} liquid phase

y_j = volume fraction of the j^{th} solid phase

ϕ = total volume fraction of resin(s)

n = number of plasticizers

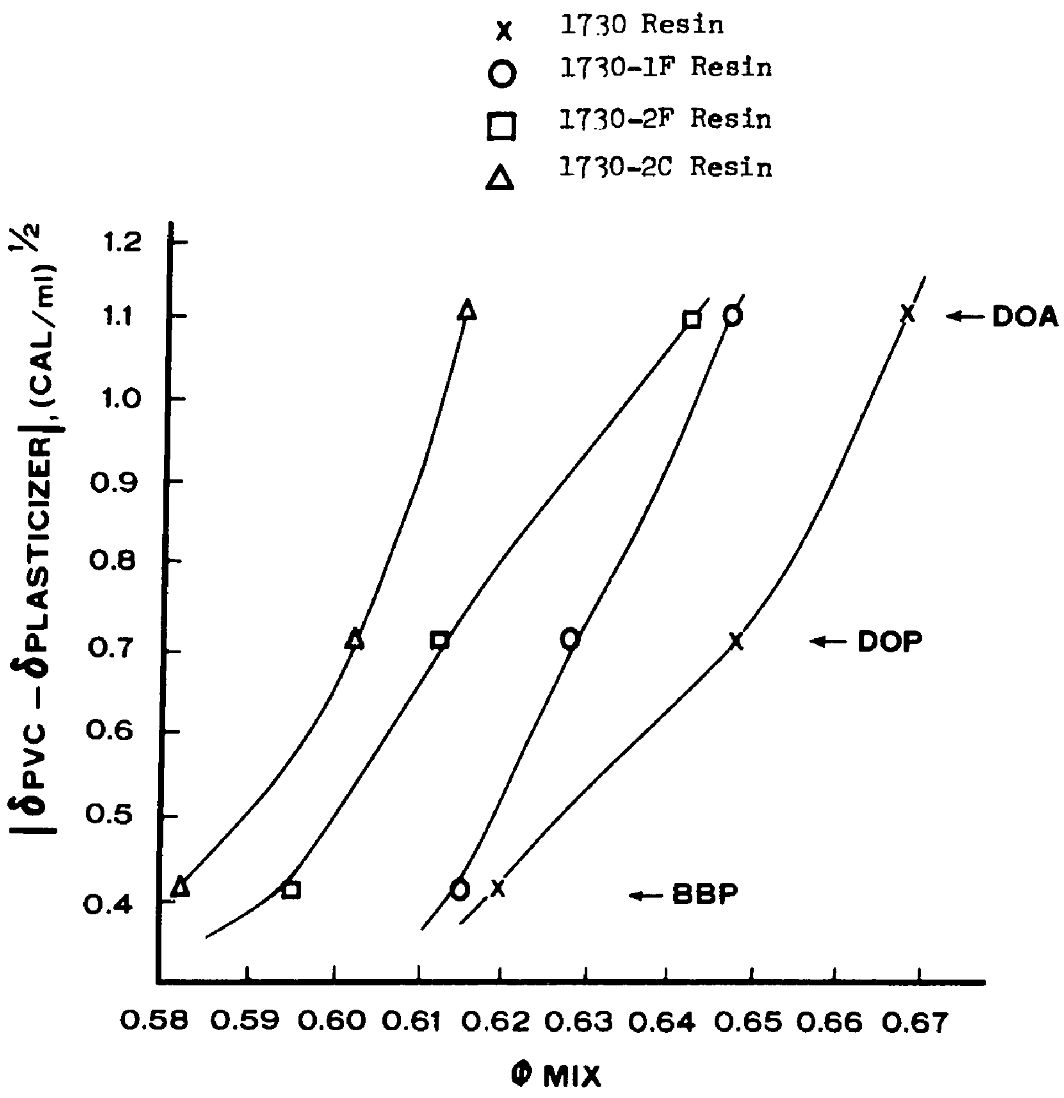
m = number of resins

and ϕ_{MIXij} = ϕ_{MIX} of i^{th} plasticizer with the j^{th} resin.

The reduced volume fraction, ϕ_R, is an indication of departure from the maximum volume fraction of resin obtainable with the resin(s)/plasticizer(s) system. This expression, which is a simple mixing

Figure 7

Φ_{MIX} of Resin/Plasticizer Systems



algorithm, permits the calculation of a reduced volume fraction, Φ_R. When using a single resin and plasticizer system, Eq. (18) reduces to expressions used by previous investigators. Reduced volume fractions were calculated using Eq. (20) for all test plastisols. Table VIII lists the results.

TABLE VIII

Reduced Volume Fractions for Test Plastisols

Experiment Designation	Plastisol Formulation	Reduced Volume Fraction Φ_R
A	0.580VF 1730 in DOA	0.870
B	0.585VF 1730 in DOA	0.877
C	0.600VF 1730 in DOA	0.900
D	0.605VF 1730 in DOA	0.907
E	0.610VF 1730 in DOA	0.915
F	0.630VF 1730 in DOA	0.945
G	0.640VF 1730 in DOA	0.960
H	0.650VF 1730 in DOA	0.975
I	0.660VF 1730 in DOA	0.990
J	0.670VF 1730 in DOA	1.00
K	0.585VF 1730 in DOP	0.911
L	0.605VF 1730 in DOP	0.938
M	0.635VF 1730 in DOP	0.989
N	0.644VF 1730 in DOP	1.00
O	0.576VF 1730 in BBP	0.929
P	0.585VF 1730 in BBP	0.944
Q	0.605VF 1730 in BBP	0.976
R	0.620VF 1730 in BBP	1.00
S	0.605VF 1730 in 0.500:0.500 DOP:DOA	0.922
T	0.605VF 1730 in 0.500:0.500 DOA:BBP	0.942

TABLE VIII, continued

Experiment Designation	Plastisol Formulation	Reduced Volume Fraction Φ_R
U	0.605VF 1730 in 0.333: 0.333:0.333: DOP:DOA:BBP	0.940
V	0.605VF 1730 in 0.250: 0.500:0.250 DOP:BBP:DOA	0.949
W	0.605VF 1730 in 0.500: 0.500 DOP:BBP	0.957
X	0.585VF 1730-2F in DOA	0.911
Y	0.586VF 1730-1F in DOA	0.906
Z	0.586VF 1730-2C in DOA	0.951

The reduced volume fraction is another qualitative measure of particle/particle interactions. The higher value of Φ_R implies a greater frequency of collisions of the resin particles, and therefore, greater particle-interaction effects. Section 4.5 discusses the specific applicability of Φ_R to this study.

4.4 Viscosity/Shear-Rate Data

Rheological data were obtained with the Haake Rotovisco Rotating Viscometer, at a constant temperature of 25°C. In order to eliminate differences among the plastisols due to the plasticizer viscosity, all viscosity determinations are compared as a ratio, η_R, of the plastisol viscosity to that of the suspending medium.

Figure 8 illustrates results obtained with 1730/DOA plastisols at concentrations varying from 0.580 to 0.670 volume fraction of resin. As the concentration of resin increases, the reduced-viscosity behavior likewise increases. The dotted line followed by an arrow (↗) in this and all subsequent flow-curve figures indicates the onset of a discontinuity in the viscosity, i.e., the viscosity approaches a very large value. The discontinuity shear rate, $\dot{\gamma}_d$, represents the highest shear rate at which the viscosity is measurable with the viscometer employed. As the concentration of resin is increased, the discontinuity shear rate decreases.

For concentrations $\geq$0.65VF resin, shear-thinning behavior is evident up to the point of viscosity discontinuity. For concentrations below 0.65VF resin, shear-thickening is observed before the onset of the discontinuity. The reason for this behavior is not clear at this time.

No hysteresis is observed when the shear rate is increased to the discontinuity range, i.e., when the material is reinvestigated at shear rates below $\dot{\gamma}_d$, the original viscosities are reproduced.

Figure 9 illustrates the flow curves for 1730/DOP plastisols at concentrations ranging from 0.585 to 0.644 volume fraction of resin. As with the 1730/DOA plastisols, when the volume fraction of resin is increased, the reduced viscosity increases and $\dot{\gamma}_d$ decreases. However, for the 1730/DOP plastisols, shear-thinning behavior at the higher concentrations is not as marked.

The flow curves for 1730/BBP plastisols at concentrations ranging from 0.576 to 0.620 volume fraction resin are illustrated in Figure 10. As is the case with 1730/DOA and 1730/DOP plastisols, an increase in the volume fraction of resin is accompanied by an increase in the reduced viscosity and by a decrease in the shear rate at which the viscosity discontinuity occurs.

Figure 11 illustrates the effect of reduced viscosity on the discontinuity shear rate for the plastisols shown in Figures 8-10. This plot shows that for a constant discontinuity shear rate, the reduced viscosity at the discontinuity varies with the particular plasticizer, i.e., (η_R for DOA)>(η_R for DOP)>(η_R for BBP). This observation indicates that the onset of discontinuous behavior is not a simple function of the reduced viscosity for a series of plastisols. This plot does indicate that for a specific family of resin/plasticizer systems, the inception of the shear-rate discontinuity increases as the reduced viscosity decreases. The reduced viscosity decreases because of a decrease in the amount of resin used to prepare the plastisol.

Figure 12 illustrates the flow curves of plastisols having reduced volume-fraction values of 1.0, representing the rheological behavior of plastisols at Φ_{MIX} concentrations. Reduced viscosity is not directly related to the onset of discontinuous-viscosity behavior; however, Figure 12 does show that at constant reduced volume fractions, viscosity discontinuity does occur at about the same shear rate. This result will be discussed in greater detail in Section 4.5.

Figure 8
Flow Curves for 1730/DOA Plastisols
at Various Concentrations

A	0.580 VF 1730 in DOA
B	0.585 VF 1730 in DOA
C	0.600 VF 1730 in DOA
D	0.605 VF 1730 in DOA
E	0.610 VF 1730 in DOA
F	0.630 VF 1730 in DOA
G	0.640 VF 1730 in DOA
H	0.650 VF 1730 in DOA
I	0.660 VF 1730 in DOA
J	0.670 VF 1730 in DOA

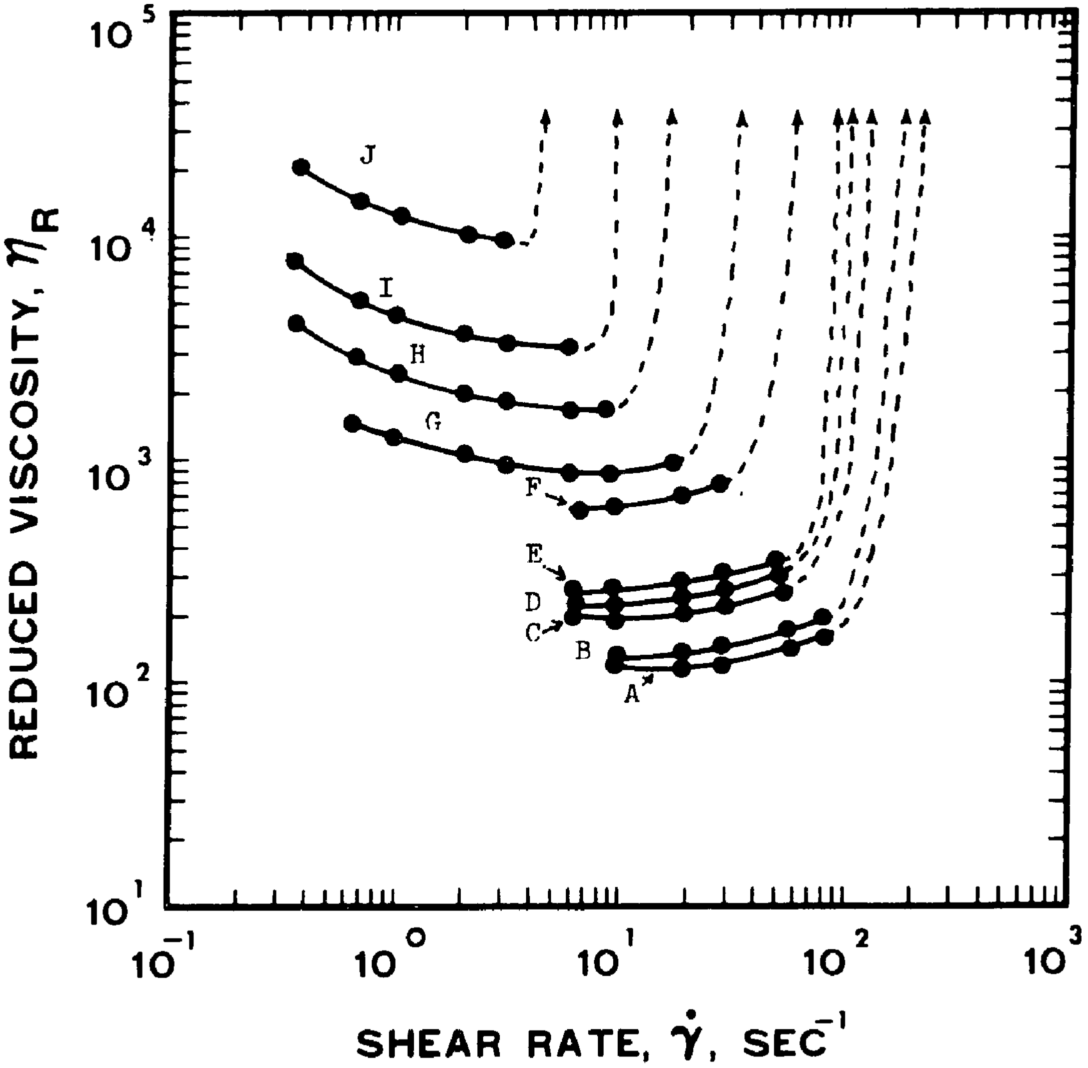


Figure 9

Flow Curves for 1730/DOP Plastisols
at Various Concentrations

K 0.585 VF 1730 in DOP
L 0.605 VF 1730 in DOP
M 0.635 VF 1730 in DOP
N 0.644 VF 1730 in DOP

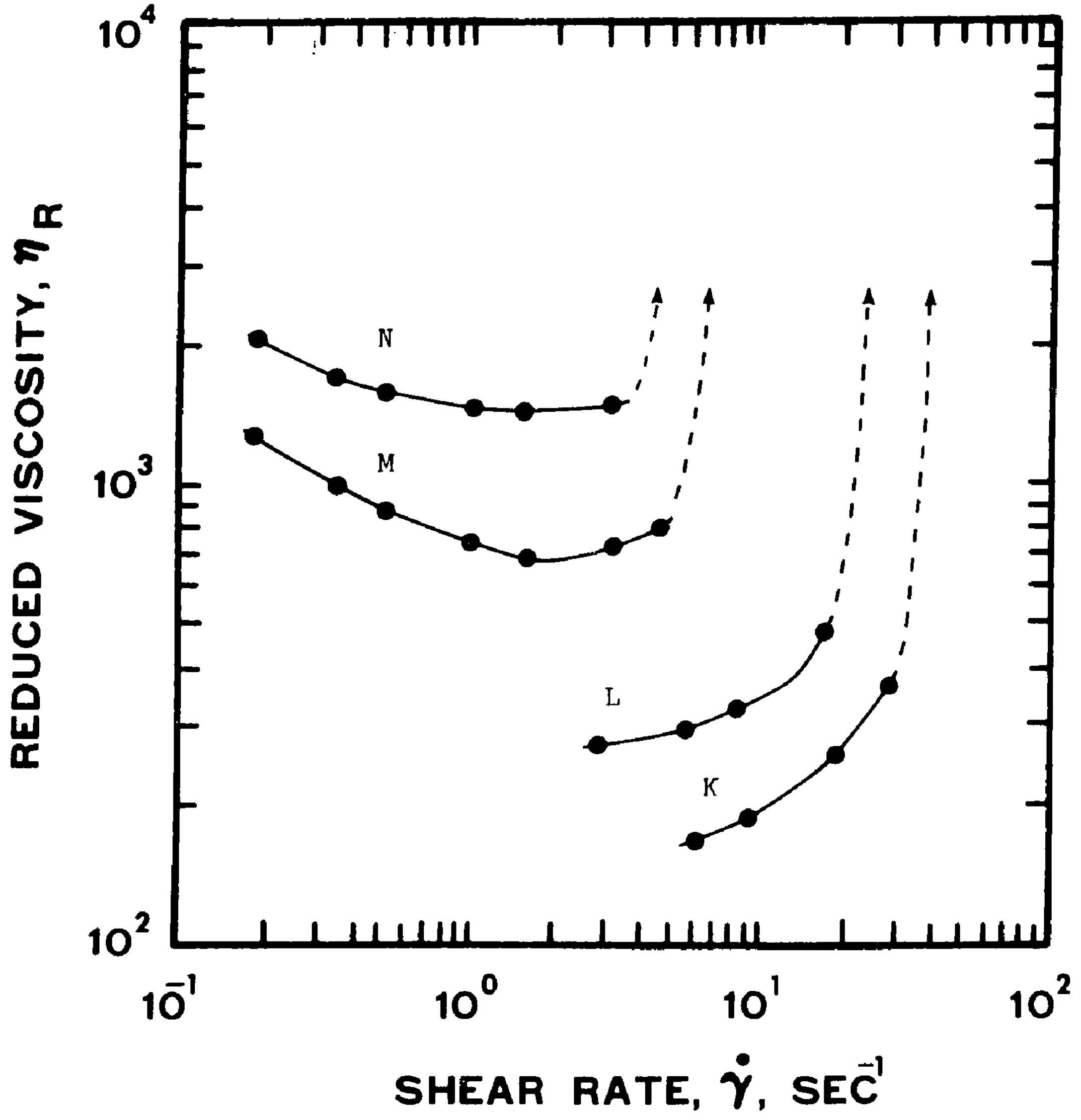


Figure 10

Flow Curves for 1730/BBP Plastisols
at Various Concentrations

O 0.576 VF 1730 in BBP
P 0.585 VF 1730 in BBP
Q 0.605 VF 1730 in BBP
R 0.620 VF 1730 in BBP

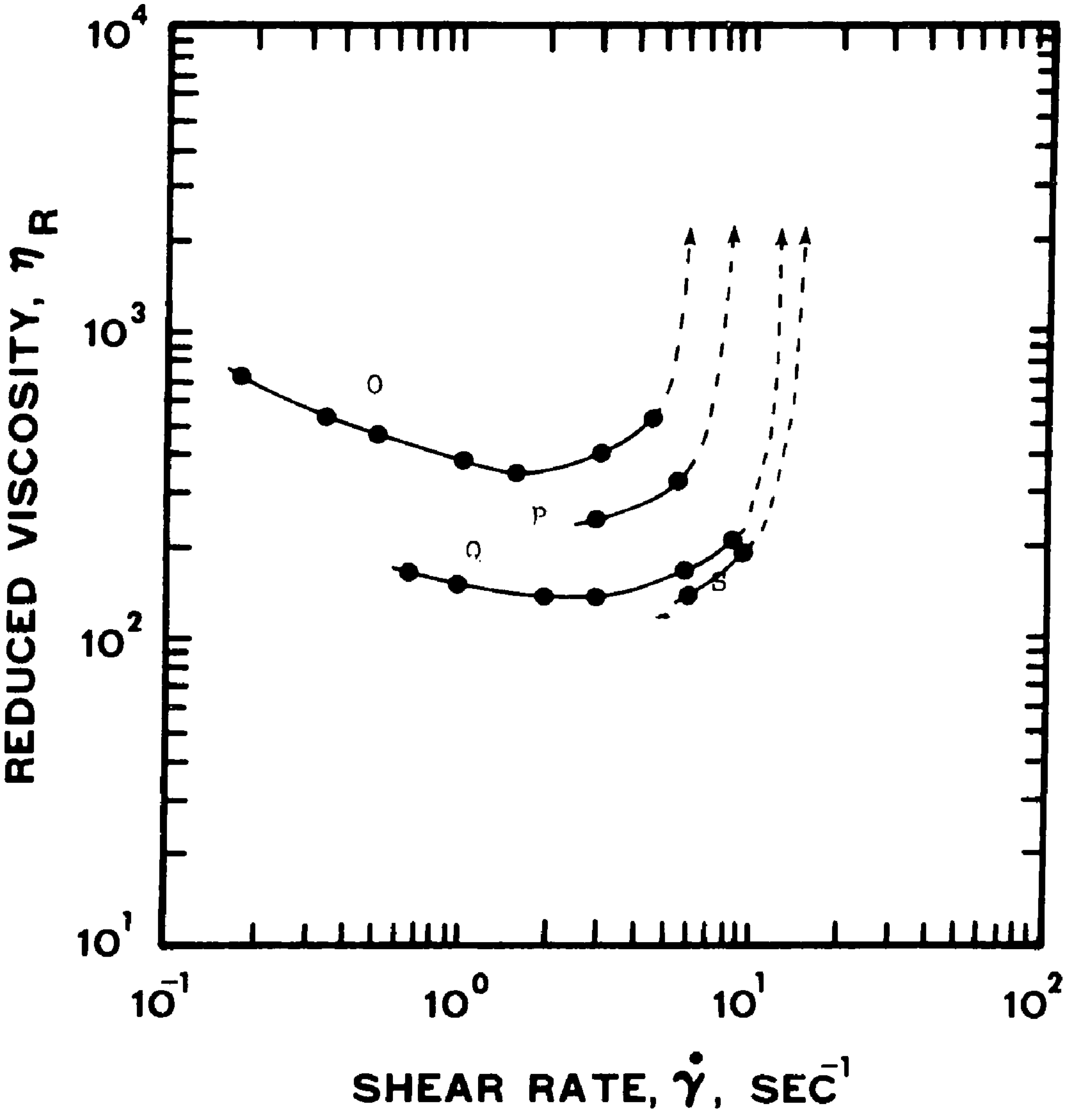


Figure 11

Reduced Viscosity at Discontinuity Shear Rate
For 1730 Plastisols Prepared with DOA, DOP & BBP

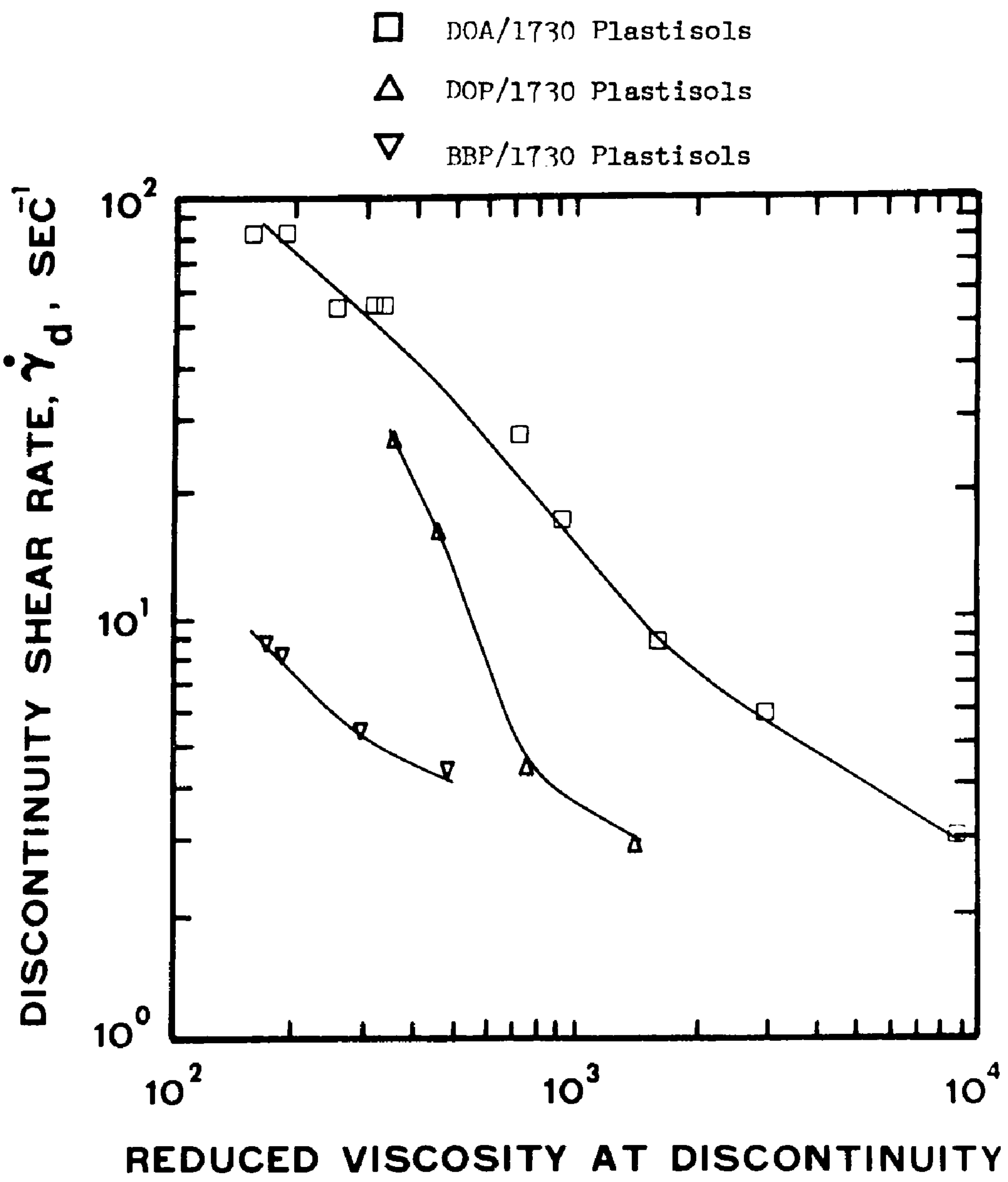


Figure 12

Flow Curves for 1730
in DOA, DOP, and BBP at $\Phi_R = 1.00$

J	0.670VF 1730 in DOA
N	0.644VF 1730 in DOP
R	0.620VF 1730 in BBP

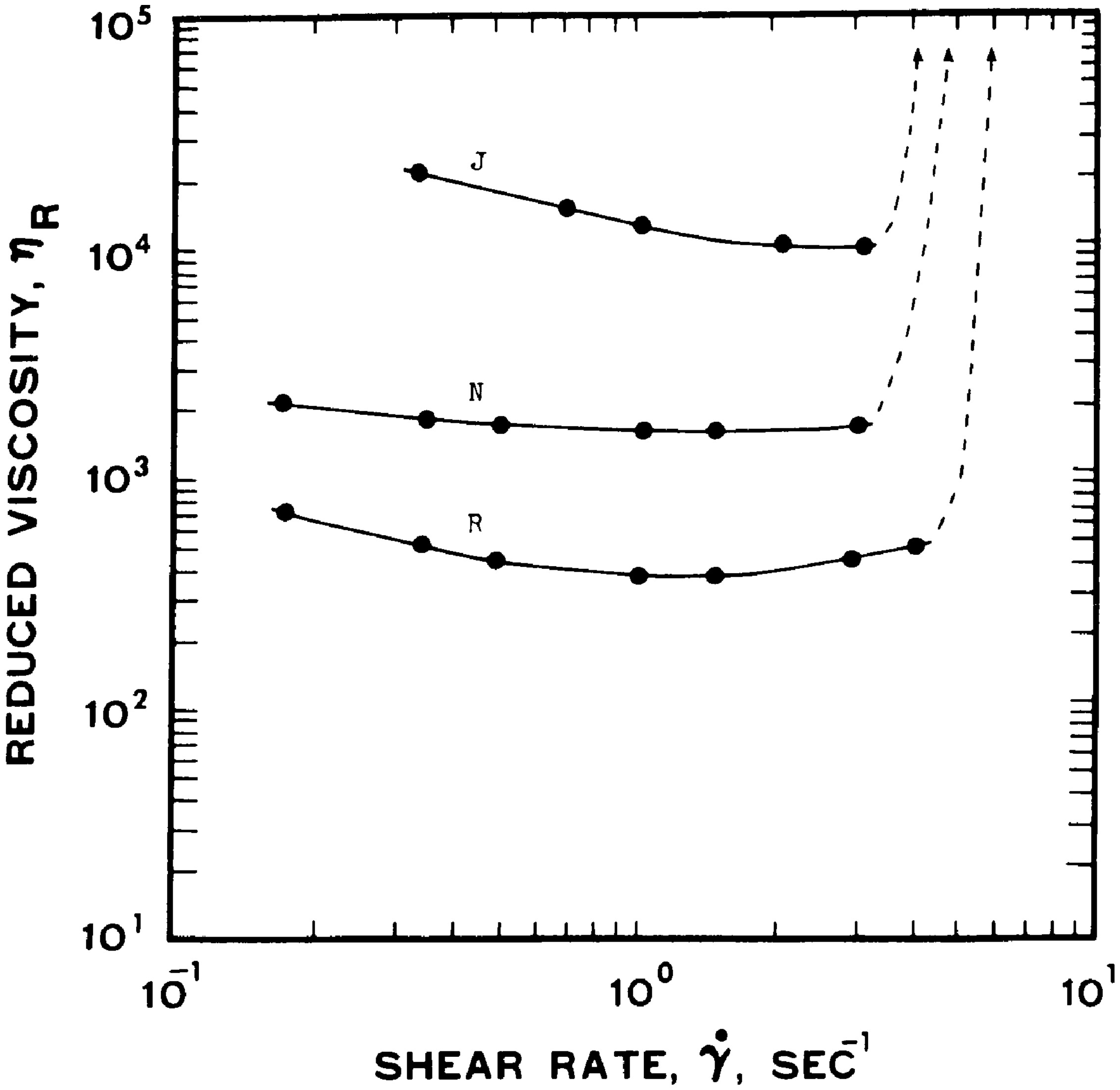


Figure 13 shows the relationship of reduced viscosity and the viscosity discontinuity among plastisols made with different plasticizers at a constant resin loading of 0.585 volume fraction of 1730 resin. The reduced viscosity of the 1730/DOA plastisol at 0.585VF resin is lower than the reduced viscosity of both the 1730/DOP and 1730/BBP plastisols. The interesting feature of this figure, however, is the comparison between the 1730/BBP and 1730/DOP plastisols. Even though the viscosities of the plasticizers differ — 0.470 poise for BBP, 0.569 poise for DOP, and 0.119 poise for DOA — the reduced viscosity of plastisols made with DOP and BBP do not differ significantly at this resin concentration. However, the onset of the flow discontinuity is at a lower shear rate for the 1730/BBP plastisol than for the 1730/DOP plastisol. This result further exemplifies the complexity of plastisol rheology.

Figure 14 illustrates the flow behaviors of plastisols made with various plasticizer blends at a 0.605VF of 1730 resin. Both the reduced viscosity and shear-rate discontinuity behaviors fall between plastisols containing all BBP (Q) and all DOA (D).

The flow behaviors among plastisols prepared with DOA and 1730, 1730-1F, 1730-2F, and 1730-2C resins at 0.585VF are shown in Figure 15. Although the flow behaviors of samples B, X, and Y seem similar, closer examination reveals a lower discontinuity shear rate for the plastisol made with 1730-2F resin, which has the finer particle size and narrowest particle-size distribution.

Figure 13

Flow Curves for 0.585 VF 1730
in DOA, DOP, and BBP

B 0.585 VF 1730 in DOA
K 0.585 VF 1730 in DOP
P 0.585 VF 1730 in BBP

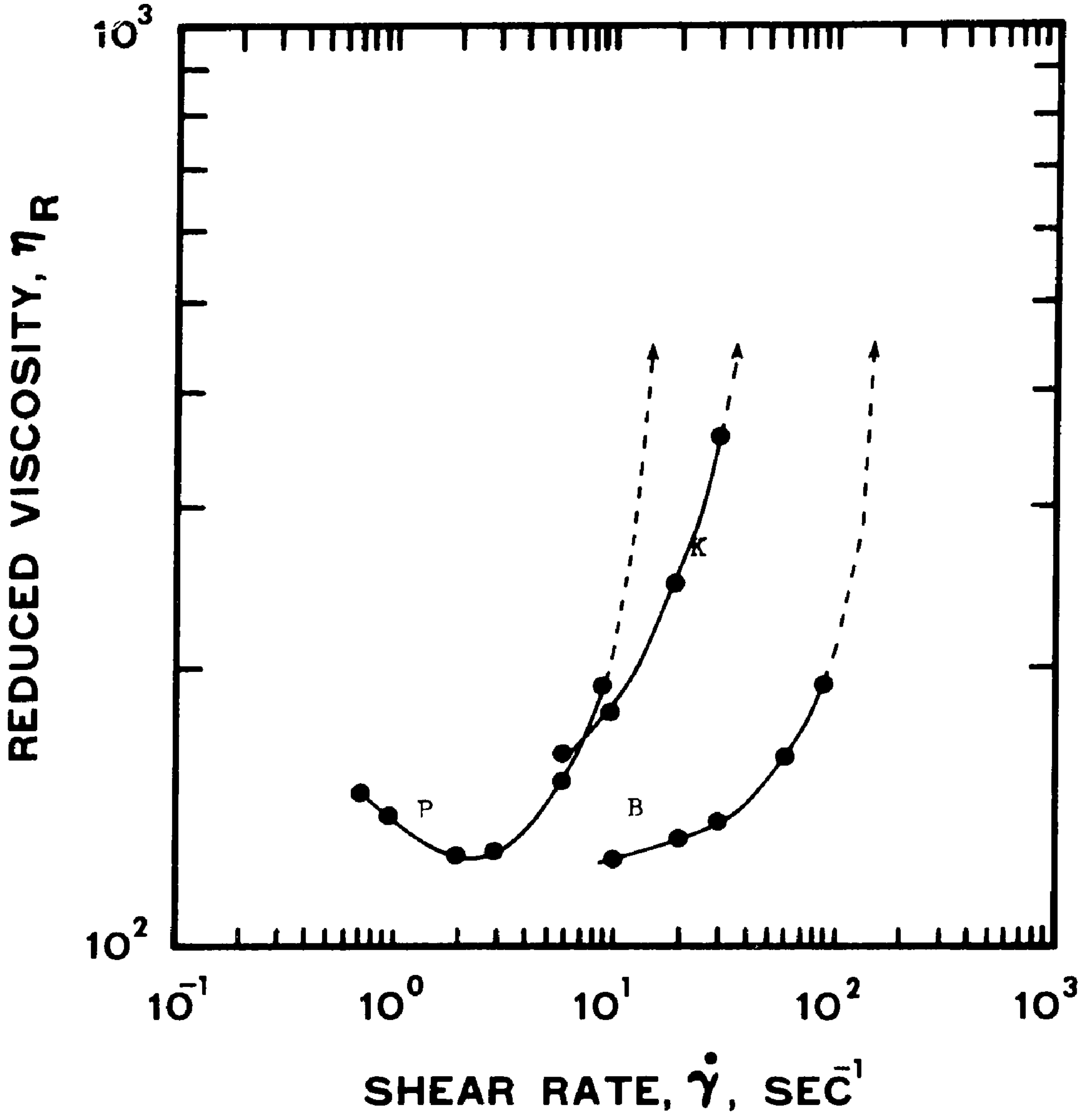


Figure 14

Flow Curves for 0.605 VF 1730 in Various Volume Fractions of DOP:DOA:BBP

D 0.605 VF 1730 in DOA
L 0.605 VF 1730 in DOP
Q 0.605 VF 1730 in BBP
S 0.605 VF 1730 in 50:50 DOP:DOA
T 0.605 VF 1730 in 50:50 DOA:BBP
U 0.605 VF 1730 in 33:33:33 DOP:DOA:BBP
V 0.605 VF 1730 in 25:25:50 DOP:DOA:BBP
W 0.605 VF 1730 in 50:50 DOP:BBP

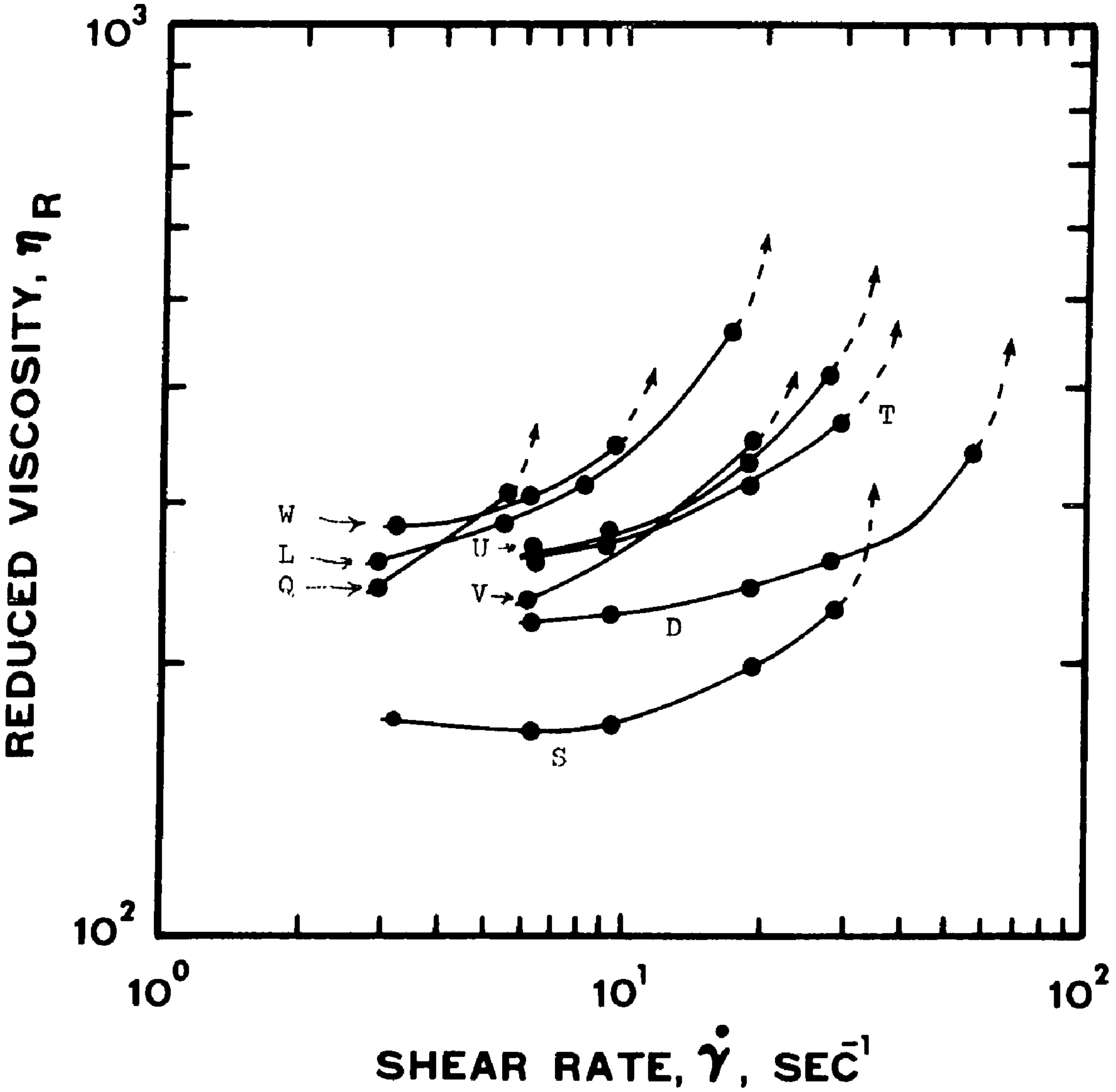
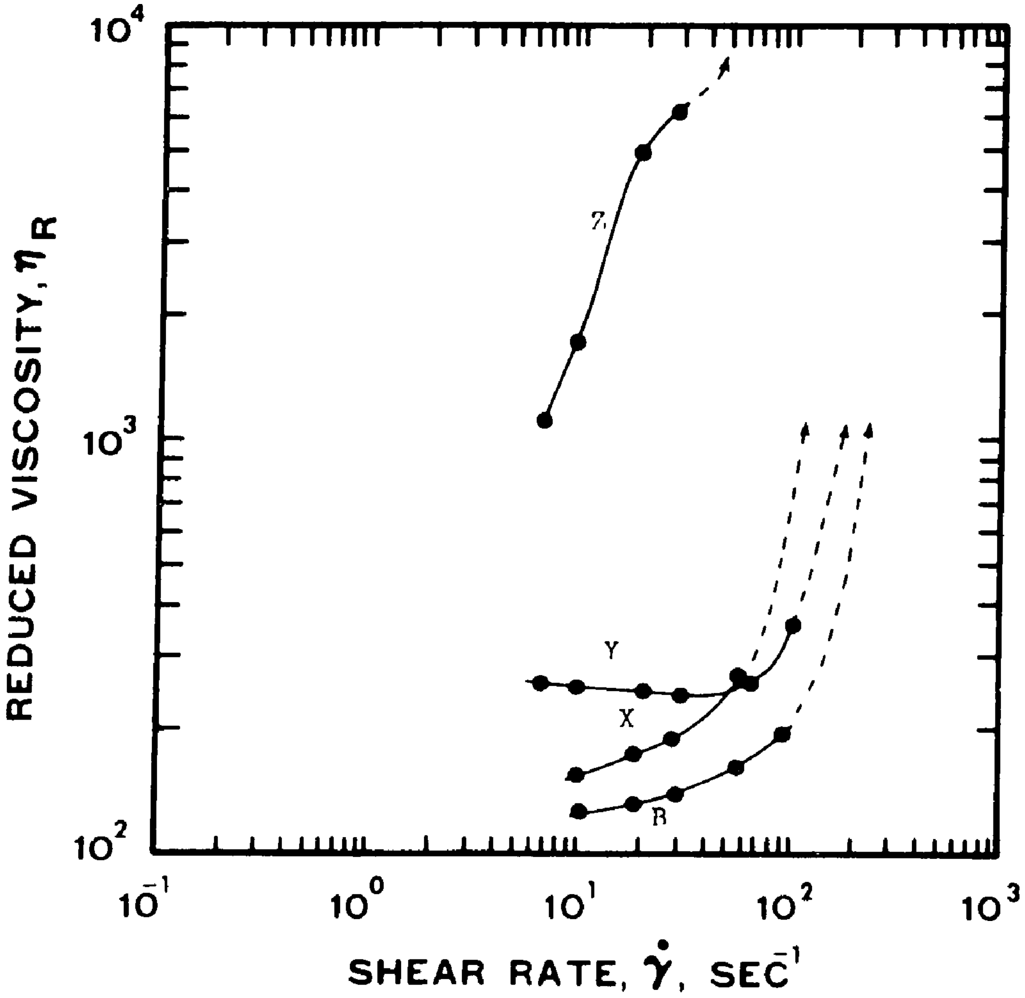


Figure 15

Flow Curves for 0.585 VF of
Various Resins in DOA

B 0.585 VF 1730 in DOA
X 0.585 VF 1730-2F in DOA
Y 0.586 VF 1730-1F in DOA
Z 0.586 VF 1730-2C in DOA



The marked difference in the behavior of the 1730-2C (Z) plastisol warrants further attention. As discussed previously, the Coulter Counter analysis did not differentiate particle size and particle-size-distribution differences between 1730 and 1730-2C resins. Scanning-electron micrographs of the two resins did show differences. Φ_{MIX} determinations suggest considerable behavior anomalies between the two resins. These differences in Φ_{MIX} are reflected in the rheological behaviors as shown in Figure 15.

4.5 Discontinuity Shear Rate, $\dot{\gamma}_d$

The occurrence of the viscosity discontinuity was first reported by Hoffman.[2] Other investigators, such as Johnston and Brower,[54] probably did not experience this discontinuity because of the relatively low shear rates ($\simeq 1$ sec^{-1}) used in their experiments.

In this study, the viscosity discontinuity has been found to vary with the type and concentration of resin and the type of plasticizer. A plot of the discontinuity shear rate versus the reciprocal of the reduced volume fraction for all the plastisol formulations used in this study is shown in Figure 16. Included is a least-squares fit represented by the expression:

$$\log_{10} \dot{\gamma}_d = 9.8568 + 10.437/\Phi_R. \qquad (21)$$

This model has a standard-error of estimate value of ± 0.1460. In addition, the r^2 value (fraction of variability accounted for) is 0.9154.

Figure 16 also contains data obtained from Hoffman's study.[2] Since Hoffman did not determine Φ_{MIX} values, Eq. (21) was used to calculate Φ_{MIX} for his systems. These calculations are detailed in Appendix F. In addition, another PVC resin supplied by the B. F. Goodrich Company was used to determine a Φ_{MIX} value with DOP. Viscosity measurements were taken on a plastisol prepared with this resin and DOP. A viscosity discontinuity was observed and is also presented in Figure 16. Both Hoffman's data and the data obtained with the plastisol prepared with the Goodrich resin are shown to be well described by the model, reinforcing the validity of the Φ_R concept for resins other than the kind used in this study.

Another important observation regarding the discontinuity shear rate is that below a certain value of Φ_R, discontinuous behavior is no longer present. Plastisol formulations investigated in this study had Φ_R values of 0.87 to 1.00. In this range, discontinuous behavior was observed. Hoffman has presented data[2] showing the absence of a viscosity discontinuity with a plastisol having a Φ_R value of 0.84, calculated as illustrated in Appendix F. The discontinuous viscosity behavior of plastisols having Φ_R values between 0.84 and 0.87 could not be investigated with the Haake Rotovisco because of shear-stress-measurement limitations at shear rates greater than 100 $\sec^{-1}$. Experimentation with other viscometers, such as the Weissenberg Rheogoniometer could be used for such an investigation.

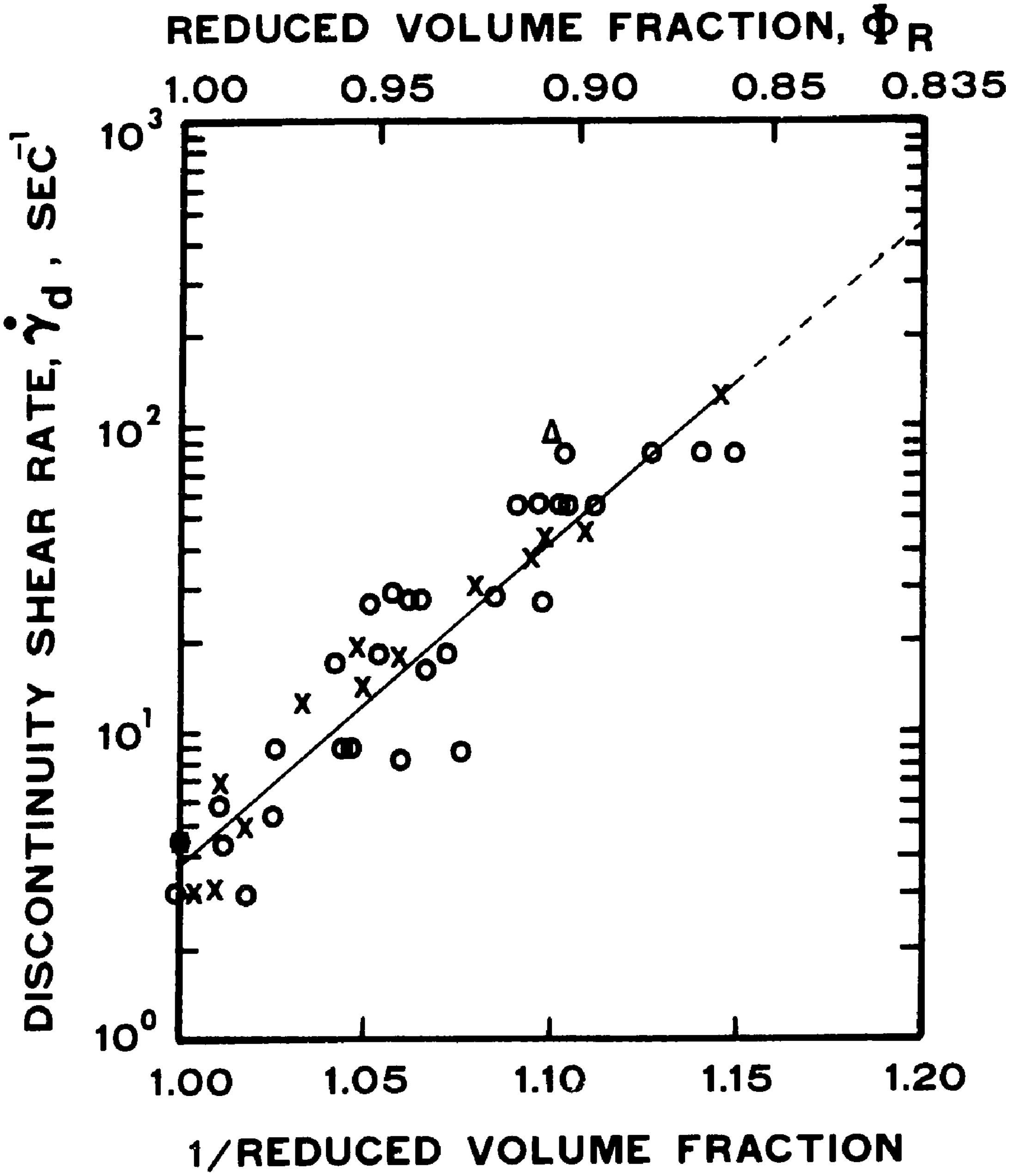
Figure 16

Relationship Between Discontinuity Shear Rate and Reduced Volume Fraction for all Plastisols

O 1730 series plastisols

X Hoffman's data

Δ B.F. Goodrich resin



Previous work has clearly demonstrated that particle/particle and particle/vehicle interactions have an important effect on rheological behavior, particularly at high resin concentrations. This study presents data that supports this contention. This study also provides a technique to measure the extent of the interactions.

The use of Eq. (20) is straightforward. One only needs to know Φ_{MIX} for the particular resin/plasticizer combination to be able to predict $\dot{\gamma}_d$ as a function of Φ_R. In formulating plastisols for use with processes having high rates of shear, Eq. (21) can be used to predict the presence of an unwanted viscosity discontinuity. This 'a priori' knowledge should be helpful in avoiding processing pitfalls.

The Φ_{MIX}, Φ_R, and $\dot{\gamma}_d$ concepts can be used in yet another important area of commercial concern--quality control. Typically, production lots of dispersion resins are compared with various quality-control standards. Such standards include the analysis of the particle size of the resin. As shown in this study, particle-size analysis can provide misleading information. The use of the Φ_{MIX} mixing technique should provide an efficient and reliable quality-control determination. The technique would not only provide meaningful data, but in combination with the Φ_R concept, it would provide guidelines for formulation adjustments.

5. SUMMARY AND CONCLUSIONS

The rheological behavior of high resin-level plastisols was studied. Four different particle-size resins were obtained for this study by classifying a commercially available resin, Tenneco 1730. These resins were characterized by determining (1) particle size and particle-size distribution using a Coulter Counter and scanning electron micrographs, (2) molecular-weight averages, (3) type and amount of surfactant present on the resin particles, and (4) density. Three different plasticizers--DOA, DOP, and BBP--were used to prepare plastisols ranging in concentration from 0.576 to 0.67 volume fraction of resin.

In the range of concentrations studied, both shear-thickening and shear-thinning behaviors were found to transform into a discontinuous-viscosity behavior as the shear rate was increased. This viscosity discontinuity was found to depend on the particle-size characteristics of the resin, and the compatibility of the plasticizer with the resin.

A technique was developed to determine the maximum or critical volume fraction of resin, designated Φ_{MIX}, that would form a suitable plastisol. This plastisol, Φ_{MIX}, was found to be related to the particle size and particle-size distribution of the resin and the compatibility of the plasticizer with the resin. The behavior of Φ_{MIX} was also found to be a useful measure of particle/particle and particle/vehicle interactions. In addition, the Φ_{MIX}

mixing technique yields information that can be used for efficient and reliable quality-control determination.

Another factor, the reduced volume fraction, Φ_R, was formed by means of a simple mixing algorithm. The reduced volume fraction was found to be dependent on the volume fraction of resin, Φ, and Φ_{MIX}. It was found that Φ_R can be used as a qualitative measure of particle/particle and particle/vehicle interactions.

A model is proposed which relates the reduced volume fraction, Φ_R, to the discontinuity shear rate, $\dot{\gamma}_d$. It is shown how this model can be used as an aid in designing plastisol flow properties.

This study further extends the work of Johnston and Brower, and of Hoffman. The development of the Φ_{MIX} mixing technique parallels the critical-volume concept of Johnston and Brower. The investigation of the factors influencing the onset of discontinuous-viscosity behavior extends results that were first presented by Hoffman. The mathematical modeling of the shear-rate discontinuity through the use of the reduced volume fraction, Φ_R, advances the important concepts previously stated by these investigators. In turn, it is intended to provide a clearer understanding of certain basic mechanisms that determine the rheological behavior of plastisols.

6. RECOMMENDATIONS

This study has demonstrated the strong influence of the reduced volume fraction on the viscosity discontinuity. An extension of this work should include the investigation of the mechanisms that cause the anomalous flow behaviors. Some work has been done in this area,[3] but more work is needed based on the results of this study.

Van der Waals-London attraction and electric double-layer repulsion forces need to be considered in the light of the effect they have on particle/particle and particle/vehicle interactions. The dielectric constant is a measure of the magnitude of the repulsive forces present, *i.e.*, the higher the dielectric constant, the greater the ability to hold a charge.

This study has shown that BBP plastisols exhibit the viscosity discontinuity at lower shear rates than either DOP or DOA plastisols at constant-volume resin fractions. Since the dielectric constant of BBP is higher than either DOA or DOP, the inference can be made that attractive forces are greater than repulsive forces. Hence, the investigation of dielectric properties as influenced by resin concentration, plasticizer type, and shear rate should provide information concerning the viscosity discontinuity on a molecular scale.

In addition, the utilization of the Φ_{MIX} and Φ_R concepts to other suspensions and plastisols prepared with other PVC-dispersion resins is an important extension of this study.

Specifically, the recommendations are as follows:

1. Determine the effects of dielectric constant as influenced by resin concentration, plasticizer type, and shear rate.
2. Investigate the use of the Φ_{MIX} and Φ_R concepts with other suspensions.
3. Evaluate PVC-dispersion resins containing various types and amounts of surface surfactants. This study could be tied in with the dielectric-constant determinations, since the protective colloid can contain various ionic species.
4. Evaluate the discontinuous-viscosity behavior in the region of reduced volume fractions lower than 0.87. This should provide information concerning the critical value of Φ_R at which discontinuous-viscosity behavior is present.

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APPENDIX A

Industrial Application of Plastisols

Knowledge of rheological properties is important for the industrial application of plastisols. In high-speed coating and spreading operations, which involve high rates of shear, shear thickening may have an adverse effect on the speed and efficiency of such processes. On the other hand, shear thinning and thixotrophy may be advantageous. Slush-molding, dipping, and casting operations will generally involve low rates of shear, and in such cases shear thickening may be desirable, although high rates of shear may be present in the pumps supplying the plastisols to the equipment. Hence, 'a priori' knowledge of the specific process is needed so that a satisfactory plastisol can be formulated.

Examples of the products produced by various plastisol processes are listed below.[1]

Spread Coating

Auto and chair upholstery, clothing and apparel, Landau roof tops, luggage, floor and wall coverings, paper coating, coil coating, and carpet backing

Casting

Toys, printing plates, bottle-cap liners, floor mats, and table cloths

Foam Molding

Athletic padding, life preservers, and auto gaskets

Rotational Molding

Inflatable balls, dolls, artificial fruit, and bicycle seats

Slush Molding

Boots, toys, and head rests

Dip Molding

Wire racks, dish drainers, gloves, tool handles, and boots

A more-detailed description of these application processes along with the range of shear rates which can be present, provides the insight necessary to appreciate how the rheology of plastisols must be engineered if optimum flow properties are to be achieved. The most important of these processes are described and analyzed below.

REVERSE-ROLL COATER

This technique is used to apply plastisol coatings to a wide variety of substrates. Basically, the substrate should be nonporous so that coating defects are minimized. Figure 17 illustrates the arrangement of the rolls in relation to the substrate.

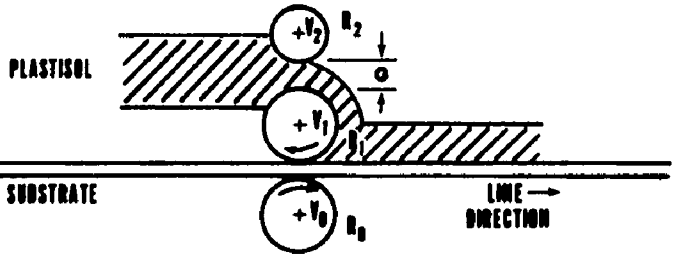

Figure 17

Reverse-Roll Coater

The plastisol is metered by the gap, G, set between rolls R_1 and R_2. The plastisol follows roll R_1 in the "reverse" direction of the traveling substrate and is wiped onto the top substrate. Roll R_0 helps to maintain constant pressure between roll R_1 and the substrate in addition to controlling the line speed. The speed of roll R_1 is usually somewhat faster than R_0. If one assumes that this arrangement is the same as the flow between two flat plates, the shear field can be defined by:

$$\dot{\gamma} \equiv (V_0 - V_1)/G. \qquad (22)$$

The entries in Table IX illustrate the range of shear rates between roll R_1 and the traveling substrate which can be present under various processing conditions.

TABLE IX

Relationship of Shear Rate to Process Variables--

Reverse-Roll Coater

V_0, feet/minute	V_1, feet/minute	G, inches	$\dot{\gamma}$, sec^{-1}
100	300	0.004	20,000
100	100	0.004	10,000
30	90	0.004	6,000
30	90	0.012	2,000
30	30	0.012	1,000

This table indicates the high magnitude of shear rates that are present and helps to point out why shear-thickening behavior can be deleterious to the product.

FORWARD-ROLL COATER

The forward-roll coater (Figure 18) is similar in nature to the reverse-roll coater except that the applicator roll (R_1) is rotating in the same direction as the back-up roll (R_0). This technique is used to apply smaller quantities of plastisol than is possible with the reverse-roll coater. The resultant coating is not as uniform as that obtained with the reverse-roll coater because the film splits somewhat irregularly between the substrate and roll R_1.

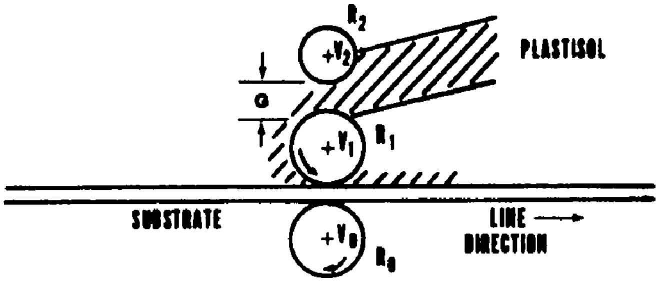

Figure 18

Forward-Roll Coater

Below is a table listing typical process conditions and the resulting rates of shear between roll R_1 and the substrate from Eq. (22).

TABLE X

Relationship of Shear Rate to Process Variables--

Forward-Roll Coater

V_0, feet/minute	V_1, feet/minute	G, inches	$\dot{\gamma}$, sec^{-1}
100	300	0.004	10,000
100	100	0.004	0
30	90	0.004	3,000
30	90	0.012	1,000
30	30	0.012	0

As has been shown for reverse-roll coating, high rates of shear can exist; however, because of the opposite direction of rotation of the rolls, low shear-rate conditions may also be achieved, if desired.

KNIFE-BLADE COATER

This coating technique can be used for porous and nonporous substrates alike because it does not rely on the contact of an applicator roll to wipe the plastisol onto the substrate.

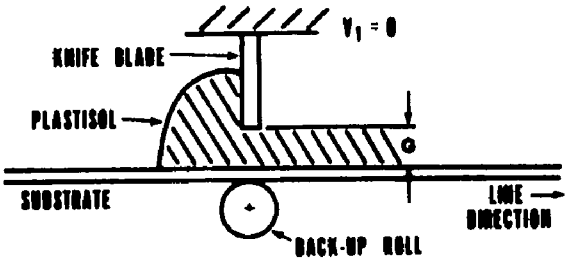

Figure 19

Knife-Blade Coater

As shown in Figure 19, the substrate moves past a stationary blade with a fixed gap setting. The plastisol is fed behind the knife blade and is "doctored" into the substrate. As before, Eq. (22) can be used to calculate approximate rates of shear existing between the blade and traveling substrate. Table XI illustrates typical conditions and the resulting rates of shear.

TABLE XI

Relationship of Shear Rate to Process Variables--

Knife-Blade Coater
($V_1=0$)

V_0, feet/minute	G, inches	$\dot{\gamma}$, sec^{-1}
100	0.004	5,000
100	0.012	1,667
30	0.004	1,500
30	0.012	500

CURTAIN COATER

This technique is different from that of the roll and knife-blade coaters. The mechanics of curtain coating involve the pumping of fluid to an elevated chamber and the continuous release of fluid from this chamber through a slot to form a fluid curtain. As shown in Figure 20, the substrate is coated as it passes through the curtain.

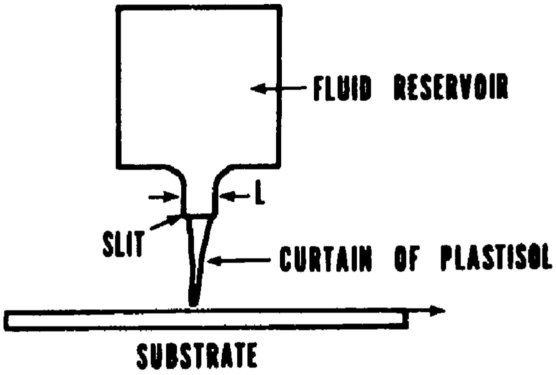

Figure 20

Curtain Coater

The flow mechanics of this coater are similar to the flow out of a rectangular duct. The maximum shear rate is governed by the equation:

$$\dot{\gamma} = 6q/wl^2, \qquad (23)$$

where w = width of slit

l = thickness of slit

and q = fluid flow rate.

Table XII illustrates a range of shear rates that can be encountered under a variety of typical process conditions.

TABLE XII

Relationship of Shear Rate to Process Variables--

Curtain Coater

q, in^3/sec	w, inches	l, inches	$\dot{\gamma}$, sec^{-1}
100	24	0.070	5,102
100	24	0.035	20,408
200	24	0.035	40,816
200	12	0.035	81,633

The shear rates encountered in this process are much higher than those present in the roll and knife-blade coaters.

DIP MOLDING

The dipping process consists of dipping a male mold into a fluid plastisol and then fusing the coating that adheres to the mold. Figure 21 illustrates a schematic of this process.

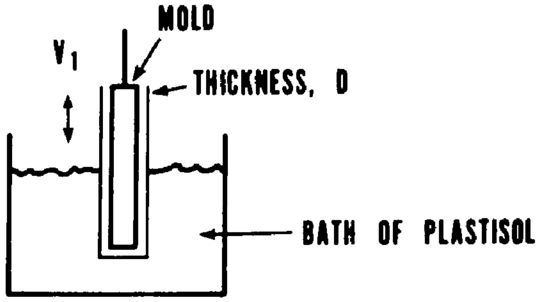

Figure 21

Dip Molding

The equation describing the shear rates present in this process can be defined by:

$$\dot{\gamma} = V_1/D, \qquad (24)$$

where V_1 = rate of mold withdrawal

and D = coating thickness.

Table XIII lists shear rates that are encountered under typical processing conditions.

TABLE XIII

Relationship of Shear Rate to Process Variables--Dip Molding

V_1, inches/minute	D, inches	$\dot{\gamma}$, sec^{-1}
3.0	0.001	50.
3.0	0.060	0.833
10.0	0.001	167.0
10.0	0.060	2.77

As one can see from Table XIII, the shear rates in this process are considerably different from those of the previous examples.

APPENDIX B

Properties of Plasticizers

A discussion of a wide range of properties that plasticizers possess should help to put their importance into perspective. A listing of the basic properties includes:

1. Compatibility

In plastics, compatibility has been defined as the ability of two or more substances to mix with each other to form a homogeneous composition of useful plastics properties.[68] Compatibility of a given plasticizer and PVC depends on the type and number of functional groups as well as the size and shape of the plasticizer molecule.

Depending on their tendency to exude, plasticizers can be classified as primary or secondary. Primary plasticizers can be used alone because of their good compatibility and resistance to exudation. Secondary plasticizers, as the name implies, are used in combination with primary plasticizers because of limited compatibility.

According to thermodynamic theory, two substances will be miscible when the free energy of mixing, as shown in Eq. (25), is negative.

$$\Delta G = \Delta H - T\Delta S, \qquad (25)$$

where ΔG = free energy of mixing

ΔH = heat of mixing

ΔS = entropy of mixing

and T = temperature.

Application of the theory to real solutions has led to the Hildebrand solubility parameter δ, the Flory-Huggins interaction parameter χ, and the Heil-Prausnitz segment interaction parameters G_1 and G_2.[69]

All early work on solubility parameters was oriented toward solvents. Recently, δ has been used in another scheme along with dielectric constant for predicting the compatibility of a plasticizer with PVC.[70] The number, kind, and arrangement of the atoms all influence the energy of vaporization and δ; they will also influence the dipole moment, hydrogen bonding, viscosity, and other properties, but not in the same proportions. Measurement of a second property of the plasticizer molecule gives a second parameter that may also be related to its compatibility. Two or more such parameters can, theoretically, describe the compatibility of a plasticizer with any given resin. Since dielectric constant ε', is strongly influenced by dipole moment and hydrogen bonding, it may be combined with the solubility parameter to predict plasticizer compatibility.[69] The common plasticizers for PVC have values of δ between 8.4 and 11.4, and values of ε' between about 4 and 8 to 10.[70,71] The merit of these modifications of the solubility-parameter concept may be that in some way they adjust for the nonideality of entropy of mixing.

The Hildebrand theory[72] was designed for solutions in which solvent and solute molecules are of the same size, so entropy behavior is ideal. Solubility is controlled primarily by ΔH, and according to theory:

$$\Delta H = n_1 v_2 V_1 (\delta_1 - \delta_2)^2, \qquad (26)$$

where n_1 = mole fraction of solvent

v_2 = volume fraction of solute

V_1 = molar volume of solution

δ_1 = solubility parameter of the solvent

and δ_2 = solubility parameter of the solute.

Although the δ value is a characteristic constant for a given material, it is the difference $(\delta_1 - \delta_2)$ between them that is significant.

The Flory-Huggins interaction parameter χ is a means of correcting for nonideality of both heat and entropy of mixing.[73] According to theory, the free energy of mixing of a polymer solution is given by Eq. (27):

$$\Delta G = RT(n_1 \ln v_1 + n_2 \ln v_2 + \chi n_1 v_2), \qquad (27)$$

where ΔG = free energy of mixing

R = gas constant

T = absolute temperature

n_1, n_2 = number of moles of solvent and solute, respectively,

and χ = interaction parameter.

If ΔG is negative, a polymer and solvent will form a solution, or, presumably, a polymer and plasticizer will be compatible. The concept has proven sufficiently useful that many equations involving χ have been developed so that various properties can be correlated with polymer/plasticizer compatibility. These include osmotic pressures of dilute solutions, equilibrium swelling, vapor pressures, viscosities, stress/strain behavior of swollen polymers, and depression of melting or freezing points.[74]

The last method gave good results in an extensive study of swelling and dissolution of PVC in plasticizers and solvents.[8,75] In these cases the more general equation is used to experimentally obtain values for χ:

$$1/T_m = 1/T_m{}^{\circ} + (R/H_u)(V_u/V_1)(v_1 - \chi v_1{}^2), \qquad (28)$$

where $T_m{}^{\circ}$ = melting point of pure polymer

T_m = depressed melting temperature

R = gas constant

H_u = heat of fusion per "mole" of repeating polymer unit

V_u, V_1 = molar volumes of polymer repeating unit and diluent, respectively,

v_1 = volume fraction of the diluent

and χ = Flory-Huggins interaction parameter.

It has been shown both theoretically[76-78] and experimentally[79] that a χ value of about 0.55 is the dividing line between poor solvents and nonsolvents. The region of poor solvency extends from about 0.31

to 0.55. Values of χ less than about 0.30 indicate good solvents. In general, the smaller the value of χ, the stronger the polymer-diluent (plasticizer) interaction and consequently the better solvent. The exact value of χ will depend on the concentration at which it is determined, because a polymer molecule responds neither as an equal number of monomer units nor as a large, completely unified molecule, but somewhere in between.

2. Solvation, Gelation, and Fusion

The ability of a plasticizer to solvate the resin is closely associated to compatibility. Certain highly compatible plasticizers show considerable solvent action to the point of gelation with time, even at room temperature, and completely solvate or fuse the resin at a relatively low temperature.

3. Heat and Oxidative Stability

Plastisols are subjected to elevated temperatures during processing and also in certain end uses. It is imperative that the plasticizer be thermally stable to temperatures of as much as 180°C and higher during processing. Plasticizers that have poor thermal and/or oxidative stability cause discoloration and ultimately embrittlement.

4. Volatilization Resistance

Plasticizers must be sufficiently low in volatility to resist loss from evaporation, since this also leads to loss of flexibility and ultimately to embrittlement. An example is automotive interiors where temperatures in excess of 140°F can develop in parked cars during the summer. In this example the result of volatilization may be the formation of a "fog" of condensed plasticizer on interior surfaces, including the windshield.

5. Low-Temperature Flexibility and Impact Strength

6. Flame Retardance

7. Economic Factors

These are important in all uses of plastisols. These factors include, in addition to the cost of the plasticizer itself, the relative efficiency (the amount of plasticizer required to achieve the desired hardness or modulus compared to a standard), the specific gravity of the plasticizer, and other considerations including volatilization loss in processing.

8. Miscellaneous Properties

These include electrical properties, fungus and mildew resistance, color, odor, and taste. Low toxicity is a further requirement in cases where the plasticizer may be in contact with food or possibly consumed by humans.

APPENDIX C

Haake Rotovisco Bob-Cup Systems

The MV and SV bob-cup systems were used in this study. Figure 22 illustrates the important dimensions.

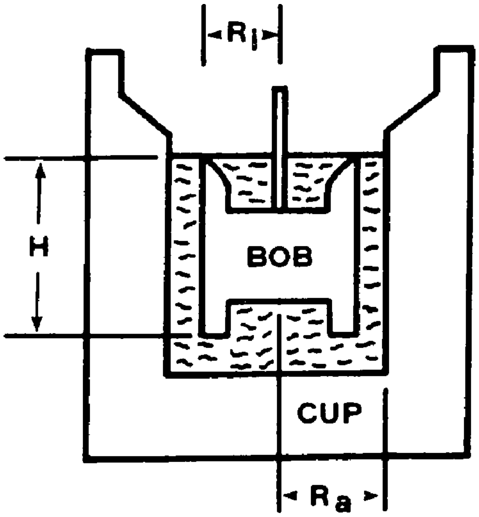

Figure 22

Rotovisco Bob-Cup System

Information concerning the systems are listed in Tables XIV and XV.

TABLE XIV

Viscosity Sensor System MV

Sensor System		MVI	MVII	MVIII
Rotor (Bob)				
Radius	R_i (mm)	20.04	18.4	15.2
Height	H (mm)	60.0	60.0	60.0
Stator (Cup)				
Radius	R_a (mm)	21.0	21.0	21.0
Radii Ratio	R_i/R_a	0.95	0.88	0.72
Sample Volume (cc)		40	55	70
Repeatability (±%)ca.		0.7	0.7	0.7
Reproducibility (±%)ca.		2.0	2.0	2.0

TABLE XV

Viscosity Sensor System SV

Sensor System		SVI	SVII
Rotor (Bob)			
Radius	R_i (mm)	10.1	10.1
Height	H (mm)	61.4	19.6
Stator (Cup)			
Radius	R_a (mm)	11.55	11.55
Radii Ratio	R_i/R_a	0.87	0.87
Sample Volume (cc)		12	6
Repeatability (±%)ca.		0.8	0.8
Reproducibility (±%)ca.		2.5	2.5

APPENDIX D

Corrections for Shear-Rate Determinations

For a power-law fluid,

$$\tau = K\dot{\gamma}^n, \qquad (29)$$

where τ = shear stress

K = empirical constant

and n = empirical constant.

From reference 67,

$$\dot{\gamma} = (2m\Omega)/(1-s^{2m}), \qquad (30)$$

where $m = 1/n$

Ω = angular velocity of bob, rpm

and s = radii ratio, R_i/R_a.

Table XVI lists data obtained with 0.67VF 1730 in DOA plastisol (Sample J) using SVII bob-cup system (s=0.87).

TABLE XVI

Uncorrected Rotovisco Data

Angular Velocity, Ω, rpm	Shear Stress, dynes/cm^2
0.36	772
0.72	1080
1.08	1338
2.16	2238
3.24	3207
6.48	----

Since the angular velocity is directly proportional to $\dot{\gamma}$, one solves for the constants K and n in Eq. (29). In this example, K = 1464 and n = 0.646.

$\therefore\ m = 1/n = 1.548$

Solving for $\dot{\gamma}$ in Eq. (30), one obtains results indicated in Table XVII.

TABLE XVII

Shear-Rate Determinations

Ω, rpm	$\dot{\gamma}$, sec^{-1}
0.36	0.330
0.72	0.667
1.08	0.998
2.16	2.00
3.24	2.99
6.48	5.99

APPENDIX E

Manipulation of Haake Rotovisco Data

Using the 0.67VF 1730 in the DOA-plastisol example discussed in Appendix D, raw data obtained with the RV1 Rotovisco is indicated in Table XVIII.

TABLE XVIII

Haake Rotovisco Test Data, 0.67VF 1730 in DOA

Rotor: SVII

Measuring Head	Ω, rpm	Scale Reading, R	Shear Stress Factor, A	Shear Stress, Dynes/cm^2, RxA
50	0.36	22.5	34.3	772
50	0.72	31.5	34.3	1080
50	1.08	39.0	34.3	1338
50	2.16	65.25	34.3	2238
50	3.24	93.5	34.3	3207
500	6.48	off scale	361	>36,100

After determining the shear rate as shown in Appendix D, the plastisol viscosity is obtained using the expression,

$$\eta = \tau/\dot{\gamma}. \qquad (31)$$

In addition, the reduced viscosity, η_R, is obtained by the expression,

$$\eta_R = \eta/\eta_S, \qquad (32)$$

where η_S = viscosity of the plasticizer.

In this case η_{DOA} = 0.119 poise. Table XIX lists the results using Eqs. (31) and (32).

TABLE XIX

Viscosity Determinations for 0.67VF 1730 in DOA

$\dot{\gamma}$, sec^{-1}	τ, $dynes/cm^2$	η, poise	η_R
0.330	772	2339	19,660
0.667	1080	1619	13,600
0.998	1338	1341	11,270
2.00	2238	1119	9,400
2.99	3207	1073	9,020
5.99	>36,100	>6027	>50,650

APPENDIX F

Calculation of Φ_R With Hoffman's Data

From reference 2, the volume fraction of resin and corresponding discontinuity shear rate for the plastisols made from the four particle-size PVC resins used by Hoffman are listed in Table XX.

TABLE XX

Listing of Hoffman's Data

Resin Particle Size, Microns	Volume Fraction of Resin, Φ	Discontinuity Shear Rate From Graphs, Sec^{-1}
1.25	0.470	--
	0.490	--
	0.510	120
	0.550	18
	0.570	4.5
0.775	0.527	42
	0.550	19
	0.573	6.7
	0.582	4.4
0.588	0.527	44
	0.550	11
	0.573	3
0.416	0.512	44
	0.527	22
	0.550	11
	0.573	3
	0.583	0

Eqs. (20) and (21) were used to calculate values of Φ_{MIX} from this data.

$$\log_{10}\dot{\gamma}_d = -9.8568 + 10.437/\Phi_R. \qquad (21)$$

For single resin/plasticizer systems, Eq. (20) reduces to

$$\Phi_R = \Phi/\Phi_{MIX}. \qquad (33)$$

Combining Eq. (21) and Eq. (33), one finally obtains, after rearranging:

$$\Phi_{MIX} = \Phi(\log_{10} \dot{\gamma}_d + 9.8568)/10.437 \qquad (34)$$

Table XXI lists the calculated Φ_{MIX} values for the various resin systems.

TABLE XXI

Φ_{MIX} Values for Hoffman's Resins in DOP

Resin Particle Size, Microns	Volume Fraction of Resin, Φ	Discontinuity Shear Rate, Sec^{-1}	Φ_{MIX} Eq. (34)
1.25	0.510	120	0.583
0.775	0.527	42	0.579
0.588	0.527	44	0.581
0.416	0.573	3	0.567

Table XXII lists the calculated values of Φ_R using Eq. (33) and the Φ_{MIX} results indicated in Table XXI.

TABLE XXII

Φ_R Values for Hoffman's Plastisols

Resin Particle Size, Microns	Volume Fraction of Resin	Reduced Volume Fraction of Resin, Φ_R	Discontinuity Shear Rate, Sec^{-1}
1.25	0.470	0.806	--
	0.490	0.840	--
	0.510	0.874	120
	0.550	0.943	18
	0.570	0.978	4.5
0.775	0.527	0.905	42
	0.550	0.950	19
	0.573	0.990	6.7
	0.582	1.00	4.4
0.588	0.527	0.907	44
	0.550	0.947	11
	0.573	0.986	3
0.416	0.512	0.903	44
	0.527	0.929	22
	0.550	0.970	11
	0.573	1.01	3
	0.583	1.03	0

VITA

Gary Edward Williams, son of Doris J. and Francis A. Williams (now deceased), was born January 30, 1947 in Allentown, Pennsylvania. He attended public school and graduated from Parkland High School in 1964. He then entered Indiana Institute of Technology, Fort Wayne, Indiana, where he graduated August 25, 1967 Cum Laude with a B.S. in Chemical Engineering. He enrolled at Lehigh University, receiving a M.S. degree in Chemical Engineering in January 1969. Since June 1969 he has been employed at the Armstrong Cork Company Research and Development Center in Lancaster, Pennsylvania. He is married to the former Nancy J. Oddou of Grabill, Indiana and has two children, a daughter, Tracy, and a son, Douglas.